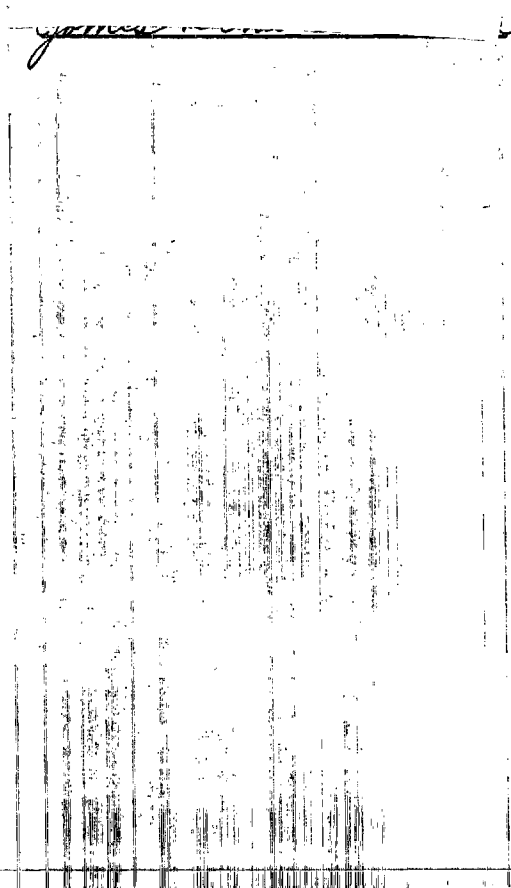


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THE EFFECT OF CERTAIN METAL IONS AS MODIFIERS
OF ADAMS' CATALYST IN THE HYDROGENATION OF CINNAMALDEHYDE

A THESIS

Presented to

The Faculty of the Graduate Division

by

James Donald Brown

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy in the School of Chemistry

Georgia Institute of Technology

June, 1963

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THE EFFECT OF CERTAIN METAL IONS AS MODIFIERS
OF ADAMS' CATALYST IN THE HYDROGENATION OF CINNAMALDEHYDE

Approved:

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Date approved by Chairman: May 31, 1963

ACKNOWLEDGMENTS

The writer wishes to thank Dr. James A. Stanfield for his suggestion of the problem and his patient guidance throughout this work. The writer also wishes to thank Dr. Dewey K. Carpenter and Dr. Raymond Kimbrough, Jr. for serving as members of the reading committee. The counsel given by Mr. D. Keith Davis and Mr. Robert T. Zimmerman of the Radioisotopes Laboratory of this institution during part of this work is also greatly appreciated.

Grateful appreciation is extended to the Offices of Isotope Development, United States Atomic Energy Commission who sponsored the early part of this work under contract number AT (38-1)-202 with the Engineering Experiment Station and to Dr. W. M. Spicer of the Chemistry Department for providing teaching assistantships throughout the latter period of this work.

The unfailing encouragement, inspiration, and patience of the author's wife, Jo Anne, is gratefully acknowledged to be a motivating factor in the pursuance and completion of this work and the graduate studies related to it.

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SUMMARY

Hydrogenation studies of cinnamaldehyde in 95 per cent ethanol and acetic acid were carried out in the presence of Adams' catalyst (PtO_2) under low H_2 pressures. The reactions were examined in terms of an initial rate and showed first order dependence in H_2 pressure over the first three to five minutes of the reaction. Not only was the time for maximum uptake of hydrogen noted, but also initial rate constants at various reaction temperatures were obtained and converted to rate constants at 30°C . by use of the Arrhenius equation. In the absence of added metal ions, the rate constants were 297 and 233 (both times 10^{-4}) $\text{min}^{-1} \text{ g}^{-1}$ for acetic acid and 95 per cent ethanol, respectively. However, H_2 absorption was greater in 95 per cent ethanol. An increase of 67 per cent in the cinnamaldehyde concentration gave 11 and 17 per cent increases in initial rates in 95 per cent ethanol and acetic acid, respectively. The use of 93 per cent acetic acid rather than glacial acetic acid caused a 30 per cent reduction in initial rate.

The addition of 0.50 ml. 3 N NaOH to cinnamaldehyde hydrogenation mixtures in 95 per cent ethanol gave after a short induction period, an initial rate constant of 315×10^{-4} .

In 95 per cent ethanol solvent, the addition of 5×10^{-6} or 20×10^{-6} mole of zinc acetate to the reaction mixtures did not affect the rate of reaction or H_2 uptake. However, in 93 per cent ethanol the presence of 100×10^{-6} mole Zn(II) caused a 28 per cent reduction in rate.

The addition of Zn(II) ions in a range from 0.05×10^{-6} to 250×10^{-6} mole caused a slight increase in rate at the lowest added level but, at the highest added level, the rate constant was reduced to 40×10^{-4} . Between these range limits, a complex dependence of rate on added Zn(II) was found. The H_2 uptake was greatest when from 50 to 100×10^{-6} mole of Zn(II) were added. The absorption of H_2 was lowest at the highest level of added Zn(II).

The extent of Zn(II) adsorption on catalyst samples isolated from cinnamaldehyde hydrogenation reaction mixtures was studied by use of radioactive (containing Zn^{65}) Zn(II) solutions. It was found that the amount of Zn(II) adsorbed on the isolated catalyst increased with an increase in the amount added, approaching a limiting value asymptotically, in the range studied. In a study of a number of variables in reaction conditions and catalyst isolation procedure the following observations were made: 1. extensive washing of the isolated catalyst samples did not affect the amount of Zn(II) adsorbed; 2. H_2 , even at atmospheric pressure, aided the adsorption of Zn(II) on the catalyst; and 3. the amount of Zn(II) adsorbed on the catalyst decreased with an increase in the time between the end of the reaction and catalyst isolation from the reaction mixture.

In connection with Zn(II) adsorption studies, techniques were developed for direct titrations of small aliquots of Zn(II) solutions using E.D.T.A. (di-sodium salt) as the titrant in the presence of Erio T indicator. These techniques permitted the determination for as little as 2.8×10^{-6} mole of Zn(II) in as little as 0.1 ml. of solution. Thus "standard" solutions and finally catalyst samples

containing known amounts of zinc could be prepared and used for comparative purposes. Direct comparison of the radioactivity of a "standard" catalyst sample with samples obtained experimentally gave values of Zn(II) adsorbed on the experimentally obtained samples.

The dependence of initial rates in terms of the amounts of Zn(II) adsorbed on the catalyst was examined, and although the form of this dependence was complex, it was of the same shape as that found between initial rates and amounts of Zn(II) added. Absorption of H_2 was greatest when the amount of Zn(II) adsorbed ranged from 3.9 to 8.1×10^{-6} mole.

In 95 per cent ethanol, the addition of Fe(II) to cinnamaldehyde hydrogenation mixtures in a range from 10 to 100×10^{-6} mole caused an increase in initial rates: added levels of 25×10^{-6} and 100×10^{-6} gave the highest rates in this range, both being essentially the same, 356×10^{-4} and 358×10^{-4} , respectively. Hydrogen absorption in these cases either reached or slightly exceeded the theoretical amount.

On the other hand, Fe(II) used as a modifier in acetic acid showed higher initial rates for cinnamaldehyde hydrogenation over the range of added Fe(II) of from 1.0 to 10×10^{-6} mole, the highest rate, 407×10^{-4} , being observed at the lowest added level. Beyond 10×10^{-6} mole Fe(II) added, the rates were lower and the lowest rate, 246×10^{-4} , was realized at the highest added level of 250×10^{-6} mole. The rate dependence on amount of added Fe(II) over the entire range studied was complex. Absorption of H_2 again either reached completion or went slightly beyond it. The use of 93 per cent acetic acid rather than

glacial acetic acid caused a 23 per cent reduction in rate in the presence of 100×10^{-6} mole added Fe(II).

Fe(III) gave a 16 per cent higher initial rate than Fe(II) at the same (100×10^{-6} mole) added level in glacial acetic acid. A 21 per cent decrease in rate was observed if 93 per cent acetic acid was used rather than glacial acetic acid in the presence of this quantity of added Fe(III).

Use of radioactive solutions of Fe(II) containing Fe^{59} showed the amount of Fe(II) adsorbed increased with an increase in the amount added, approaching a limiting value asymptotically, in the range from 1.0 to 250×10^{-6} mole added. The asymptotic limiting value of adsorbed Fe(II) was near 16×10^{-6} mole which was also indicated from Zn(II) adsorption experiments. Greater amounts of Fe(II) were adsorbed at lower added levels than were found for Zn(II) at the same added levels. A 67 per cent increase in cinnamaldehyde concentration resulted in lower amounts of Fe(II) adsorbed for the same added levels. This difference was greatest at the lower added levels and became negligible at higher added levels (beyond 50×10^{-6} mole Fe(II) added).

A complex dependence of initial rates on the amount of Fe(II) adsorbed was found. This dependence showed the same general shape as that found for the rate dependence on the amount of Fe(II) added.

Surface area determinations on a sample of reduced PtO_2 showed its specific surface to be $8.3 \text{ m}^2/\text{g}$. Calculations for the highest level of adsorbed Fe(II) or Zn(II) showed only about 20 per cent of this surface was covered by the metal ions. However, additional calculations, using the idea of two acetate ions associated with each

metal ion, showed these counter ions could effectively cover 79 per cent of the total catalyst surface available.

The difference in initial rates found for Fe(II) and Zn(II) (246×10^{-4} and 40×10^{-4} , respectively) at near the same level (16×10^{-6} mole) of adsorbed ions was attributed to differences in electronic alterations of the catalyst surface by the two ions.

Reaction mixtures from cinnamaldehyde hydrogenations were analyzed by vapor phase chromatography (V.P.C.). These reactions were stopped at either 83 or 50 per cent completion. Acetic acid or 95 per cent ethanol was used as the reaction solvent. Zn(II) or Fe(II) ions were added in certain runs while others contained no added metal ion. The V.P.C. results showed 3-phenyl-propanal to be a major component in the reaction mixtures stopped at 83 or 50 per cent completion. At 83 per cent completion, Fe(II) in ethanol solvent favored the highest (35 to 40 per cent) amount of 3-phenylpropanal in the reaction mixture. In the absence of added metal ions or in the presence of Zn(II), in either solvent, the amount of the same compound at 83 per cent completion was 25 to 30 per cent of the mixture. Fe(II) in acetic acid gave essentially this same result at 83 per cent completion. At 50 per cent completion in acetic acid solvent the amount of 3-phenylpropanal in the mixture was 25 per cent when either ion was present or no added ions were present. Only a slightly greater amount of this compound was found at the same level of completion in 95 per cent ethanol containing Zn(II). Variation of the amounts of added ions from 2×10^{-6} to 50×10^{-6} mole did not significantly affect the composition in either solvent. Cinnamyl alcohol was not found in significant

amounts in any of the reaction mixtures analyzed. In a number of cases the composition of the mixture was accounted for completely in terms of starting material (cinnamaldehyde), 3-phenylpropanal, and fully hydrogenated product (3-phenyl-1-propanol). However, these results did not define the reaction path from cinnamaldehyde to 3-phenyl-1-propanol.

CHAPTER I

INTRODUCTION

Heterogeneous catalytic reactions may be defined as catalytic reactions which take place in a system having two or more phases present. A common example of such a reaction involves the addition of hydrogen (gas phase) to an organic compound dissolved in a suitable liquid solvent (liquid phase) in the presence of a finely divided metal catalyst (solid phase). The carbon-carbon (ethylenic) double bond and the carbon-oxygen (carbonyl) double bond in a wide variety of organic compounds are two groups which have been frequently reduced by such catalytic hydrogenation reactions. Among those metals which have demonstrated their ability to catalyze such reactions, platinum has proven to be of general utility in the laboratory. One practical reason for its usefulness is the fact that low pressures (one to three atmospheres) of hydrogen may be used for the reaction. Such is not always the case for other metal catalysts.

Since the inception of its use as a catalyst, the relatively high cost of platinum has made the development of a platinum catalyst with maximum activity of practical necessity. The term maximum activity means that for a given amount of reactants, the minimum amount of catalyst giving the highest yield of desired products per unit of time is that catalyst of highest activity. Expressing it in another way, for a given amount of catalyst, that catalyst is of highest activity which gives the highest yield of desired products per unit of time.

Since the activity of a catalyst may be a function of its surface area the suspension of finely divided platinum in a colloidal form, using natural or synthetic high polymers has been found useful (1) in furnishing a very large surface area per unit weight of catalyst. In addition, the colloid also appears to prevent gross coagulation of the catalyst particles which tends to occur in certain reaction media. Another method of attaining a high surface area is to support a quantity of platinum on some inert material of high surface area such as carbon in the form of charcoal, bone black, or lamp black.

Other factors, however, besides surface area influence the activity of the catalyst in heterogeneous catalytic reactions. Low pressure platinum-catalyzed hydrogenations of organic substrates in a liquid phase are certainly no exception. One such factor is the very large effect on catalyst activity that the presence of minute traces of materials foreign to the metal may show. If such impurities increase the activity of the catalyst they are termed promoters. On the other hand, if they decrease the catalyst activity they are termed poisons.

The fact that some early workers (2)(3) with platinum as a hydrogenation catalyst suggested oxygen in the catalyst was necessary for hydrogenations of oxygen containing groups led directly to the preparation of an unusually active catalyst for many hydrogenations. Voorhees and

(1) L. D. Rampino and F. F. Nord, J. Am. Chem. Soc., 63, 2745 (1941).

(2) M. G. Vavon, Compt. rend., 158, 409 (1914).

(3) R. Willstätter and E. Waldschmidt-Leitz, Ber., 54, 113 (1921).

Adams (4) concluded that if oxygen was necessary, a platinum oxide might prove to be an excellent catalyst. Their preparation of an oxide, PtO_2 , was accomplished by the fusion of chloroplatinic acid and sodium nitrate. A temperature of 500°C . for this fusion gave the best results (5) in terms of catalyst activity. In the presence of hydrogen the platinum oxide is reduced to the metal which is the effective catalyst. Oxygen promotion of the platinum catalyzed reduction of the ethylenic double bond as well as the aldehyde carbonyl has been indicated by Maxted and Akhtar (6). It is common practice to refer to the platinum oxide-platinum catalyst system as Adams' catalyst.

In spite of the great improvement shown by Adams' catalyst over other platinum catalysts it was still necessary to reactivate it several times during the reaction when aldehydes were being reduced. Such reactivations were accomplished simply by shaking the reaction mixture in the presence of air or oxygen (7). In view of this difficulty in aldehyde reductions, it was of considerable interest when Carothers and Adams (8) reported that small amounts of iron, as Fe(II) or Fe(III) , added to the reaction mixture greatly decreased the time required for the hydrogenation of benzaldehyde and heptaldehyde in alcohol solution when using Adams' catalyst. Furthermore, the number of reactivations required was

-
- (4) V. Voorhees and R. Adams, J. Am. Chem. Soc., 44, 1397 (1922).
(5) R. Adams and R. L. Shriner, J. Am. Chem. Soc., 45, 2171 (1923).
(6) E. B. Maxted and S. Akhtar, J. Chem. Soc., 1959, 3130.
(7) W. E. Kaufmann and R. Adams, J. Am. Chem. Soc., 45, 3029 (1923).
(8) W. H. Carothers and R. Adams, J. Am. Chem. Soc., 45, 1071 (1923).

greatly reduced and in some instances completely eliminated. This promoting effect of iron salts was demonstrated by Adams and co-workers (7)(9)(10)(11)(12) for a variety of other aldehydes. Similar effects were noted by Faillebin (13) who found the addition of FeCl_3 to chloroplatinic acid before its reduction to platinum black gave a catalyst much more active toward aldehyde and ketone hydrogenation than the usual platinum black.

Carothers and Adams (14) also showed that added Zn(II) ions were effective promoters for Adams' catalyst in benzaldehyde reduction. More recently, Maxted and Akhtar (6) found a number of different metal ions act as promoters in the reduction of valeraldehyde using Adams' catalyst. It was generally noted in these cases that for a given set of reaction conditions the amount of added salt was a critical factor in determining the optimum promoting effect of a particular metal ion. Thus, the promoting effect, as judged by the rate of hydrogenation, passed through a maximum as the amount of added metal ion increased. This implied that a metal ion may act either as a promoter or poison in aldehyde reductions with Adams' catalyst, depending on its concentration in the reaction

(9) W. H. Carothers and R. Adams, J. Am. Chem. Soc., 46, 1675 (1924).

(10) R. Adams and B. S. Garvey, J. Am. Chem. Soc., 48, 477 (1926).

(11) W. F. Tuley and R. Adams, J. Am. Chem. Soc., 47, 3061 (1925).

(12) R. H. Bray and R. Adams, J. Am. Chem. Soc., 49, 2101 (1927).

(13) M. Faillebin, Compt. rend., 175, 1077 (1922).

(14) W. H. Carothers and R. Adams, J. Am. Chem. Soc., 47, 1047 (1925).

mixture. The presence of metallic impurities in Adams' catalyst -- added intentionally (15) or inadvertently (16) during its preparation -- has also been shown to exert similar promoting-poisoning effects in the hydrogenation of benzene nucleus in acetic acid solvent.

The presence in the organic substrate of two or more groups susceptible to hydrogenation is a common occurrence in catalytic hydrogenation procedures. It is often desirable to effect a selective reduction of such compounds, i.e., to reduce one group without concomitant reduction of the other. If the groups differ greatly in their susceptibility to hydrogenation it may be possible to achieve selective reduction simply by stopping the reaction after the absorption of the theoretical amount of hydrogen needed to reduce the most active group present. If selective reduction is considered to be related to the relative rates of hydrogenation of the groups present, it should be possible to add a promoter or poison specific for one group and thus achieve a degree of selective reduction of the promoted or unpoisoned group or groups. This technique has proven to be practical in a number of cases. For example, furfural (7) could be hydrogenated to furfuryl alcohol in the presence of FeCl_2 . The selectivity achieved was attributed to the greater poisoning effect Fe(II) ions have on the catalytic hydrogenation of the ethylenic group than on the carbonyl group. A similar example is provided by the work of Csűrös, et al., (17) who reported a variety of α , β -unsaturated

(15) R. H. Earle, Unpublished Master's Thesis, Georgia Institute of Technology, 1950.

(16) C. W. Keenan, B. W. Giesemann, and H. A. Smith, J. Am. Chem. Soc., 76, 229 (1954).

(17) Z. Csűrös, K. Zech, and I. Géczy, Hung. Acta Chim., 1, 1 (1946). Chemical Abstracts, 41, 109 (1947).

ketones were hydrogenated to the unsaturated alcohols using a colloidal palladium catalyst in the presence of ferrous sulfate or zinc acetate.

Another factor which can influence the relative rates of hydrogenation of groups present in the organic substrate is the amount of catalyst used in the reaction. Csürös (18), in discussing this factor, made the following observations: 1. the rate of hydrogenation of a particular group passes through a local minimum and maximum as the amount of catalyst is increased; 2. molecules containing both an ethylenic double bond and a carbonyl group exhibit their respective maxima and minima in rates at different amounts of catalyst; and, 3. as a result of this, a degree of selective reduction of either group could be achieved by choosing the proper amount of catalyst. However, it is stated, such a reversal of selectivity is possible only when the rates of hydrogenation of the two groups are of similar magnitude. It was further shown that the variation of hydrogenation rates according to a minimum-maximum curve could be attributed to a simultaneous variation of the rate constant and the reaction order, relative to the substrate, both of these being functions of the amount of catalyst used. The relationships just mentioned were observed with many different substrates and a variety of different dispersed catalysts indicating a general validity for such relationships.

Cinnamaldehyde ($\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$) is typical of α , β -unsaturated aldehydes commonly encountered in organic chemical work and as such it is of interest to review briefly its behavior in catalytic hydrogenations. Cinnamaldehyde has been catalytically hydrogenated using a variety of

(18) Z. Csürös, Research (London), 4, 52 (1951).

catalysts under varying conditions with varying results. Freidlin (19) (20) reported that hydrogenation of cinnamaldehyde over a zinc or zinc-copper catalyst prepared from a Raney type alloy gave selective reduction of the carbonyl group. These reactions were carried out at 50 to 100 atmospheres pressure and 50° to 140° C. Delépine and Hanegraff (21), using a Raney nickel catalyst to hydrogenate cinnamaldehyde in alcohol, found that the ethylenic group was reduced faster than the carbonyl group. Thus, after the absorption of 1.32 mole equivalents of hydrogen the reaction mixture contained only 8 per cent of the original ethylenic group content and 54 per cent of the original carbonyl group content. Straus and Grindel (22) used a colloidal palladium catalyst to hydrogenate cinnamaldehyde and observed the carbonyl group was reduced first. Skita used a colloidal palladium catalyst (23) and a colloidal platinum catalyst (24) to hydrogenate cinnamaldehyde but reported that the ethylenic double bond was reduced first. Csürös (18), in the work noted earlier, found that either the carbonyl or the ethylenic double bond of cinnamaldehyde could be selectively hydrogenated depending on the amount of colloidal palladium catalyst used. Using colloidal palladium or palladium on

(19) L. Kh. Freidlin and V. I. Gorschkov, Izvest. Akad. Nauk S.S. S.R. Otdel Khim Nauk, 1959, 2027. Chemical Abstracts, 54, 10813 (1960).

(20) L. Kh. Freidlin, Problemy Kinetiki i Kataliza Akad. Nauk S.S.S.R., 1960, No. 10, 187. Chemical Abstracts, 55, 15415 (1961).

(21) M. Delépine and C. Hanegraff, Bull. Soc. Chim. France, 4, 2087 (1937).

(22) F. Straus and H. Grindel, Ann. 439, 276 (1924).

(23) A. Skita, Ber., 48, 1685 (1915).

(24) A. Skita, Ber., 48, 1486 (1915).

barium sulfate in a semimicro apparatus, Csűrös and co-workers (25) reported that with the proper amount of catalyst, the carbonyl group of cinnamaldehyde could to a large extent be hydrogenated before the ethylenic double bond. Rampino and Nord (1) isolated and identified n-propylbenzene, 3-phenylpropanal, and 3-phenyl-1-propanol from the hydrogenation mixture of cinnamaldehyde using a colloidal palladium catalyst. This catalyst was prepared using a synthetic high polymer as the colloid forming material. Vavon (26) used a platinum black catalyst to hydrogenate cinnamaldehyde and isolated from the reaction mixtures 3-phenyl-1-propanol in 80 to 100 per cent yield. Cinnamaldehyde has also been hydrogenated using a platinized charcoal catalyst containing a trace of palladium (27). This catalyst gave a rate of hydrogen absorption of one to five millimoles per minute with the absorption of two mole equivalents of hydrogen. The product was presumably 3-phenyl-1-propanol though it was not isolated.

In agreement with the observed difficulties in using Adams' catalyst for aldehyde reductions, Tuley and Adams (11) noted that 0.2 mole cinnamaldehyde in 100 ml. of 95 per cent ethanol with 0.2 g. PtO_2 absorbed in five hours only about 10 per cent of the hydrogen required for both ethylenic and carbonyl reduction. However, if 2×10^{-5} mole of FeCl_2 was present in the reaction mixture the reaction proceeded to completion with the absorption of the first mole equivalent of hydrogen taking place in 165 minutes. The time required for the second mole equivalent of

(25) Z. Csűrös, K. Zech, and T. Pfliegel, Hung. Acta Chim., 1, 24 (1947). Chemical Abstracts, 41, 110 (1947).

(26) M. G. Vavon, Compt. rend., 154, 359 (1912).

(27) R. Baltzly, J. Am. Chem. Soc., 74, 4586 (1952).

hydrogen was not recorded. If the same level, 2×10^{-5} mole, of zinc acetate was used, the time required for the reaction of the first mole equivalent of hydrogen was eight hours. The second mole equivalent of hydrogen was absorbed slowly but the time required for its reaction was not recorded. On the other hand, if a mixture of 2×10^{-5} mole FeCl_2 and 3×10^{-5} mole $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ was used, the reaction stopped completely after one mole equivalent of hydrogen was absorbed. The time required for this seemed to vary from 275 to 390 minutes. Distillation of the reaction mixtures obtained in the presence of the metal ions revealed that the carbonyl group of cinnamaldehyde was first being reduced selectively under each of these conditions to give cinnamyl alcohol. However, the product after the absorption of one mole equivalent of hydrogen in the case using $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ alone showed the presence of some 3-phenyl-1-propanol. If this was true, cinnamaldehyde was also probably present though it is stated that no aldehyde was found in this mixture. The procedure used in these experiments involved pre-reduction of the PtO_2 before the reactants were added. If the PtO_2 was reduced in the presence of the reactants, it was noted that selectivity was affected only to the extent that conditions were not found whereby the reaction could be made to stop completely after one mole equivalent of hydrogen had been absorbed. The results obtained by Adams and co-workers in similar experiments on two other α,β -unsaturated aldehydes, citral (10) and furfuracrolein (12), seemed to indicate in general the carbonyl group of such compounds is reduced first in the presence of Fe(II) or Zn(II) or mixtures of the two ions. It might be noted here that Sokol'skii (28)

(28) D. V. Sokol'skii, *Trudy Inst. Khim, Nauk, Akad. Nauk Kazakh. S.S.R.*, 5, 146 (1959). *Chemical Abstracts*, 54, 13836 (1960).

showed that Adams' catalyst used in the hydrogenation of cinnamaldehyde in neutral or alkaline 96 per cent ethanol produced 3-phenylpropanal as the product. Metal ions, other than sodium in the alkaline media, are presumably absent in these cases.

In light of these early results obtained in the study of Fe(II) and Zn(II) as selective promoters in the hydrogenation of cinnamaldehyde using Adams' catalyst, it was deemed advisable to investigate this problem from three viewpoints. The first area of study would involve an examination of the effect these metal ions have on the initial rates of reaction, *i.e.*, the rate over the first three to five minutes. The comparison of the initial rate constants obtained in such a study could offer a convenient method of measuring poisoning or promoting effects observed in such systems. The second area of study would be that of the extent to which these metal ions are adsorbed on the catalyst surface. Such measurements are fundamental to any attempts to explain the action of these ions as poisons or promoters. The ready availability of radioactive isotopes, Fe⁵⁹ and Zn⁶⁵, has made possible the development of a rapid, convenient, and rather precise method of making such measurements. Maxted and co-workers (29)(30) had earlier developed another method which was suitable for a wide variety of substances, both molecular and ionic, in a study of poisoning effects on a platinum black catalyst. Their method was based on the following procedure: the catalyst sample was allowed to stand under a known volume of solution containing a known

(29) E. B. Maxted and H. C. Evans, J. Chem. Soc., 1938, 2071.

(30) E. B. Maxted and A. Marsden, J. Chem. Soc., 1940, 469.

of poison, an aliquot portion of the supernatant liquid over the catalyst was removed and added to a hydrogenation reaction mixture containing a sample of "standardized" catalyst, and the amount of the poison in the aliquot portion was measured by its effect on the rate of hydrogen absorption over the "standardized" catalyst. The standardization procedure for the catalyst involved measurements of hydrogenation rates for varying known amounts of added poison. A plot of the rate of hydrogen absorption for the "standard" catalyst vs. the amount of added poison permitted the amount of poison in the aliquot to be read directly from such a plot. The amount of adsorbed poison on the first catalyst was then the difference between the total amount added and the amount found present in supernatant liquid. The principal disadvantage to their method is that the metal ion adsorption takes place in the absence of the organic substrate, hydrogen, and agitation -- conditions quite different from an actual hydrogenation experiment. The third area of study would involve an investigation of the products of the hydrogenation of cinnamaldehyde in the presence of Fe(II) and Zn(II). Analysis of reaction mixtures at various stages of reaction is necessary in the confirmation of earlier results or the obtaining of new evidence on the selectivity of reduction of the carbonyl or ethylenic group in cinnamaldehyde. The use of vapor phase chromatography (V.P.C.) as an analytical tool is extremely valuable in cases such as this where the reaction mixture may contain as many as four components besides solvent and water. This method is simple and rapid while giving analysis results that range from semi-quantitative to quantitative depending on the conditions of the analysis. Besides

these three principal areas of investigation, any interrelationships between the areas would be of particular value in attempts to offer explanations for the experimental results obtained.

CHAPTER II

EXPERIMENTAL

All temperatures reported herein are uncorrected.

Apparatus

Hydrogenation Equipment

The hydrogenation equipment used in this work was manufactured by the Parr Instrument Company of Moline, Illinois. The Parr apparatus was mounted on a heavy metal base and consisted of the following principal parts: a four liter cylindrical tank which served as the hydrogen reservoir; a reaction bottle holder affixed at the top to rigid supports by means of a bearing-bushing assembly and affixed at the bottom to an eccentric wheel by a connecting rod; and an electric motor connected to the eccentric wheel by a rubber drive belt. The four liter tank was equipped with a thermometer well on the outside of the tank, a two-way valve equipped with a pressure gauge at the end of the tank leading to the hydrogen supply cylinder, and a three-way valve at the other end of the tank leading to the reaction bottle and to the evacuation system. The pressure gauge on the two-way valve was an Ashcroft Laboratory Test Gauge graduated in 0.25 lb. intervals. The three-way valve permitted the reaction bottle to be opened to the evacuation system or to the hydrogen reservoir. The electric motor-eccentric wheel-connecting rod assembly permitted the reaction bottle and its contents to be shaken by the rocking motion imparted to the bottle holder. Thick walled, cord reinforced, rubber pressure tubing was used to connect the two-way valve

of the hydrogen reservoir tank to the pressure reducing valve of the hydrogen supply cylinder. This reducing valve was a standard type valve equipped with a double gauge and a simple needle valve. The same type pressure tubing mentioned above was used for connections between the three-way valve and the reaction bottle and between the three-way valve and the evacuation system.

The reaction bottles used in the work were of two types. One type was a commercial "citrate of magnesia" bottle holding 460 ml. when full. The other type was also a commercially available bottle of the same style but holding when full 465 ml. The reaction bottle was placed in the holder and clamped tightly in place. Connection of the bottle with the three-way valve was achieved by the use of a tight-fitting, one-hole rubber stopper. Through the rubber stopper, a short piece of copper tubing was attached to the pressure tubing from the three-way valve. As a safety precaution the reaction bottle was encased in a snug-fitting, perforated, welded metal jacket open at both ends. As a further precaution when radioactive materials were used, the entire bottle holder assembly was surrounded by a plywood box open at the bottom, with a removable lid, and equipped with slots for the tubing and connecting rod to pass through. Furthermore, when radioactive materials were used the entire Parr apparatus was placed in a large plastic tray as another safety precaution.

The evacuating system for the hydrogenation apparatus consisted of an ordinary laboratory vacuum pump of the oil-sealed type, protected from vapors from the reaction bottle by suitable traps. These traps were of two types. One type consisted of a series of four glass tubes, the

first two filled with soda lime and the second two filled with potassium hydroxide pellets. An exposed needle valve was placed between the last tube and the pump so that the reaction bottle and the pump could be opened to the air. The other trap was a common glass cold trap placed in a Dewar flask and surrounded by crushed dry ice. A three-way thick walled glass stopcock was placed between the trap and the pump to permit the reaction bottle and the pump to be opened to the air.

Radioactivity Measuring Equipment

The radioactivity of certain catalyst samples obtained in this work was measured by placing the catalyst sample, contained in a cork-stoppered plastic (cellulose acetate) test tube, in a lead shielded sample holder. This sample holder, suitable for gamma radiation sources, was Model DS5-1 of the Nuclear Chicago Company. The detectable radiation was transformed into electrical impulses by means of an NaI(Tl) activated scintillation crystal and photo-multiplier tube in this instrument. These electrical impulses were then recorded as "counts" by a Nuclear Chicago Model 182 scaler. This scaler was equipped with a timer having a manual on-off switch. However, in most cases an auxiliary set-timer was used which stopped the counting process after a pre-set duration of time had elapsed. Use of either timer permitted the radioactivity of the sample to be expressed in terms of a count rate, usually as counts per minute (cpm).

Two different combinations of sample holders and scalers were used in this work. However, each combination involved the use of the same model instruments just described.

Distillation Equipment

Distillations required in this work were carried out using a Todd Precision Distillation assembly made by Todd Scientific Company of Springfield, Pennsylvania. In some cases a one-half inch diameter Vigreux type column was used. In other cases a one-inch diameter column filled with one-eighth and one-fourth inch, single turn glass helices was used. Each of the columns was three feet in length. In cases where low pressure distillations were required, the low pressure was achieved by the use of a Welch Duo-Seal vacuum pump protected by suitable cold traps. A type of McLeod gauge was used to note the pressures during such distillations.

Vapor Phase Chromatography (V.P.C.) Equipment

A Perkin Elmer Vapor Fractometer, Model 154 was used for V.P.C. analyses in this work. This apparatus provides for the use of different columns and varying conditions of operation. Of the various columns used there were four that gave qualitative to semi-quantitative results. One was a Perkin Elmer "R" column three feet long, made of stainless steel tubing, and packed with diatomaceous earth coated with "UCON," a polypropyleneglycol. The second was a Perkin Elmer "O" column, made of a three-foot length of stainless steel tubing and packed with diatomaceous earth coated with a silicone grease. The third column designated B59, was made of a nine-foot length of 4 mm. O.D. copper tubing packed with Chromasorb P coated with a silicone grease (S.E.-30 from General Electric Corporation). The preparation of this column is given in Appendix A. The fourth column designated B132A, was a six-foot column made of 4 mm. O.D. copper tubing packed with chromasorb P coated with a silicone grease

(S.E.-30 from General Electric Corporation). This column was prepared by Dr. R. G. Jones (31) according to procedures similar to those described in Appendix A.

In order to achieve column equilibrium, the column heating assembly was kept at the desired temperature for four to six hours before samples were analyzed. The samples were introduced into the vaporizing chamber of the instrument by means of a Hamilton Microsyringe inserted through a self-sealing Neoprene rubber gasket. Helium was used as the carrier gas in this instrument. The fractionation of the sample was recorded on cross-hatched chart paper as a series of peaks of varying sizes and shapes by a Leeds and Northrup Laboratory Recorder.

Reagents and Other Materials

Adams' Catalyst

The catalyst used throughout this work was obtained from Baker and Company, Incorporated (now known as Englehard Industries, Incorporated) of Newark, New Jersey. This sample was designated as lot number eight and contained 84.12 per cent platinum.

Hydrogen

The hydrogen used in this work was obtained from several local distributors -- Southern Oxygen Company of Atlanta, Georgia, Marks Oxygen Company of Atlanta, and National Cylinder Gas Company of Atlanta. In each case the hydrogen was used as received.

(31) R. G. Jones, Unpublished Ph. D. Thesis, Georgia Institute of Technology, 1961, p. 97.

Acetic Acid

Acetic acid, C.P. grade from Baker and Adamson or reagent grade from du Pont, was distilled at atmospheric pressure in the Todd assembly. Both the Vigreux type column and the glass helices filled column were used for this distillation. In a typical distillation, material boiling at 114.8°C . under 730 mm. pressure was collected for use. The quality of the distilled acid did not appear to vary with the source of supply.

Ethanol

Both 95 per cent and absolute ethanol, C.P. grades, were used without further purification.

Methanol

Synthetic methanol, C.P. grade, was used as obtained.

Benzoic Acid

Benzoic acid, Analytical Reagent Grade from Mallinckrodt Chemical Company, used in certain hydrogenation experiments was not purified further prior to its use.

Cinnamaldehyde

This compound was obtained as the trans isomer from Distillation Products Industries division of Eastman Kodak Company. The compound was "white label" grade designated lot number 77. In some few cases it was used as received but for the majority of the work it was fractionally distilled at reduced pressure under a nitrogen atmosphere. As the aldehyde thus distilled was consumed during the work it was necessary to repeat twice the fractional distillation procedure to obtain an additional supply of cinnamaldehyde. See Appendix B for the data obtained in the

first fractional distillation. The various fractions obtained were stored in glass stoppered bottles under nitrogen away from sunlight. The fractions chosen for use in this work were those fractions whose boiling points at the given pressures seemed to agree best with the vapor pressure-temperature data presented by Stull (32) for cinnamaldehyde.

Cinnamyl Alcohol

This alcohol was needed as a reference compound in the V.P.C. analysis experiments. It was obtained from Distillation Products Industries division of Eastman Kodak Company as a practical grade material. It was distilled under reduced pressure in the Todd apparatus using the Vigreux column. The fraction boiling from 113° to 114° C. at four mm. was chosen for use in this work.

3-Phenylpropanal

Experiments in the V.P.C. analysis required this compound as one of the reference materials. It was obtained from Distillation Products Industries division of Eastman Kodak Company as a practical grade material. Preliminary V.P.C. analysis of this compound alone showed it to be of suitable purity as received. Accordingly, it was used without further treatment.

3-Phenyl-1-propanol

This compound was also needed as a reference material in V.P.C. analysis experiments. It was obtained by the catalytic hydrogenation of cinnamyl alcohol (practical grade) in absolute ethanol using Adams' catalyst. See Appendix C for details of the preparation and distillation of

(32) D. R. Stull, Ind. Eng. Chem., 39, 517 (1947).

the crude product. The fraction boiling at 67° C. under one mm. pressure was chosen for this work.

Ferrous Chloride

The $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, reagent grade, was used as received from Matheson, Coleman, and Bell Chemical Company.

Ferric Chloride

This material was obtained from Baker and Adamson Chemical Company as the hexahydrate in "purified lump" form. It was used without further treatment.

Radioactive Iron⁵⁹

The radioactive sample of $\text{Fe}^{59}\text{Cl}_3$ in $\text{HCl}(1.3\text{N})$ solution was obtained from the Oak Ridge, Tennessee facility of the United States Atomic Energy Commission. The sample had a volume of 0.7 ml. with a concentration of 0.098 mg. Fe per ml. The activity of the sample was 32.244 millicuries (mc.) per mg. This isotope had a half-life of 46 days and emitted gamma radiation of 1.1 and 1.3 Mev. It was also an emitter of 0.46 and 0.27 Mev. beta radiation. In order to prepare a radioactive solution of suitable activity and concentration of Fe ions, the following procedure was employed. The 0.7 ml. original sample was diluted to 25 ml. with distilled water and one ml. of this solution mixed with a solution of 0.2485 g. of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in 225 ml. of acetic acid containing approximately 5 per cent water. Finally, using a 250 ml. volumetric flask, this mixture was diluted with pure glacial acetic acid to 250 ml. This solution was then 5×10^{-3} M with respect to Fe ions and had a calculated count rate of approximately 5.2×10^4 cpm. per ml. which was suitable for the counting instruments available.

Zinc Acetate

The zinc acetate was obtained from Matheson, Coleman, and Bell Chemical Company as the dihydrate with 303162 as the lot number. It was used without further treatment.

Zinc Chloride

The zinc chloride used in certain titration experiments with ethylenediamine tetraacetic acid (E.D.T.A.), disodium salt as the titrant was of two types. One was C.P. grade from Baker Chemical Company while the other was a technical grade product obtained from Merck and Company. Both were used as received.

Radioactive Zinc⁶⁵

The radioactive sample of $\text{Zn}^{65}\text{Cl}_2$ in HCl solution (0.90N) was obtained from the Oak Ridge, Tennessee facility of the United States Atomic Energy Commission. The volume of this sample was 0.2 ml. with a concentration of 71.1 mg. Zn per ml. The activity of the sample was 7.13 ± 10 per cent mc. per ml. or 0.100 mc. per mg. This isotope had a half-life of 250 days and emitted 1.1 Mev. gamma radiation.

Determinations of the molarity of the original Zn^{65} sample diluted to 10 ml. were made by titrating small samples of about 0.1 ml. with E.D.T.A.-disodium salt. See Appendix D for the experimental details of this analysis. The molarity of this 10 ml. solution was found to be 0.033 with respect to ZnCl_2 . Using this result, the same type of procedure as that described for Fe^{59} was used in obtaining radioactive solutions of Zn(II) of suitable activity and concentration. In this case $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ was the "diluting" salt for the radioactive ZnCl_2 .

Ethylenediamine Tetraacetic Acid-Disodium Salt

This material was used as received from Distillation Products Industries division of Eastman Kodak Company.

Aqueous Ammonia

This product, containing 28 to 30 per cent NH_3 , was obtained from du Pont. It was used as received.

Ammonium Chloride

This material, along with the aqueous ammonia, was used in preparing a buffer solution for the E.D.T.A. titrations. The NH_4Cl used was obtained from Merck and Company as C.P. grade material.

Eriochrome Black R (Erio T)

This compound, mixed with NaCl in 1 to 100 weight proportions, served as the indicator for the E.D.T.A. titrations of Zn(II) . It was furnished by Dr. H. A. Flaschka of this institution.

S.E.-30 Silicone Grease

In the preparation of the V.P.C. column (Appendix A), this material was used as the liquid phase. It was used as obtained from the General Electric Company.

Chromasorb P

This product was obtained from the Johns-Manville Company. It was treated before use in the V.P.C. column according to procedures given in Appendix A.

ProcedurePreparation of Hydrogenation Equipment

Careful techniques of cleaning and handling of apparatus and equipment in this work was necessary for two reasons. The first reason

was the well-known effect impurities of various types may have on catalytic hydrogenations. This was especially significant in this work because the effect of added "impurities" was studied in cinnamaldehyde hydrogenation using Adams' catalyst. The second obvious reason was the necessary precautions against spreading radioactive contamination when radioactive materials were used.

All pressure tubing used with the Parr apparatus was boiled with concentrated NaOH solution with at least three changes of solution being made. The tubing was then boiled with several changes of tap water and finally with at least three changes of distilled water.

The inside of the short piece of copper tubing used to connect the reaction bottle with the pressure tubing from the three-way valve was cleaned with a length of pipe-cleaner soaked in methanol followed by drying with a length of dry pipe cleaner. The rubber stopper attached to this tubing was cleaned with a piece of paper towel soaked in methanol with the excess methanol being removed by a piece of dry paper towel. This cleaning procedure of the stopper and copper tubing was performed before and after each hydrogenation experiment.

The reaction bottles were cleaned thoroughly with a brush using a common detergent and tap water, rinsed well with tap water and then filled with $\text{H}_2\text{SO}_4\text{-Na}_2\text{Cr}_2\text{O}_7$ cleaning solution. This cleaning solution was left in the bottles for at least six hours. Following this period, the bottles were rinsed well with tap water and then three times with about 200 ml. portions of distilled water. After the final rinse the excess water was permitted to drain from the bottles and they were placed in an electric drying oven for drying at 110°C . After at least six hours in

the drying oven they were removed and capped with aluminum foil until needed. It was found that the same procedure for cleaning the reaction bottles could be used when radioactive materials were used provided a rinse was used before cleaning with detergent and water. This rinsing liquid was added to the radioactive liquid waste collected during the course of this work.

Hypodermic syringes used in this work were rinsed several times with acetone after each use and kept in an electric drying oven until used again.

Pipettes were cleaned with the chromic acid solution followed by rinsing in tap water and finally by rinsing in distilled water. Pipettes used in handling radioactive solutions were not cleaned after each use. However, these pipettes were used only for a given radioactive solution and were rinsed well in that solution prior to their use.

Hydrogenation Procedure

After the hydrogenation apparatus and other equipment had been cleaned it was then ready for use. The following procedure is typical of the many hydrogenations carried out during this work. Exceptions to this general procedure will be noted at the appropriate points in this description.

The solvent was measured into the reaction bottle from a 100 ml. graduated cylinder. A given volume of cinnamaldehyde was next added by use of a hypodermic syringe. A given weight of catalyst, which had been weighed to the nearest tenth of a mg. on a tared watch glass, was then placed in the bottle by use of a camel's hair brush. If benzoic acid was used as the hydrogen acceptor it was added to the solvent in the same

manner as that used for the catalyst. If solutions of Fe(III), Fe(II), or Zn(II) were added, they were pipetted into the bottle following addition of the catalyst. In such cases the volume of original solvent was adjusted so that the final total volume would be the same in all such cases. In a few experiments the total volume of solvent came from the ion solutions. In these experiments the charge order was ion solution (pipetted), cinnamaldehyde (by syringe), and then catalyst.

The reaction bottle, charged with reagents, was next placed in the bottle holder of the Parr apparatus and connected to the three-way valve. By proper use of the valves the following procedure was carried out: the reaction bottle was opened to the evacuation system until the solvent began to boil; hydrogen was admitted to the reaction bottle at about 50 lbs. pressure; and again the bottle was opened to the evacuation system until the solvent boiled or at least for several minutes. This purging cycle was repeated twice more to assure that essentially all of the air had been removed from the system.

Following the final purge, the reaction bottle was opened to the hydrogen reservoir and the pressure adjusted so that the gauge pressure indicated at least 50.00 p.s.i. The barometer was read to ascertain the atmospheric pressure. The total pressure, gauge plus atmospheric, was then recorded to the nearest 0.05 lb. The temperature of the hydrogen reservoir was recorded. The system was allowed to remain at this stage for at least five minutes while the gauge pressure was watched in order to assure that pressure leaks were absent in the system. If the pressure remained constant during this period, the reaction was started by switching on the electric motor which powered the bottle shaking assembly. At

the same time a stopwatch was started. Gauge pressure readings at one-half minute intervals were continued for the first 6 to 10 minutes. After this period, one or two minute intervals were used up to 30 to 50 minutes. Usually, the reaction was complete or else very slow at the end of the first 30 minutes. In some cases the reaction was permitted to continue for several hours. Besides giving information on "final" values of hydrogen absorption for the slow reactions, these extended reaction periods permitted a further check on the presence of leaks in the system.

At the conclusion of the reaction period the bottle shaker was switched off and the three-way valve was adjusted so that the reaction bottle was opened to the evacuation system but closed to the hydrogen reservoir. The bottle was evacuated until the solvent began to boil or at least for several minutes. After the excess hydrogen had been removed the bottle was opened to the atmosphere. The bottle was then removed from its holder and capped with aluminum foil. In those experiments in which the catalyst was not isolated for metal ion adsorption measurements, the catalyst was filtered with suction from the reaction mixture by use of a fine porosity sintered glass filter tube. In these instances the reaction mixture was then discarded or else retained for V.P.C. analysis.

Catalyst Isolation Procedure

For those experiments in which radioactive metal ion solutions were added to the reaction mixture, the isolation of the catalyst from each reaction mixture required a different procedure from that just described. This procedure involved the use of a small, 15 ml. capacity,

Buchner type funnel and suction flask equipped with two traps as a safety precaution. Suction was obtained by either a water-aspirator or house vacuum. The filter paper for use on the small funnel was cut to fit the bottom of the funnel from analytical grade filter paper of very fine porosity. After the reaction bottle and its contents had been permitted to stand for the desired length of time, the contents were swirled vigorously and then poured in several portions on the funnel while suction was being applied. As the last liquid passed through the filter the suction was stopped and 15 ml. of reaction solvent which had been used to rinse out the reaction bottle was placed on the funnel. This liquid was stirred in contact with the catalyst for three to five minutes before suction was reapplied. In some cases additional washes of the catalyst were performed with 10 to 15 ml. portions of the reaction solvent using the procedure just described with the exception that these portions were not used to rinse the bottle. While suction was being applied after the last washing, several ml. of distilled water was used to wash down catalyst particles adhering to the walls of the funnel. Suction was stopped before the catalyst was completely dry and the catalyst and filter paper was transferred to a plastic counting tube with the aid of a stainless steel spatula and pair of tweezers. Any catalyst remaining on the funnel after this step was wiped up with a small piece of dampened filter paper held by tweezers. This paper was also added to the counting tube. The transfer of the catalyst while it was still slightly damp was necessary since the dry catalyst could become a source of air-borne radioactive contamination, and in addition would be difficult to handle in terms of loss during

transfer. The outside and stopper of the counting tube containing the catalyst was wiped thoroughly with a dampened piece of paper towel before it was used to measure radioactivity of the catalyst sample.

Certain radioactive "standard" catalyst samples were required in this work. Their preparation involved weighing out a given amount (0.200 g.) of PtO_2 into a 10 ml. beaker, carefully pipetting a known volume of the radioactive Fe(II) or Zn(II) solution whose concentration is known on to the PtO_2 , covering the beaker loosely with aluminum foil, and then allowing the solvent to evaporate at room temperature in a hood. This standard sample was then carefully transferred to a counting tube by means of a stainless steel spatula. The fact that the standard catalyst sample is PtO_2 whereas the catalyst samples obtained in the hydrogenation experiments are reduced PtO_2 is considered to be of little significance since the primary concern is to obtain a standard that is only approximately the same in size and composition as the experimental samples.

Counting Procedure for Radioactive Catalyst Samples

The use of a gamma scintillation counter in this work required the establishment of reliable and reproducible operating conditions for the instrument. This was accomplished by measuring the count rate vs. applied voltage at 50 volt intervals for each of the two combinations of gamma counters and scalers used in this work. Such measurements were also required for each of the two sources of radiation used, i.e., Fe^{59} and Zn^{65} in a given counter combination. The purpose of these measurements was to locate precisely the voltage range where the count rate did not change appreciably with a change of voltage. The voltage

from the middle to lower end of this plateau region was found suitable for an operating voltage. In all cases it was found that from 1,000 to 1,100 volts was best suited for this work.

The overall efficiency of counting of the scintillation counters used in this work was 65 per cent for I^{131} gamma rays according to the manufacturer's specifications. However, since measurements of radioactivity in this work were all related to a standard sample, compensation for the efficiency factor was automatically made. The geometry factor in counting efficiency was also of no importance in this work since all samples were of approximately the same size and shape. Furthermore, the geometric efficiency was very high for these counters because the material containing the TII activated NaI scintillation crystals completely surrounded the sample tube except for the space directly above the tube.

The background count was determined before and after each period of extended counting in which the radioactivity of a number of catalyst samples was determined. The background determinations were necessary to assure the proper operation of the instrument and also to assure that extraneous sources of radiation had not contaminated the sample holder. If the background count was in the correct range for the instrument in use, the counting of the standard and experimental samples was begun. The standard was usually counted first which established a direct relationship between the count rate and the amount of Fe(II) or Zn(II) ions present on that sample. Using this established relationship, the amount of ions adsorbed on the samples of catalyst obtained from the hydrogenation experiments could be easily found by comparison

of their count rates with that of the standard. The use of this simple relationship depends on the reasonable assumption that there is no selective adsorption of either the radioactive ions or non-radioactive ions on the catalyst during the hydrogenation experiments. Kinetic data using non-radioactive ion solutions and radioactive ion solutions indicated the radiation emitted by the radioactive ions was not affecting the activity of the catalyst to a noticeable degree. This agrees with the results of Graham (33) who found a negligible effect on the activity of a carbon supported platinum catalyst when this catalyst was irradiated with two Mev. x-rays.

In order to cancel out decay effects of the radioactive samples, the standard catalyst was counted each time a counting session was performed on catalyst samples obtained from experiments using the same radioactive solution as that which was used in preparing the standard.

Kinetic Data Treatment

General Rate Behavior in Heterogeneous Catalytic Reactions

Investigations of many different reactions occurring at the surface of a catalyst have shown the presence of the following elementary consecutive steps (34): 1. diffusion of reactants to the catalyst surface; 2. chemisorption of the reactants on the surface; 3. chemical reaction on the surface; 4. desorption of products from the surface; and 5. diffusion of products away from the surface. Any one of

(33) D. Graham, J. Phys. Chem., 66, 510 (1962).

(34) W. J. Moore, Physical Chemistry, Second Edition, Prentice-Hall, Inc., New York, 1955, p. 581.

these steps may be the rate-controlling step if it is much slower than all the others. Cases are known in which diffusion, steps 1 or 5, are rate controlling. Other cases are known where steps 2 or 4 become rate controlling. Generally speaking, however, step 3 is found to be the rate-determining step for most heterogeneous catalytic reactions. For such reactions, the data obtained in kinetic experiments should be amenable to treatment by the usual methods of expressing rates of reactions.

The rate of a reaction is usually defined (35) as the rate of change of concentration of a substance involved in the reaction with a minus or plus sign attached, depending on whether the substance is a reactant or product, respectively. Thus, for a general reaction of the stoichiometry indicated,



the rate may be expressed by

$$- d [A]/dt \quad (2)$$

where t is time and the brackets indicate molar concentration. Corresponding terms with the appropriate sign may be written for B, C, and D. In any case, the proper sign is chosen so that the rate will be positive numerically. The functional relationship between the rate and concentration

(35) A. A. Frost and R. G. Pearson, Kinetics and Mechanism, Second Edition, John Wiley and Sons, Inc., New York, 1961, p. 9.

found for a reaction under a given set of experimental conditions is termed the rate expression. For many reactions this rate expression may be written as a product of powers of concentrations. Using equation (1) as an example, the rate expression would be written as

$$- d[A]/dt = k [A]^{n_1} [B]^{n_2} [C]^{n_3} [D]^{n_4} . \quad (3)$$

For such cases, the order of the reaction, n , is defined (36) by the sum of the exponents as

$$n = n_1 + n_2 + n_3 + n_4 . \quad (4)$$

Furthermore, each individual exponent is called the order with respect to that reaction component. It should be noted that these individual exponents may be simple positive integers, but if the reaction is complex they may be fractional or even negative. The k in equation (3) is called the rate constant for that reaction. It is also seen from equation (3) that k has the dimensions of concentration¹⁻ⁿ time⁻¹.

If experimental conditions are chosen such that one or more of the concentration factors remains very nearly constant during the kinetic experiment, these factors may be included in the constant k . The reaction then is said to be of pseudo- n th order and the new rate constant may be called a pseudo rate constant or apparent rate constant. For example, if the reaction conditions for equation (1) are chosen such

(36) Ibid, p. 10.

that the concentration factors of B, C, and D remain essentially constant, equation (3) reduces to

$$- d[A]/dt = k' [A]^{n_1}, \quad (5)$$

where k' is the apparent rate constant. Rearranging of this equation gives

$$- d[A]/[A]^{n_1} = k' dt \quad (6)$$

Equation (6) can now be integrated choosing as the limits of integration $[A] = [A_0]$ at $t = 0$ and $[A] = [A_t]$ at $t = t$. This integration gives

$$\log \frac{[A_0]}{[A_t]} = \frac{k' t}{2.303} \quad (7)$$

after conversion to base 10 logarithms. A value for k' can now be obtained by plotting $\log \frac{[A_0]}{[A_t]}$ vs. t for the reaction which, of course, presupposes an accurate rapid method of determining $[A_0]$ and especially $[A_t]$. From such a plot a straight line is obtained whose slope multiplied by 2.303 gives the value for k' in reciprocal time units.

For many reactions the variation of rate with temperature can be expressed by the Arrhenius equation:

$$d \log k/dT = E/2.303RT^2 \quad (8)$$

The integrated form of this equation,

$$\log \frac{k_2}{k_1} = \frac{E}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (9)$$

where k_2 and k_1 are the rate constants at the respective temperatures, T_2 and T_1 , and E is an activation energy, can be used to convert a rate constant determined at one temperature to a rate constant valid for a second temperature. This is possible if the activation energy, E_a , is known for the reaction and provided E_a does not change appreciably with temperature in the range of temperature involved. The use of equation (9) can usually be made regardless of whether the rate constants involved are "true" or "apparent" rate constants.

Rate Expressions for Catalytic Hydrogenations at Low Pressures Using Adams' Catalyst in a Liquid Phase

Smith and co-workers (37)(38)(39) and others (40) have shown the rate expression for a variety of hydrogenations using Adams' catalyst in a liquid phase has the form

$$-\frac{dp}{dt} = k'p \quad (10)$$

(37) H. A. Smith, D. M. Alderman, and F. W. Nadig, J. Am. Chem. Soc., 67, 272 (1945).

(38) H. A. Smith and E. F. H. Pennekamp, J. Am. Chem. Soc., 67, 276 (1945).

(39) Ibid., p. 279.

(40) R. H. Baker and R. D. Schuetz, J. Am. Chem. Soc., 69, 1250 (1947).

where p is the hydrogen pressure. This means the reaction is zero order with respect to the substance being hydrogenated and first order with respect to H_2 pressure. If one assumes H_2 is behaving as an ideal gas, equation (10) also indicates the H_2 concentration is directly proportional to its pressure as would be expected from the use of the Ideal Gas Law.

Treatment of equation (10) in the same manner as that used for equation (5) gives

$$\log \frac{P_o}{P} = \frac{k' t}{2.303} \quad (11)$$

as the result.

If comparisons of rate constants are to be made which were obtained by the use of reaction vessels and reservoirs of different volumes it is necessary (41)(42) that a volume term be included in equation (11) thus giving

$$\log \frac{P_o}{P} = \frac{k'' t}{2.303V} \quad (12)$$

(41) J. F. Fuzek and H. A. Smith, J. Am. Chem. Soc., 70, 3743 (1948).

(42) H. A. Smith, W. C. Bedoit, Jr., and J. F. Fuzek, J. Am. Chem. Soc., 3769 (1949).

By comparing equations (11) and (12) it is seen that

$$k'' = k' V \quad (13)$$

In this work the volume of the apparatus used was approximately 4.4 liters. Since the volume was kept essentially constant throughout this work, the values for the rate constants reported are those obtained from the use of equation (11).

An equation of an even more general nature than (12) has been derived by Schuetz, et al., (43). This equation makes allowance for the fact that the temperature of the reaction chamber may be different from the rest of the hydrogen containing apparatus. This equation has the following form:

$$\log \frac{P_o}{P} = \frac{R k''' t}{V_1/T_1 + V_2/T_2} \quad (14)$$

where R is the gas constant, V_1 and T_1 are the volume and temperature of the reaction chamber, and V_2 and T_2 are the volume and temperature of the remainder of the apparatus. At temperatures above usual room temperatures equation (14) gives better results than equation (12) according to these workers. These same workers also noted "puzzling" results with the use of high pressures in their studies, i. e., the apparent activation energy of benzene hydrogenation over Adams' catalyst

(43) R. D. Schuetz, L. R. Caswell, and J. C. Sternberg, J. Org. Chem., 34, 1080 (1959).

was essentially zero at 1,200 p.s.i. H_2 pressure. Since high pressures and high temperatures were not used in this work, the use of equation (11) was justified for this work.

In some cases (37) the rate was directly proportional to the amount of catalyst used. However, Csürös (18) noted a rather complex relationship between the rate and the amount of catalyst and claimed this to be generally valid, although Adams' catalyst was apparently not used in that work. Since the work reported herein used a constant weight of catalyst in the kinetic runs, the rate dependence on catalyst amount was not determined. For this reason, it is assumed that the order of the reaction relative to the catalyst is zero for purposes of this work. In accordance with common practice in catalytic work, the rate constants found were divided by the weight of catalyst used so that the k' finally obtained had the dimensions of $g.^{-1} \text{ time}^{-1}$.

In order to make convenient comparisons of rate constants obtained in this work at varying room temperatures it was necessary to refer such constants to a standard temperature by use of equation (9), the integrated Arrhenius equation. The temperature chosen as the standard was 30°C . The use of equation (9) required a knowledge of E_a . Since this value was not known for cinnamaldehyde, an arbitrary value of 8,000 calories per mole, which is an average value for many hydrogenations, was chosen.

If $\log \frac{P_0}{P}$ was plotted against t for cinnamaldehyde hydrogenations it was observed that the plot was linear for the first 3 to 5 minutes. This indicated a first order dependence on H_2 pressure over the time range indicated. However, like many catalytic hydrogenations,

deviation from linearity appeared as the reaction progressed. This deviation was observed in the form of a rate that became progressively slower as t increased. Several explanations for this behavior might be given. One likely explanation is found in the possibility of competition for the catalyst surface between cinnamaldehyde and a half-hydrogenated intermediate. If this intermediate reacts at a slower rate than cinnamaldehyde, then such a rate decrease with time would be expected. Furthermore, if the rate of cinnamaldehyde reaction is not too much greater than that of the intermediate, one would not expect to obtain a rate curve made of two straight lines of different slopes but would instead obtain an initial linear plot followed by a curving plot of changing slope. Regardless of what the cause may be, the incursion of this change of rate with time required that only the initial linear portion of the rate curve be used to obtain the rate constant for cinnamaldehyde hydrogenation. Therefore, in this work the presentation of rate data will be in terms of "initial" rate constants.

An item of practical interest might be noted here. Observations of pressure changes in these kinetic runs and other hydrogenations permitted a calibration of the pressure gauge used in terms of lbs. of hydrogen pressure change and moles of hydrogen reacted. It was found a mole of hydrogen absorbed would correspond to a drop in pressure of 85 lbs. on the gauge. Use of this factor permitted the reaction to be stopped at any desired state of completion. This was particularly useful in the product analysis work.

CHAPTER III

DISCUSSION OF RESULTS

Hydrogenation of Benzoic Acid

In the beginning of this work, the hydrogenation of benzoic acid was used as a familiarization procedure with the apparatus and experimental techniques involved. These experiments also serve as a convenient standard for comparing the activity of the catalyst used in this work to that which might be used by other workers under otherwise similar conditions. This is possible because benzoic acid is readily obtained in a pure state and undergoes a convenient rate of hydrogenation. In addition, certain experiments were carried out in which benzoic acid was hydrogenated in the presence of a radioactive Zn(II) solution. The primary purpose of these experiments was to note any large effects on the extent of Zn(II) adsorption on the catalyst caused by a change in the substance being reduced. In order to avoid repetition of data, presentation of the data obtained with benzoic acid as the hydrogen acceptor is shown in Table 1.

The data in Table 1 show k'_{30} g.⁻¹ min.⁻¹ x 10⁴ had an average value of 174 in the absence of Zn(II) ions. These reactions went to completion in 26 to 30 minutes. On the other hand, if 10×10^{-6} mole Zn(II) was present k'_{30} had an average value of 162. The reaction was not followed to completion in these cases, but for B 42 the reaction was 92 per cent complete in 44 minutes and the same was true for B 40 in 50 minutes.

Table 1. Hydrogenation of Benzoic Acid in the Absence and Presence of Added Zn(II) Ions

Conditions: 0.020 mole benzoic acid, 0.200 g. PtO_2 ; 50 ml. acetic acid solvent; 64.5 ± 0.3 p.s.i.a. initial H_2 pressure.

Experiment Number	P_0 in P.s.i.a.	Moles Zn(II) Added $\times 10^6$	Moles Zn(II) Adsorbed $\times 10^6$	Per Cent Adsorbed	$k_{30}^{\text{g.}} \cdot \text{min.}^{-1} \times 10^4$
A 6	64.40	-	-	-	179
A 7	64.35	-	-	-	174
A 8	64.30	-	-	-	170
B 42	64.65	-	-	-	173
B 38	64.65	10	2.3	23	160
B 40	64.60	10	2.4	24	165

The results showed a definite poisoning effect of Zn(II) on the hydrogenation of benzoic acid under the conditions involved. Inspection of the data also seemed to indicate no observable dependence of the rate on P_0 in the range involved. This fact simplified the kinetic runs since it was time consuming to adjust P_0 to the same value for each experiment. The Zn(II) ion adsorption data for benzoic acid hydrogenations will be discussed later when similar data for cinnamaldehyde are presented and the results compared.

Hydrogenation of Cinnamaldehyde in the Absence
of Added Fe(III), Fe(II), or Zn(II) Ions

Purity of the Cinnamaldehyde

In the initial stages of this work it was of interest to compare

the hydrogenation behavior of cinnamaldehyde used as received with that obtained by fractional distillation of the material.

In three experiments using undistilled cinnamaldehyde, it was evident that reliable kinetic data could not be obtained unless pressure readings at less than two-minute intervals were used. In the work with benzoic acid, two-minute time intervals could be used since the reaction rates appeared to remain constant for the first 16 to 18 minutes of the reaction period. The reaction rate plots for cinnamaldehyde, however, began to deviate from linearity at about four to five minutes. In view of this behavior, 0.5 minute intervals were chosen for all further kinetic experiments. One further experiment then was carried out using undistilled cinnamaldehyde. The results of this experiment, A 13, are included in Table 2 with the results of a number of other runs using fractionally distilled cinnamaldehyde. The results shown in Table 2 for moles of H_2 absorbed represent values obtained for the particular reaction temperature at times after which the reaction appeared to be extremely slow, *i.e.*, no additional hydrogen was absorbed in 12 to 20 minutes after the time indicated. However, no attempt was made in these cases to determine if the reaction went to completion.

Calculations show the reduction of PtO_2 (0.200 g.) should require 0.0018 mole of H_2 if it is non-hydrated or 0.0016 mole if it is the mono-hydrate as indicated by Adams and Shriner (5). Expressing this in terms of the pressure drop shown by the gauge, meant the first 0.15 lb. of H_2 absorbed was used to reduce the PtO_2 to Pt, if it was assumed this reduction was complete before hydrogenation of the cinnamaldehyde commenced. Thus, complete hydrogenation of the ethylenic

Table 2. Hydrogenation of Cinnamaldehyde in the Absence of Added Metal Ions

Conditions: 0.012 mole cinnamaldehyde; 0.200 g. PtO_2 ; 50 ml. solvent; 64.6 ± 0.5 p.s.i.a. initial H_2 pressure.

Experiment Number	Moles H_2 , Absorbed @ Time, Min.	Solvent	$k'_{30} \text{ g.}^{-1} \text{ min.}^{-1} \times 10^4$
A 13 ^a	0.022 @ 18	$\text{C}_2\text{H}_5\text{OH}(95\%)$	346
A 18	0.018 @ 14	$\text{C}_2\text{H}_4\text{O}_2(\text{glacial})$	271
A 20	0.021 @ 16	$\text{C}_2\text{H}_4\text{O}_2(\text{glacial})$	324
A 22	0.021 @ 26	$\text{C}_2\text{H}_4\text{O}_2(\text{glacial})$	296
C 30	0.022 @ 18	$\text{C}_2\text{H}_4\text{O}_2(\text{glacial})$	283
A 24	0.024 @ 24	$\text{C}_2\text{H}_5\text{OH}(95\%)$	220
A 26	0.025 @ 22	$\text{C}_2\text{H}_5\text{OH}(95\%)$	245
A 28	0.021 @ 20	$\text{C}_2\text{H}_5\text{OH}(95\%)$	235

(a) This run used undistilled cinnamaldehyde

and carbonyl groups in 0.012 mole cinnamaldehyde, including catalyst reduction, should have required 0.026 mole H_2 . From Table 2, only experiments A 24 and A 26 approached this value at the times indicated.

The rate constants in Table 2 permit some useful observations to be made. The average value of k'_{30} for runs in glacial acetic acid was 294, while in 95 per cent ethanol the average value of k'_{30} was 233. All of these results were obtained using distilled cinnamaldehyde. In glacial acetic acid the average deviation from the mean value was 5 per cent. In 95 per cent ethanol, the average deviation was 4 per cent.

For the first four experiments in Table 1 this value was 1 per cent. It was thus generally observed in this work that the agreement between individual rate constants was better for those reactions which had "moderate" rates. While it is clear the rates in glacial acetic acid were greater than those in 95 per cent ethanol, it appears the H_2 absorption was slightly greater for the latter solvent.

Experiment A 13 using undistilled cinnamaldehyde in 95 per cent ethanol showed a somewhat surprising result. The rate obtained in this case was greater even than those using distilled cinnamaldehyde in glacial acetic acid. The lower initial rates for experiments using distilled cinnamaldehyde indicated the accelerated rate observed for A 13 was not truly indicative of "pure" cinnamaldehyde. This effect may have been due to cinnamic acid or some other impurity present in the undistilled material. However, it was not investigated further.

Experiment C 30 was actually a control experiment in a series when radioactive Fe ions were to be used. It was included in Table 2 to indicate reproducibility of results since it was carried out at a much later date using completely different "batches" of distilled cinnamaldehyde and solvent. It also involved the use of a reaction bottle which was five ml. larger than those used for the other experiments in Table 2. The result tended to show the solvent and cinnamaldehyde could be reproducibly purified by distillation and the minor change in apparatus did not observably affect the rate of the reaction.

Effect of Added NaOH in 95 Per Cent Ethanol as Solvent

The use of ethanol as a solvent for hydrogenation of aldehydes may sometimes be complicated by hemiacetal and/or acetal formation. The

presence of a small amount of NaOEt or NaOH is said (9) to prevent the formation of these compounds in ethanol. Since 95 per cent ethanol was one of the solvents used in cinnamaldehyde hydrogenations it was of interest to obtain an indication of the effect of added NaOH in these cases. Two duplicate experiments were performed to observe this effect, A 30 and A 32. In each case P_0 was 64.30 p.s.i.a. with 0.200 g. catalyst, 0.012 mole cinnamaldehyde, 0.5 ml. 3 N NaOH, and 50 ml. 95 per cent ethanol as the reaction mixture. In both cases an initial slow absorption of H_2 was observed followed by a rapid absorption which stopped abruptly after a total of only 0.018 mole had been absorbed. The "induction period" for A 30 appeared to last for 4.5 minutes while for A 32 it appeared to last for 3.0 minutes. The values of $k'_{30} \text{ g.}^{-1} \text{ min.}^{-1} \times 10^4$ were determined from the linear portions of the rate curves just following the induction periods. For A 30 k'_{30} was 297 and for A 32 k'_{30} was 333.

It was of considerable significance that the induction periods lasted until approximately 0.15 lb. H_2 had been absorbed. The agreement of this value with the value calculated for complete reduction of PtO_2 to Pt is not likely to be merely coincidental. If it is not coincidence, it indicates the added NaOH under these conditions has a marked effect on the rate of PtO_2 reduction to Pt, a reaction thought to be auto-catalytic. While it cannot be said with certainty what the reason is for this effect, it may very well be a poisoning of the PtO_2 surface by Na ions which prevents or hinders the adsorption and reaction of H_2 on the PtO_2 . Evidence to support such a view is indicated by the work of Smith, et al., (16) who found benzene could be reduced without

the use of a solvent using sodium-free Adams' catalyst. On the other hand, Adams' catalyst, which contained a sodium compound as an impurity from its preparation, required the use of solvents or additives to hydrogenate benzene. The function of these solvents or additives appeared to be to remove the sodium compound from the catalyst, according to these workers.

From a practical standpoint, the results obtained from A 30 and A 32 show the addition of base to ethanolic hydrogenation mixtures of cinnamaldehyde probably will not aid these reactions in going to completion. In fact, for these specific experiments, the addition of base caused the "final" absorption of H_2 to be less than those cases (see Table 2) where no base was added. Based on these results, it was decided to discontinue this particular area of work in cinnamaldehyde hydrogenations.

Hydrogenation of Cinnamaldehyde
in the Presence of Added Zn(II) Ions

Effect of Added Zn(II) on the Initial Rate

Although acetic acid was chosen as the solvent for the majority of the experiments which dealt with kinetic and ion adsorption data, a few experiments were used to observe the effect of added Zn(II) in 95 per cent ethanol. The results obtained in these experiments are shown in Table 3.

Comparison of the results from A 52, A 54, and A 56 with those in Table 2 obtained using the same solvent indicated that Zn(II) at the 5×10^{-6} mole level had no effect on the rate. However, at the 2×10^{-5} mole level a very slight increase in rate was found and the reaction appeared to go to completion in this case.

Table 3. Hydrogenation of Cinnamaldehyde in the Presence of Zn(II) Ions in 95 Per Cent Ethanol

Conditions: 0.012 mole cinnamaldehyde; 0.200 g. PtO_2 ; 50 ml. 95 per cent ethanol solvent; 64.4 ± 0.1 p.s.i.a. initial H_2 pressure; and Zn(II) added as acetate (5×10^{-3} M in 95 per cent $\text{C}_2\text{H}_5\text{OH}$).

Experiment Number	Moles H_2 , Absorbed @ Time, Min.	Moles Zn(II) Added, $\times 10^6$	k'_{30} g. ⁻¹ min. ⁻¹ $\times 10^4$
A 52	0.021 @ 38	5	237
A 54	0.022 @ 28	5	232
A 56	0.026 @ 36	20	245

Two other experiments, B 122 and B 130, used 93 per cent ethanol as solvent. Table 4 shows the results obtained in these experiments.

Table 4. Hydrogenation of Cinnamaldehyde (0.020 mole) in the Absence or Presence of Zn(II) Ions

Conditions: 0.020 mole cinnamaldehyde; 0.200 g. PtO_2 ; 54 ml. 93 per cent ethanol solvent; 64.4 ± 0.1 p.s.i.a. initial H_2 pressure; and Zn(II) added as acetate (10^{-2} M in absolute $\text{C}_2\text{H}_5\text{OH}$).

Experiment Number	Moles H_2 , Absorbed @ Time, Minutes	Moles Zn(II) Added, $\times 10^6$	k'_{30} g. ⁻¹ min. ⁻¹ $\times 10^4$
B 122	0.026 @ 114	100	187
B 130	0.039 @ 90	None	259

If the slight change in solvent is neglected, the single experiment, B 130, when compared with the results of A 24, A 26, and A 28 in

Table 2, indicated an 11 per cent increase in rate when the concentration of cinnamaldehyde was increased 54 per cent. On the same basis, B 122 showed a significant decrease in rate in spite of the increase in cinnamaldehyde concentration over that used in A 56. The difference here was in the level of Zn(II) added, 20×10^{-6} mole in A 56 and 100×10^{-6} in B 122.

Based on the results of these few experiments in ethanolic solvents, it appeared that the relationship between the amount of added Zn(II) and the initial rate was not an exceedingly simple one. Evidence for a complex dependence of k'_{30} on the amount of added Zn(II) was more clearly shown in the experiments using glacial acetic acid as the solvent. Such experiments are discussed in the following section.

A total of 51 experiments in acetic acid were performed from which values of the initial rate constants and H_2 absorption could be obtained when Zn(II) ions had been added to the hydrogenation mixtures. Of this number, 43 used comparable reaction conditions. The remaining eight experiments involving a change in cinnamaldehyde concentration and other variables will be reserved for discussion later in this section. The majority of the 43 experiments used radioactive solutions of Zn(II) as the source of Zn(II) ions. Those experiments using a non-radioactive Zn(II) solution are noted in Table 5. In Table 5 the rate constants and H_2 absorptions for a range of added Zn(II) from 0.05×10^{-6} mole to 250×10^{-6} mole are given.

Variations in the solvent for the Zn(II) ions are noted in Table 5. If it was assumed that these changes in solvent for the Zn(II) ions had a negligible affect on the initial rates, at least in the volume range

Table 5. The Effect of Added Zn(II) on k'_{30} and H_2 Absorption

Conditions: 0.012 mole cinnamaldehyde; 0.200 g. PtO_2 ; 64.5 ± 0.6 p.s.i.a. initial H_2 pressure; and 50 ml. acetic acid solvent. Zn(II) added as acetate and chloride in acetic acid.

Experiment Number	Moles H_2 , Absorbed @ Time, Minutes	Moles Zn(II) Added, $\times 10^6$	k'_{30} g. ⁻¹ min. ⁻¹ $\times 10^4$	
A 84 ^a	0.021 @ 20	0.050	334	
A 92 ^a	0.017 @ 18	0.050	300	
A 86 ^a	0.018 @ 28	0.250	265	
A 94 ^a	0.016 @ 22	0.250	232	
A 96 ^a	0.015 @ 20	0.250	220	238(ave.)
A 98 ^a	0.015 @ 20	0.250	227	
A 106 ^a	0.017 @ 12	1.25	266	
A 108 ^a	0.017 @ 16	1.25	263	
A 102 ^a	0.017 @ 16	2.50	276	
A 104 ^a	0.017 @ 18	2.50	275	
A 70 ^a	0.021 @ 20	5.00	314	
A 90 ^a	0.020 @ 16	5.00	300	
A 100 ^a	0.018 @ 20	5.00	261	288(ave.)
A 120	0.018 @ 18	5.00	279	
A 122	0.018 @ 18	5.00	295	
A 124	0.017 @ 18	5.00	279	
A 74 ^a	0.020 @ 22	10.0	252	
A 78 ^a	0.016 @ 18	10.0	253	
A 80 ^{*b}	0.016 @ 14	10.0	266	
A 82 ^{*c}	0.016 @ 14	10.0	274	
A 114	0.019 @ 18	10.0	230	
A 116	0.018 @ 24	10.0	232	
A 118	0.019 @ 20	10.0	220	
A 140	0.020 @ 28	10.0	253	
A 142	0.021 @ 24	10.0	261	252(ave.)
A 144	0.020 @ 12	10.0	253	
A 146	0.021 @ 22	10.0	253	
B 10	0.021 @ 20	10.0	271	
B 12	0.020 @ 26	10.0	251	
B 14	0.019 @ 24	10.0	242	
B 24	0.018 @ 16	10.0	261	
B 26	0.021 @ 38	10.0	261	
B 28	0.021 @ 26	10.0	256	

(Continued)

Table 5 (continued). The Effect of Added Zn(II) on k'_{30} and H_2 Absorption

Conditions: 0.012 mole cinnamaldehyde; 0.200 g. PtO_2 ; 64.5 ± 0.6 p.s.i.a. initial H_2 pressure; and 50 ml. acetic acid solvent. Zn(II) added as acetate and chloride in acetic acid.

Experiment Number	Moles H_2 , Absorbed @ Time, Minutes	Moles Zn(II) Added, $\times 10^6$	k'_{30} g. ⁻¹ min. ⁻¹ $\times 10^4$
A 130	0.021 @ 24	25.0	203
A 132	0.021 @ 24	25.0	211
A 134	0.025 @ 28	50.0	167
A 136	0.026 @ 28	50.0	159
A 148	0.025 @ 32	100	138
A 150	0.025 @ 28	100	137
B 16	0.012 @ 32	250	40
B 18	0.014 @ 50	250	38
B 30	0.012 @ 60	250	45
B 32	0.012 @ 50	250	39

40(ave.)

(a) These experiments used a Zn(II) addition as the acetate and chloride (5×10^{-3} M or 5×10^{-5} M) in water.

(b) This experiment used a Zn(II) addition as the acetate in acetic acid (5×10^{-3} M).

(c) This experiment used a Zn(II) addition as the acetate in absolute ethanol (5×10^{-3} M).

(*) Indicates non-radioactive Zn(II) solution was used.

of added solutions involved, then it was possible to trace the dependence of k'_{30} on the amount of Zn(II) added over the entire range of Zn(II) levels used. The form of this dependence of k'_{30} on the amount of Zn(II) added and the amount of Zn(II) adsorbed is shown in Figure 1.

Although a detailed analysis of the H_2 absorption data was not made, it does appear from the data in Table 5 that a maximum for H_2

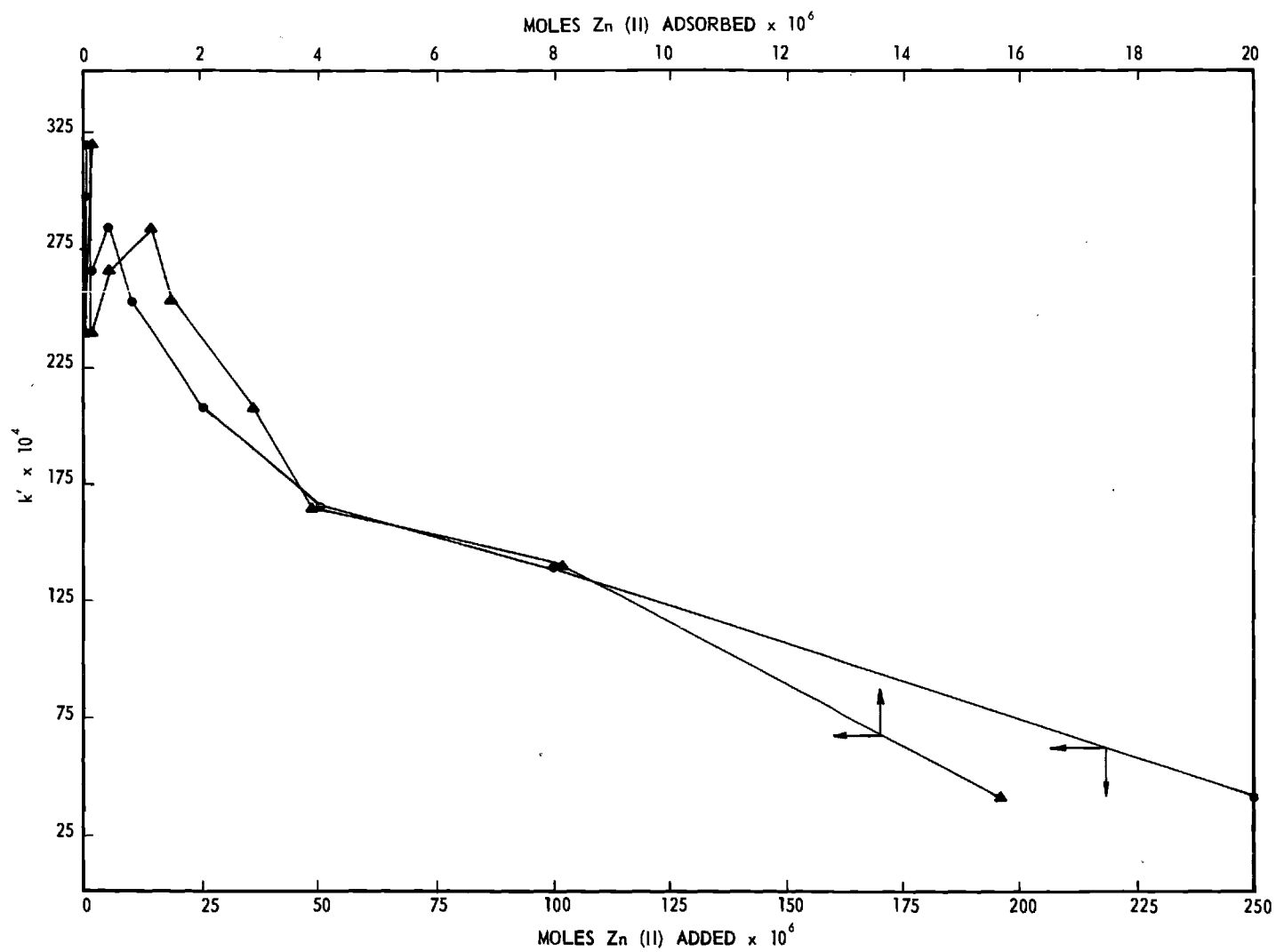


Figure 1. Dependence of k' on Amount of Zn(II) Added and Amount of Zn(II) Adsorbed.

absorption occurred at about 5×10^{-5} mole of added Zn(II). Indeed, only experiments A 134, A 136, A 148, and A 150 appeared to approach completion of the reaction under the conditions used.

Some experiments were carried out in acetic acid under experimental conditions significantly different from those just discussed. The results obtained in these experiments are shown in Table 6. Although some interesting observations can be made on the results in this table, such observations must be tentative since the amount of data is limited.

As was the case in ethanolic solvents, increasing the cinnamaldehyde concentration of 54 per cent gave an increase in rate. In acetic acid, this rate increase was about 17 per cent, whereas in ethanol a rate increase on only 11 per cent was noted (see page 48).

If the change in total volume of solvent is ignored, then an interesting effect of added H_2O is observed. In the case of experiments B 106 and B 112 the added H_2O did not affect the rate. On the other hand, in experiments B 94, C 14, and B 110 where no Zn(II) was present, the addition of H_2O appeared to decrease the rate.

At a 100×10^{-6} mole level of Zn(II) the reaction approached completion in these experiments. In Table 5 (Runs A 48 and A 50) it was shown that the same level of added Zn(II) ions gave a similar result for the series of experiments using 0.012 mole cinnamaldehyde. However, comparison of these same experiments indicated a slightly lower rate for those using the larger amounts of cinnamaldehyde, but the opposite result appears at the 10×10^{-6} mole level and, of course, when no Zn(II) was added.

Table 6. Hydrogenation of Cinnamaldehyde Under Modified Experimental Conditions

Conditions: 0.020 mole cinnamaldehyde; 0.200 g. PtO_2 ; 64.5 ± 0.2 p.s.i.a. initial H_2 pressure.

Experi- ment Number	Moles H_2 , Absorbed @ Time, Min.	Moles Zn(II) Added $\times 10^6$	Solvent Vol. in ml. and Composition	$k'_{30} \text{ g.}^{-1}$ $\text{min.}^{-1} \times 10^4$
B 88	0.024 @ 26	1.8	50 - glacial acetic acid	370
B 90	0.026 @ 18	9.1 ^a	50 - glacial acetic acid	390
B 92	0.026 @ 42	10.0	50 - glacial acetic acid	338
B 112	0.038 @ 92	100	50 - glacial acetic acid	121
B 106	0.040 @ 70	100	54 - 93% acetic acid	125
B 94	0.024 @ 26	None	50 - glacial acetic acid	330
C 14	0.023 @ 32	None	50 - glacial acid	360
B 110	0.019 @ 26	None	54 - 93% acetic acid	241

(a) In this experiment the Zn(II) was added as the chloride ($2.8 \times 10^{-2} \text{ M}$) in H_2O . For the remainder the Zn(II) was added as the acetate in glacial acetic acid ($5 \times 10^{-3} \text{ M}$).

Relation Between the Amount of Zn(II) Added and the Amount of Zn(II) Adsorbed on the Catalyst

One of the primary objectives of this work was to obtain measurements of the amount of Zn(II) ions adsorbed on the catalyst after its isolation from the reaction mixture to which Zn(II) ions had been added. Radioactive Zn(II) solutions were employed for this purpose according to the procedure described previously.

A simple but significant area of this work was the determination of the amount of Zn(II) adsorbed on the catalyst as a function of the amount of Zn(II) added to the reaction mixture. It was of particular interest to see if a linear relationship could be obtained in the range of added Zn(II) employed. Such a "linear poisoning curve" has been obtained by Maxted and co-workers (29)(44)(45) in a study of variety of different poisons on platinum catalyzed hydrogenations in solution. Of special significance to this work were the results obtained by Maxted and Evans (29). These workers hydrogenated crotonic acid (0.1 mole) in 10 ml. of acetic acid solvent using 0.05 g. of platinum black in the presence of added ZnSO_4 . They showed that a linear relationship between the amount of Zn(II) adsorbed and the amount of Zn(II) added existed in the range from 0 to about 1×10^{-6} moles of added Zn(II). At the latter level an inflection point occurred after which another linear portion of smaller slope appeared. Later (46) it was indicated the inflection in such curves took place over a region rather than at a point on the curve.

This same determination of the relation between the amount of adsorbed Zn(II) and the amount of Zn(II) added could provide information on the formation of a double layer of Zn(II) ions as the amounts of added Zn(II) increased. The double layer formation would be detected as a plateau in the plot of added vs. adsorbed Zn(II) followed by an increase in adsorbed Zn(II) as added Zn(II) increased.

(44) E. B. Maxted, J. Chem. Soc., 117, 1501 (1920).

(45) Ibid., 119, 225 (1921)

(46) E. B. Maxted, Trans. Faraday Soc., 41, 406 (1945).

The data for a number of experiments in which the amount of Zn(II) adsorbed on the isolated catalyst was determined are presented in Table 7. A plot of these data in terms of the amount adsorbed vs. the amount added is shown in Figures 2 and 3. Figure 2 is an expanded plot over the first portion of the range of Zn(II) used. Figure 3 is a complete plot of all the data. In making these plots only the averages of the amounts adsorbed at a given added amount were used. The doubtful results in Table 7 were not used in computing these averages.

The purpose of showing the expanded plot over the initial portion of the curve is to show that if an initial linear portion of this curve exists, it apparently must be between 0 and 0.05×10^{-6} or not more than 0.07×10^{-6} mole Zn(II) if a smooth curve is to be obtained in this lower region. It should be noted such a linear portion would be significantly shorter than the 0 to 1×10^{-6} range shown by Maxted and Evans (29). Since the curve shown in Figure 2 has the same number of points in about the same region as a like figure shown by Maxted and Evans, the difference in the curves merits some discussion. First, the obvious differences in conditions used must be kept in mind. The conditions used by these workers were noted earlier (see above p. 52). Foremost among these differences would be the amount of solvent and catalyst employed and also the amount and nature of the substrate being hydrogenated. With regard to this last difference, Herington and Rideal (47) have shown in a theoretical paper that if random adsorption is permitted on a catalyst surface the more complex the molecule being

(47) E. F. G. Herington and E. K. Rideal, Trans. Faraday Soc., 40, 505 (1944).

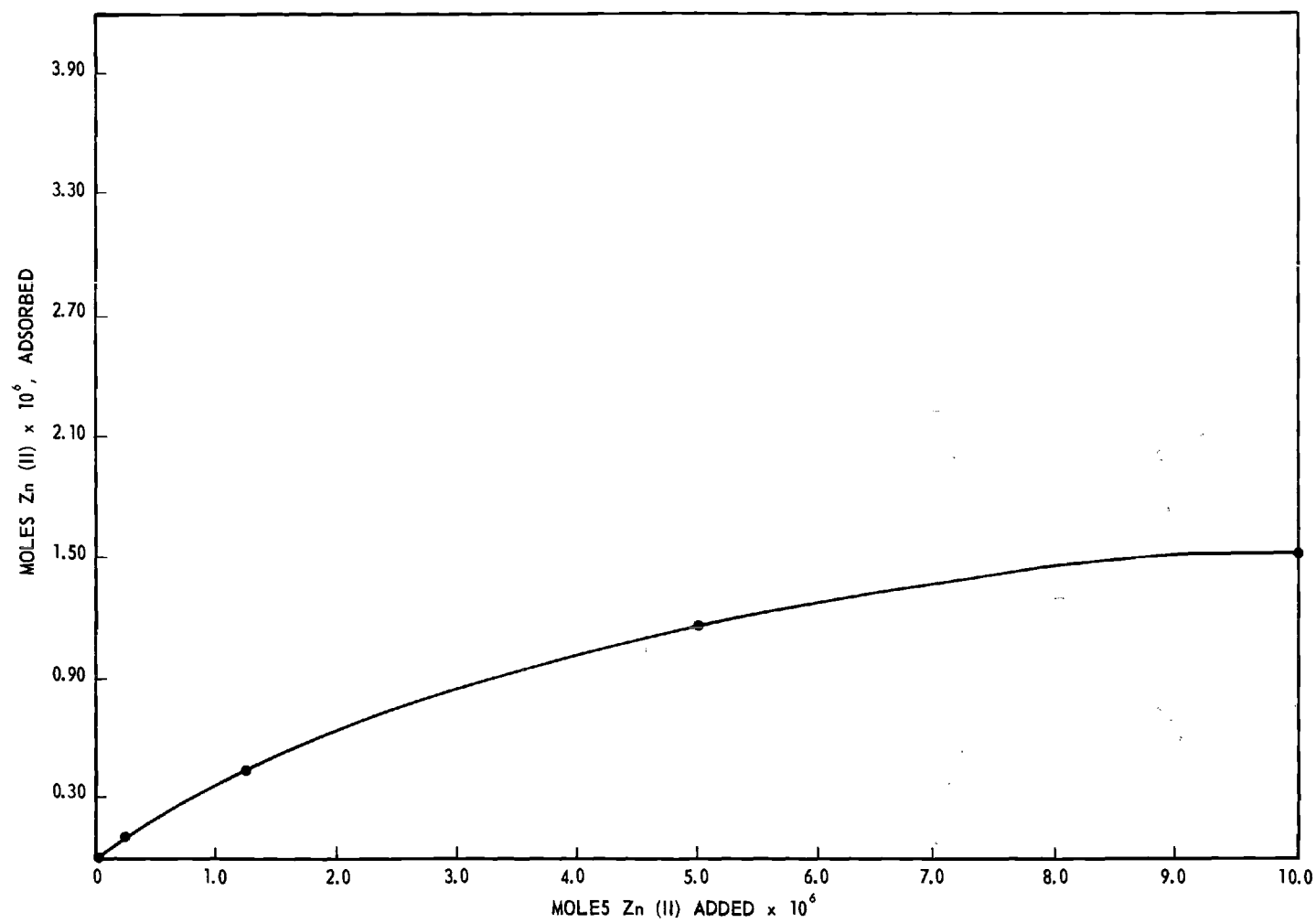


Figure 2. Amount Zn(II) Adsorbed vs. Amount Zn(II) Added in the Range from 0 to 10 x 10⁻⁶ Mole Added.

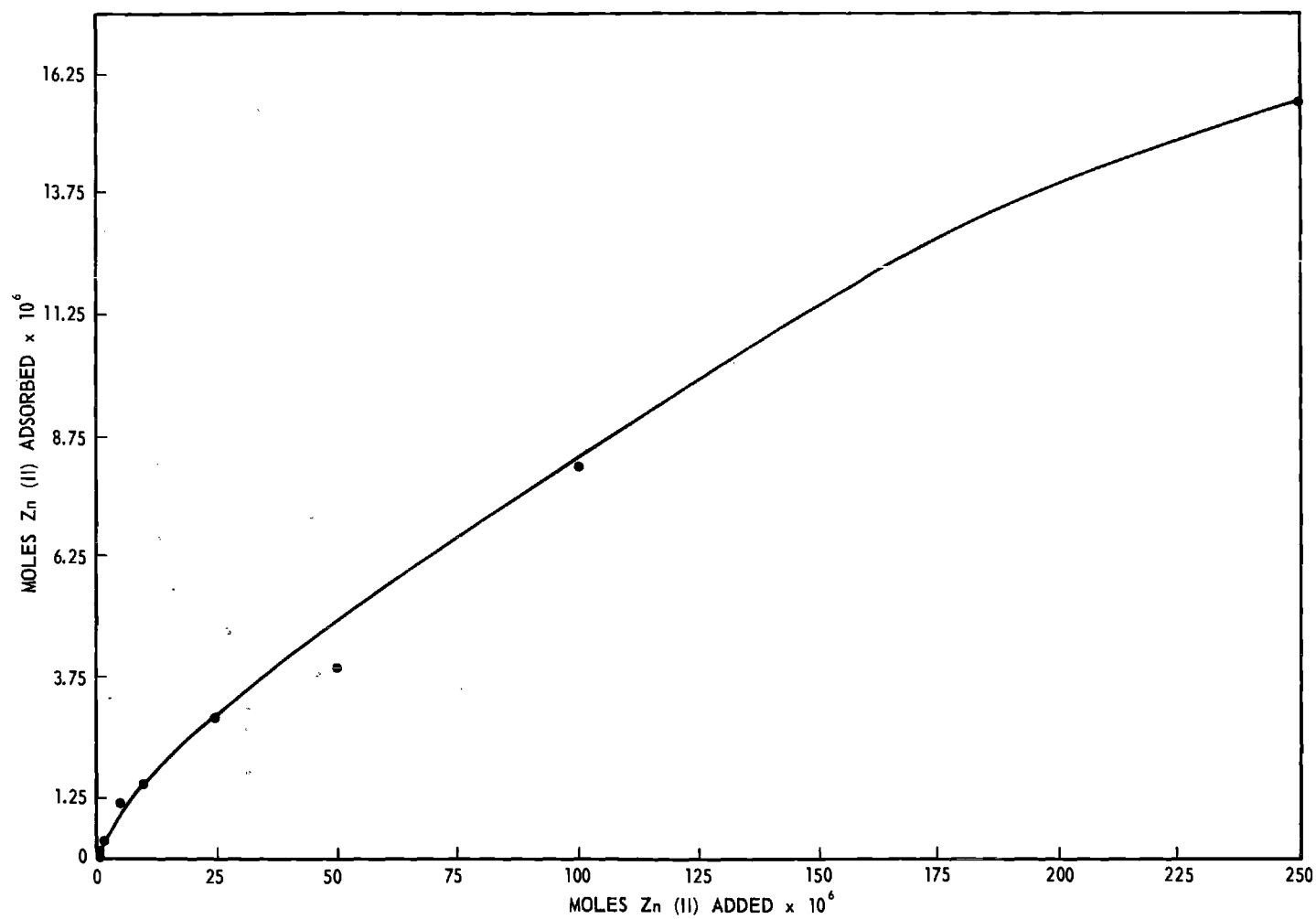


Figure 3. Amount Zn(II) Adsorbed vs. Amount Zn(II) Added in the Range from 0 to 250×10^{-6} Mole Added.

Table 7. Comparison of Zn(II) Added to Zn(II) Adsorbed

Conditions: Time after reaction is stopped until catalyst is isolated, >24 hours; 0.012 mole cinnamaldehyde; 0.200 g. PtO_2 ; 64.5 ± 0.6 p.s.i.a. initial H_2 pressure; and 50 ml. acetic acid solvent.

Experiment Number	Moles Zn(II) Added $\times 10^6$	Moles Zn(II) Adsorbed $\times 10^6$	Per Cent Adsorbed
A 84	0.050	0.026	52.0
A 92	0.050	0.026	52.0
A 86	0.25	(0.088) ^a	(35.2)
A 94	0.25	0.104	41.6
A 96	0.25	0.104	41.6
A 98	0.25	0.105	42.0
A 106	1.25	0.45	36.0
A 108	1.25	0.44	35.2
A 102	2.50	0.76	30.4
A 104	2.50	0.78	31.2
A 70	5.00	1.23	24.6
A 90	5.00	1.12	22.4
A 100	5.00	1.00	20.0
A 120	5.00	1.19	23.8
A 122	5.00	1.10	22.0
A 124	5.00	1.17	23.4
A 74	10.0	(0.88) ^a	(8.8)
A 78	10.0	(1.32) ^a	(13.2)
A 114	10.0	1.56	15.6
A 116	10.0	1.49	14.9
A 118	10.0	1.55	15.5
A 142	10.0	1.47	14.7
A 144	10.0	1.51	15.1
B 14	10.0	1.36	13.6
A 130	25.0	2.82	11.3
A 132	25.0	2.96	11.8
A 134	50.0	3.88	7.8
A 136	50.0	3.99	8.0
A 148	100	8.08	8.1
A 150	100	8.21	8.2

(Continued)

Table 7 (Continued). Comparison of Zn(II) Added to Zn(II) Adsorbed

Conditions: Time after reaction is stopped until catalyst is isolated >24 hours; 0.012 mole cinnamaldehyde; 0.200 g. PtO₂; 64.5 ± 0.6 p.s.i.a. initial H₂ pressure; and 50 ml. acetic acid solvent.

Experiment Number	Moles Zn(II) Added x 10 ⁶	Moles Zn(II) ₆ Adsorbed x 10 ⁶	Per Cent Adsorbed
B 16	250	14.9	5.9
B 18	250	15.4	6.2
B 30	250	15.7	6.3
B 32	250	16.8	6.7

(a) These results are doubtful since the count rate was too high for accurate results to be obtained from the counters employed in this work. This was corrected in later experiments by the use of a standard radioactive solution of lower Zn⁶⁵ content.

hydrogenated becomes the more deviation from a linear poisoning curve is observed. Linear poisoning curves are directly reflected in linear curves for amounts of added poison vs. amounts adsorbed in the work of Maxted and Evans. Cinnamaldehyde used here is certainly more complex than crotonic acid used by Maxted and Evans. But, with respect to the other differences, it might be expected the larger amounts of solvent and catalyst used in this work should make the linear range even larger than that found by Maxted and Evans since these workers attribute the inflection from linearity to incipient saturation of the catalyst surface.

Of even more direct significance is the method used by Maxted and Evans to determine the amount of adsorbed Zn(II). The method has been described earlier on page 11 in this work. Briefly, it depended on rate measurements in terms of ml. H₂ absorbed per unit of time (min.).

From the data given it was not possible to ascertain the reproducibility of such rates. An early step in their procedure involved permitting the catalyst whose ion adsorption was to be measured to stand under a volume of liquid containing the Zn(II). The time allowed for this step was not specifically stated; however, some early work by Maxted (48) in a similar investigation denotes this period as being "overnight." Under the conditions used in the work presented here, it was found (see below, page 68) the time required for an "equilibrium" value of Zn(II) ions adsorbed on the isolated catalyst to be reached was greater than 24 hours. From the work of Maxted and Evans it cannot be ascertained if a similar effect was found or even investigated. Neither the method used in this work nor the method of Maxted and Evans is able to provide a measurement of adsorbed Zn(II) ions during the reaction. The Maxted method measures Zn(II) adsorption on a catalyst sample in the absence of H_2 and H_2 acceptor. At least, in this work, the H_2 and H_2 acceptor are permitted to exert their effects on Zn(II) adsorption, whatever they may be, before a measurement is made of the adsorbed Zn(II). Furthermore, in this work an indication of the effects of H_2 and substrate on Zn(II) adsorption was found (see below, page 69). It is felt then, that the method used in this work, besides being more direct, is also more realistic in terms of Zn(II) adsorption under reaction conditions than the Maxted method. Based on the foregoing discussion, it is suggested that the difference in the type of curves for adsorbed Zn(II) vs. added Zn(II) found in this work and the work of

(48) E. B. Maxted, J. Chem. Soc., 127, 73 (1925).

Maxted and Evans is primarily due to the difference in the methods employed to measure the amount of adsorbed Zn(II). Although a direct comparison of the relative state of subdivision of the catalysts used in the work of Maxted and Evans and in this work could not be made, the possible difference in this respect may also be a factor in the difference of the curves obtained.

If straight lines are drawn through consecutive points starting at the origin it was observed that these lines showed a continued decrease in slope over the entire plot in Figure 3, except for the line between 50×10^{-6} and 100×10^{-6} mole of added Zn(II). This line had a greater slope than the preceeding one drawn between 25×10^{-6} and 50×10^{-6} mole of added Zn(II). The reason for the deviation of the point at 5×10^{-5} mole added Zn(II) from a smooth curve drawn through the other points is not known. However, it is not felt this deviation is indicative of the formation of a double layer of adsorbed Zn(II) ions for the following reasons: 1. a plateau region would be essentially non-existent even if the curve was drawn through this point; 2. the variation of the number of washes given the isolated catalyst did not noticeably affect the amount of adsorbed Zn(II) even at high levels of added Zn(II); and 3. similar experiments with added Fe ions, whose size is comparable to Zn(II), showed virtually no deviation from a smooth curve (see below Figure 4) over the entire range of added Fe ions (1×10^{-6} to 2.5×10^{-4} mole).

From the appearance of the curve in Figure 3 it seemed the curve was approaching a limiting value of adsorbed Zn(II) in an asymptotic manner though at a slow rate. This limiting value was apparently not reached even at 250×10^{-6} mole of added of Zn(II).

Comparison of experiments B 38 and B 40 in Table 1 with those experiments (A 114, A 116, etc.) in Table 7 which used the same amount of added Zn(II) showed a higher level of Zn(II) adsorption when 0.020 mole benzoic acid was used as the hydrogen acceptor than those using 0.012 mole cinnamaldehyde. In some experiments which studied Fe(II) adsorption, it was found an increase in cinnamaldehyde from 0.012 to 0.020 mole caused a significant decrease in the amount of Fe(II) adsorbed especially at lower levels of added Fe(II) (see below, p. 81). These results seemed to indicate the nature of the substrate being hydrogenated rather than simply the amount in moles of any substrate was a factor in determining the amount of ions adsorbed.

Effect of Adsorbed Zn(II) on the Initial Rate

An examination of the Zn(II) adsorption data in Table 7 and the rate constants shown in Table 5 for the same experiments showed the absence of a simple relationship between the amount of Zn(II) adsorbed and the initial rates. In a plot of the rate constants vs. the amount of adsorbed Zn(II) (see Figure 1, page 50) it was found the form of this dependence of k'_{30} on adsorbed Zn(II) was very close to the same form found for a similar plot of k'_{30} vs. the amount of Zn(II) added. It is emphasized later that the amount of Zn(II) found on the catalyst when isolated is apparently an "equilibrium" value. From this standpoint then, a simple relationship between k'_{30} and the adsorbed Zn(II) might not have been expected.

Other Factors Influencing the Amount of Zn(II) Adsorbed on the Isolated Catalyst

It was recognized that if reproducible adsorption results were to be obtained, a "standard" procedure of catalyst isolation should be used.

In this connection it was also of interest to observe any effects that variations in the isolation procedure might have on the amount of Zn(II) found adsorbed on the isolated catalyst. These observations could give an indication of the strength of the adsorptive forces holding the Zn(II) to the surface and could also serve to eliminate simple occlusion of the Zn(II) in the catalyst as a source of error in this work.

Variation of the catalyst wash procedure was of obvious import in terms of the preceding discussion. Changes in the number of washes given the catalyst were performed at low and high levels of added Zn(II). For example, experiment A 94 used a single wash, A 96 two washes, and A 98 three washes with each wash using 10 to 15 ml. of solvent according to the procedure described on page 27. The results in Table 7 show that 42 per cent of the same amount of added Zn(II) was adsorbed in each experiment. In experiment A 134 a single wash was used while in A 136 a triple wash was used. From Table 7, the results show essentially the same amount of adsorbed Zn(II) for both experiments. It seemed then, occlusion of Zn(II) was not a problem in this work and the use of a multiple wash was unnecessary.

The results of Maxted and Ball (49) are noteworthy in regard to the results just mentioned. These workers studied the hydrogenation of cyclohexene (1 ml.) in acetic acid (8.5 ml.) using a platinum black (0.025 g.) in the presence of $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ (10^{-5} mole in 0.5 ml. H_2O). They found the Zn(II) ions could be completely removed from the isolated catalyst by stirring the catalyst in 10 ml. H_2O for 15 minutes. There

(49) E. B. Maxted and G. T. Ball, J. Chem. Soc., 1952, 4284.

was also reported the almost complete removal of Zn(II) ions by simply making one change of supernatant liquid over the catalyst, i.e., without isolating and washing the catalyst. Again, the differences in these results with those found in this work are worthy of discussion.

The differences in conditions might be expected to cause some differences of results but certainly not in the magnitude observed. Even if the single wash used by Maxted and Ball is considered to be more thorough than a single wash used in this work, the fact that three washes used in this work did not change the amount of adsorbed Zn(II) is difficult to explain in terms of their results. Moreover, the almost complete removal of adsorbed Zn(II) by a change of the supernatant liquid over the catalyst as reported by Maxted and Ball makes the results found here even more unusual.

It should be emphasized the method of Maxted and Ball in judging the removal of Zn(II) from the catalyst was dependent on the catalyst originally poisoned being restored to an activity equal to that observed for a catalyst which had no Zn(II) present. A control experiment in which a catalyst containing no adsorbed Zn(II) was washed in the same manner as that used for the Zn(II) poisoned catalyst was not mentioned by these workers. In the absence of such a control experiment, the only conclusion that appears to be justified from the results is that washing of the catalyst greatly increased its activity. It does not necessarily follow that the Zn(II) ions had been removed by such a treatment. One might postulate the restoration to original activity by the washing treatment is merely a coincidental combination of washing effects on the catalyst and the continued presence of Zn(II) ions on the catalyst.

In contrast to the method of Maxted and Ball, the method used in this work is more direct in that it measures the radioactivity of the isolated catalyst sample without recourse to additional kinetic runs. These measurements were made after the variations in wash procedures had been used. It would be hard to visualize the radioactivity of the washed samples as being due to anything other than Zn^{65} adsorbed on the catalyst.

A further comment on the work of Maxted and Ball seems to be in order here. In this work cited (49), these workers found mercury ions to be considerably more difficult to remove from the platinum catalyst by washing than the case using Zn(II) at the same level. It was not stated whether the mercury was added as the Hg(I) or Hg(II) acetate salt. However, it is likely the mercury was present as Hg(I) under hydrogenation conditions (30). The reasonableness of this assumption is also indicated by the fact that Fe(III) is apparently reduced to Fe(II) under conditions used in this work (see below, page 71). Maxted and Ball showed in the same work that mercury ions were more "toxic" (caused slower hydrogenation rate) than Zn(II) ions at the same added level. The greater difficulty of Hg(I) removal was then attributed to its longer adsorbed life on the catalyst. This should be related to the relative strengths of the chemisorptive bonds between the ions and the catalyst. But, these statements seem to be in contradiction to a scale of "relative effective toxicities" presented by Maxted and Marsden (30) in which Zn(II) had a value of 3.6 and Hg(I) was 1.8. These values were found in hydrogenations of crotonic acid in ethanol or acetic acid using a platinum black catalyst from linear portions of

hydrogenation rate vs. added ion curves. Although the magnitudes of the toxicity coefficients may change with a change of catalyst sample, the relative values apparently (30) do not change, provided a given sample is used to compare the poisons in question. With regard to the substrates, Maxted and Stone (50) found that mercury showed the same toxicity coefficient in hydrogenations of several different substrates in acetic acid using a platinum black catalyst. Thus, the apparent contradiction is not explained by a change in catalyst sample or a change in the hydrogen acceptor because of these observations by Maxted, et al., (30)(50). If the contradiction in relative toxicity of Hg(I) and Zn(II) is unexplained, its presence tends to cast doubt on the results obtained by Maxted and Ball (49) concerning ease of Zn(II) removal from a platinum catalyst.

Since the top layer of ions in a multilayer adsorption should be much easier to remove by washing than the monolayer ions, it appeared again from these results that a double layer of ions is not found on the catalyst after its isolation. This is not to say, however, that the formation of a multilayer of ions does not occur on the catalyst as it remains in the reaction mixture. In fact, based on the results to be discussed next, it appeared the amount of Zn(II) ions adsorbed on the catalyst during the reaction was considerably higher than the amount found on the isolated catalyst.

An important variable in the isolation procedure was found to be the time elapsed between the end of the reaction and the isolation

(50) E. B. Maxted and V. Stone, J. Chem. Soc., 1934, 672.

of the catalyst from the reaction mixture. The importance of this variable was not recognized in the early stages of this work. Fortuitously, however, the time periods used proved to be of suitable length so the early results remained useful. The results obtained in a series of experiments examining this variable are shown in Table 8. These results show the catalyst, if isolated immediately from the reaction mixture, had almost double the amount of adsorbed Zn(II) ions than if it was permitted to stand in the reaction mixture for 36 to 42 hours. Furthermore, it appeared the amount of Zn(II) adsorbed approached a limiting value rapidly as the time interval increased. Figure 4 shows the data of Table 8 in graphical form. Experiments A 148 and A 150 are included in Table 8 to show the degree of precision that could be achieved in determining the amounts of adsorbed Zn(II) when the isolation times were identical. From a practical standpoint, Figure 4 shows the choice of a time interval between 24 and 42 hours should give results that were within experimental error of each other under otherwise similar conditions. This would be especially true of the higher levels of added Zn(II).

The reason for this behavior is not clear. One possible explanation is in the tendency of the adsorbed Zn(II) ions to minimize repulsive interactions by a desorption of some of the ions, assuming this tendency could not be realized while the mixture was being shaken under H_2 pressure. Using this idea, one might then term the amount of Zn(II) ions found on the catalyst after 24 to 32 hours an "equilibrium" value of adsorbed Zn(II) ions.

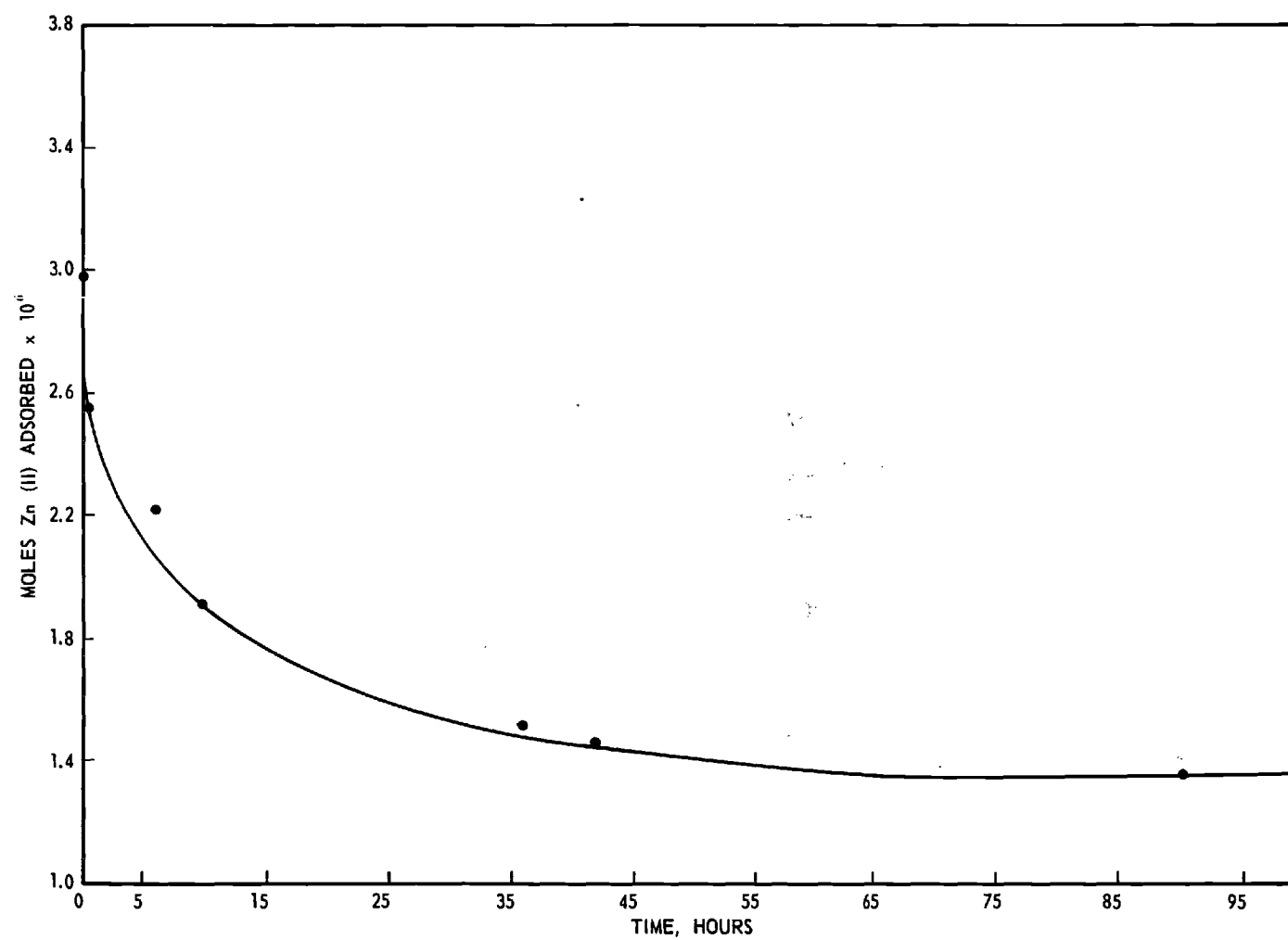


Figure 4. Amount Zn(II) Adsorbed vs. Time Between End of Reaction and Catalyst Isolation.

Table 8. Comparison of Adsorbed Zn(II) Values in Relation to the Time Between End of Reaction and Isolation of Catalyst

Conditions: 0.012 mole cinnamaldehyde; 0.200 g. PtO₂; 50 ml. glacial acetic acid.

Experiment Number	Catalyst Isolation Time, Hours	Moles Zn(II) Added x 10 ⁶	Moles Zn(II) ₆ Adsorbed x 10 ⁶	Per Cent Adsorbed
A 140	0.03	10.0	2.97	29.7
B 12	0.08	10.0	2.54	25.4
B 10	5.8	10.0	2.22	22.2
A 146	9.5	10.0	1.91	19.1
A 144	36.0	10.0	1.51	15.1
A 142	42.0	10.0	1.47	14.7
B 14	90.0	10.0	1.36	13.6
A 148	24.0	100	8.08	8.1
A 150	24.0	100	8.21	8.2

Since the reaction mixtures at the end of a reaction period were exposed to the air, it was suspected this air (probably O₂) contact with the mixture may have been a factor in decreasing the amount of Zn(II) adsorbed with increasing time. Three experiments were performed to obtain information on this point. In each case the reaction conditions were the same with 10×10^{-6} mole added Zn(II) being used. In experiment B 24 the reaction was terminated, air was admitted to the bottle, and then shaking of the bottle was resumed for one hour. At the conclusion of this period the catalyst was isolated as quickly as

possible. In experiment B 26 the reaction was terminated and the excess H_2 was bled off until five p.s.i.a. registered on the gauge. Shaking of the bottle was commenced and continued for one hour after which the catalyst was isolated as quickly as possible. For experiment B 28 the additional one hour shaking of the bottle was performed after the bottle had been evacuated for several minutes and then closed off. Again, the catalyst was isolated as quickly as possible. The values of Zn(II) adsorbed were as follows: B 24 - 2.12×10^{-6} mole or 21.2 per cent of the added amount, B 26 - 2.90×10^{-6} mole or 29.0 per cent and B 28 - 2.56×10^{-6} mole or 25.6 per cent. These results indicated that air did act to decrease the Zn(II) adsorption and H_2 even at low pressure acted to increase the Zn(II) adsorption.

Some additional experiments gave more evidence on the effect of H_2 on Zn(II) adsorption. In essence, what was done in these experiments was to observe the effect of the absence or presence of the components of the hydrogenation mixture under otherwise similar conditions. The results of these experiments are given in Table 9.

It is apparent the results of A 126 and A 128 represent Zn(II) adsorption on PtO_2 rather than Pt. It is interesting to note this pair of experiments indicated cinnamaldehyde decreased the amount of adsorbed Zn(II) on the PtO_2 surface. But, interestingly enough, when H_2 was present cinnamaldehyde did not appear to affect the Zn(II) adsorption either in its presence (A 124) or its absence (A 127).

A qualitative explanation for these effects shown by hydrogen on Zn(II) adsorption might be based on the suggestions of Boudart (51)

(51) M. Boudart, J. Am. Chem. Soc., 74, 3556 (1952).

Table 9. Effect of Hydrogenation Mixture Components
on Zn(II) Adsorption

Conditions: 0.200 g. PtO_2 ; 50 ml. glacial acetic acid solvent; and 5×10^{-6} mole Zn(II) present. Time before catalyst isolation > 24 hours.

Experi- ment Number	Initial H_2 Pressure @ 64.50 p.s.i.a.	0.012 Mole Cinnamaldehyde	Moles Zn(II) ₆ Adsorbed $\times 10^6$	Per Cent Adsorbed
A 124	Present	Present	1.17	23.4
A 126	Absent	Present	0.43	8.6
A 127	Present	Absent	1.15	23.0
A 128	Absent	Absent	0.82	16.4

concerning changes in the electronic nature of the catalyst surface caused by adsorption of electropositive or electronegative species. These changes in the electronic nature of the surface were evidenced by an increased ease or an increased difficulty in adsorption of the next adsorbed substance over the case where the surface was free from other adsorbed species. It might be suggested here then, the adsorbed H_2 changes the nature of the surface so as to aid Zn(II) adsorption. The effect of cinnamaldehyde in these cases is unclear but it might be tentatively suggested that it acts to decrease the extent of Zn(II) adsorption. At least in the case of adsorbed Fe(II) (see below, page 81) it was found an increase in cinnamaldehyde concentration caused a decrease in the amount adsorbed especially at lower levels of added Fe(II). These results may or may not be analogous to cases using Zn(II).

Hydrogenation of Cinnamaldehyde in the Presence of Fe Ions

Effect of Added Fe Ions on the Initial Rate

The beneficial effect of added Fe(II) or Fe(III) on aldehyde hydrogenations using Adams' catalyst, originally observed by Carothers and Adams (8) has been cited earlier. It was desirable in the present work to obtain more precise information on the effect certain amounts of added Fe ions show on the initial rates of cinnamaldehyde hydrogenations using Adams' catalyst. As in the cases using Zn(II) ions, it will be convenient to group the results together in terms of the solvent used for the experiments. It also will be convenient to reserve the discussion of those results obtained using "modified" experimental conditions for the latter part of a particular discussion section.

It should be pointed out in the beginning of this discussion that the differences between Fe(II) and Fe(III) in these reactions were not completely investigated in this work. There were good indications that Fe(III) was reduced to Fe(II) under the reaction conditions used. For example, the characteristic orange-yellow color of Fe(III) was completely absent in the final reaction mixture which originally contained added Fe(III) or "old" Fe(II). Furthermore, Carothers and Adams (8) reported the reduction of Fe(III) to Fe(II) to take place under the conditions they used. They also observed induction periods in H_2 absorption if greater than 1×10^{-4} mole $FeCl_3$ was present. In these cases HCl was liberated and the hydrogen uptake was said to proceed beyond the alcohol state. Slight induction periods were also observed in this work if either "old" Fe(II) solutions or Fe(III)

solutions were used and in a number of cases the H_2 absorption proceeded beyond the amount required to reduce the PtO_2 and hydrogenate the ethylenic and carbonyl groups of cinnamaldehyde. In spite of this apparent reduction of Fe(III) to Fe(II), there seemed to be significant differences in the rate results depending on whether the ion was added as Fe(III) or Fe(II). The results which are relevant to this area of discussion will be pointed out as they are presented in the main body of data. Keeping these points in mind, the presentation of results for Fe ions will be in terms of Fe(II) unless Fe(III) was specifically used in an experiment.

A number of experiments were performed using comparable conditions in which various amounts of $FeCl_2$ were present in 95 per cent ethanol as solvent. These results, shown in Table 10, indicate that the addition of Fe(II) in the amounts used gave considerably higher initial rates than those cases where no Fe(II) was present in 95 per cent ethanol. If the single result obtained at a level of 2.5×10^{-5} mole added Fe(II) is reliable, then the initial rate showed a maximum near this level and also near the 100×10^{-6} mole Fe(II) level in the range studied. If a trend is present in this limited range of added Fe(II) it appears to be one of increasing k'_{30} with increasing amounts of added Fe(II), at least up to 100×10^{-6} mole of Fe(II).

It is also seen from Table 10 that the H_2 absorption increases with an increase in added Fe(II). In all cases the reaction either approached completion or went slightly beyond the theoretical amount required for PtO_2 reduction and hydrogenation of the ethylenic and carbonyl groups of cinnamaldehyde. No attempt was made to examine the products in any of these cases.

Table 10. Effect of Added Fe(II) on the Initial Rate and H_2 Absorption in 95 Per Cent Ethanol Solvent

Conditions: 0.012 mole cinnamaldehyde; 0.200 g. PtO_2 ; 64.5 ± 0.4 p.s.i.a. initial H_2 pressure; and 50 ml. 95 per cent ethanol solvent.

Experiment Number	Moles H_2 , Absorbed @ Time, Minutes	Moles Fe(II), as $FeCl_2$ Added $\times 10^6$	k'_{30} g. ⁻¹ min. ⁻¹ $\times 10^4$
A 34	0.024 @ 36	10.0	296
A 40	0.024 @ 28	10.0	295
A 46	0.027 @ 42	10.0	301
A 42	0.028 @ 18	25.0	356
A 36	0.029 @ 12	50.0	319
A 44	0.028 @ 14	50.0	305
A 48	0.028 @ 32	50.0	311
A 38	0.029 @ 26	100	357
A 50	0.029 @ 30	100	360
A 24	0.024 @ 24	None	220
A 26	0.025 @ 22	None	245
A 28	0.021 @ 20	None	235

A single experiment (B 96) was carried out in 95 per cent ethanol solvent using 0.020 mole cinnamaldehyde with other conditions being the same as those in Table 10 in regard to solvent volume and catalyst weight. The initial H_2 pressure was 64.45 p.s.i.a. in this run. The reaction mixture also contained 10×10^{-6} mole $FeCl_2$. For this experiment k'_{30} was found to be 445 and the H_2 absorption was 0.034 mole at 50 minutes.

Thus, an increase in cinnamaldehyde concentration of 67 per cent gave an increase in the initial rate of 50 per cent by a comparison of B 96 with A 34, A 40, and A 46.

A series of experiments using acetic acid as the solvent for these reactions was carried out. The results obtained using conditions comparable to those in Table 10 are shown in Table 11.

Some difficulty was experienced in dissolving completely the FeCl_2 in glacial acetic acid for the preparation of a 5×10^{-3} M solution. It was found necessary to add a small amount of water to aid the solution of the FeCl_2 in glacial acetic acid. However, it was calculated that the maximum amount of water present in the reaction mixture using 50 ml. of this 5×10^{-3} M solution was 2 per cent. Obviously, it would be less than 2 per cent for all other experiments in this series. However, this fact should be kept in mind when the results of Table 11 are examined because it will be shown later the presence of water at a level of 7 per cent appeared to decrease the initial rate of hydrogenation of cinnamaldehyde in acetic acid. In any case, precipitates due to hydrolysis of Fe(III) were not observed in any of the Fe solutions prepared in 95 per cent ethanol or acetic acid during the length of time they were used in this work.

Although duplicate experiments were not run in the series of experiments shown in Table 11, it does appear that a downward trend in initial rate existed as the amount of added Fe(II) increased. This decrease in k'_{30} appeared to be at first rapid but then showed a plateau region followed by another region of slowly decreasing k'_{30} with increasing amounts of added Fe(II) (see below, Figure 6, p.83). It is apparent

Table 11. Effect of Added Fe(II) on the Initial Rate and H_2 Absorption in Acetic Acid Solvent

Conditions: 0.012 mole cinnamaldehyde; 0.200 g. PtO_2 ; 64.5 ± 0.4 p.s.i.a. initial H_2 pressure; and 50 ml. acetic acid solvent.

Experiment Number	Moles H_2 , Absorbed @ Time, Minutes	Moles Fe(II) as $FeCl_2$, ^a Added $\times 10^6$	k'_{30} g. ⁻¹ min. ⁻¹ $\times 10^4$
C 32	0.022 @ 18	1.00	407
C 34	0.024 @ 40	5.00	340
C 36	0.025 @ 22	10.0	334
C 38	0.026 @ 24	25.0	282
C 40	0.028 @ 24	50.0	278
C 42	0.029 @ 22	75.0	274
C 44	0.028 @ 24	100	278
C 46	0.029 @ 24	175	264
C 48	0.029 @ 22	250	246
A 18	0.018 @ 14	None	271
A 20	0.021 @ 26	None	324
A 22	0.021 @ 26	None	296
C 14	0.023 @ 32	None	283

(a) The source of Fe(II) in these experiments is a radioactive solution prepared from $FeCl_2 \cdot 4H_2O$ in acetic acid and $Fe^{59}Cl_3$ in 1.3 N HCl. It was calculated the maximum amount of Fe(III) present in the reaction mixtures (C 48) would be 9.6×10^{-9} mole from this source and could thus be ignored as a significant source of Fe ions in these experiments.

from these results that only the first three numbers of this series showed initial rates higher than those shown in the absence of added Fe(II) ions.

The results for H_2 absorption in Table 11 are similar to those shown in Table 10 for 95 per cent ethanol solvent. Here again, the reactions either approached completion or went slightly beyond the theoretical amount of H_2 to be absorbed.

A number of other experiments were run in acetic acid solvent using modified experimental conditions. The results obtained under these modified conditions are shown in Table 12.

A somewhat surprising result is observed when the initial rate of C 16 is compared with C 32. In spite of the higher concentration of cinnamaldehyde in C 16, its initial rate was significantly lower than that of C 32. A possible explanation for this behavior may be found in a comparison of the relative amounts of Fe(II) adsorbed on the catalyst in the same two experiments (see below, Table 14, page 81). At the low levels of added Fe(II) used in these two experiments such large relative differences may be reflected in significant differences in initial rates.

Comparison of experiment B 118 with experiment B 116 showed a deleterious effect on the rate caused by "aging" the Fe(II) solution. The same effect to almost the same degree is evidenced in comparing B 134 with B 136. The effect of aging the solutions for long periods is difficult to account for in terms of a simple oxidation of Fe(II) to Fe(III) because it will be shown later Fe(III) ions added to the reaction mixture give a considerably higher rate than Fe(II) ions at the same level. Although precipitates due to hydrolysis of Fe(III) were not observed, the possibility of a colloidal suspension of Fe(III) hydrolysis products was not ruled out. The "aged" solutions did show the intense orange color characteristic of Fe(III) which seemed to grow more intense as "aging" progressed.

Table 12. Effect of Added Fe(II) on the Initial Rate and H_2 Absorption Under Modified Conditions

Conditions: 0.020 mole cinnamaldehyde; 0.200 g. PtO_2 ; 65.6 ± 0.4 p.s.i.a. initial H_2 pressure; and 50 ml. acetic acid solvent.

Experiment Number	Moles H_2 , Absorbed @ Time, Minutes	Moles Fe(II) as $FeCl_2$ Added $\times 10^6$	$k'_{30} \text{ g.}^{-1} \text{ min.}^{-1} \times 10^4$
C 16 ^a	0.025 @ 30	1.00	348
C 18 ^a	0.024 @ 26	5.00	331
C 20 ^a	0.032 @ 60	25.0	301
C 22 ^a	0.041 @ 220	50.0	292
C 24 ^a	0.048 @ 240	125	277
B 116 ^b	0.040 @ 76	100	251
B 118 ^c	0.040 @ 60	100	279
B 134 ^{c,d}	0.035 @ 108	100	214
B 136 ^{b,d}	0.029 @ 128	100	196

(a) These experiments used the radioactive Fe(II) solution described in Table 10.

(b) The Fe(II) solutions used in these experiments were about nine weeks old.

(c) The Fe(II) solution used in this experiment was freshly prepared.

(d) These experiments contained an additional four ml. water besides the 50 ml. acetic acid.

From a comparison of B 134 and B 118 the effect of 7 per cent water in the acetic acid in decreasing the rate can be observed. A similar result was cited earlier in the cases where no added metal ion

was present in the reaction mixture (see above, page 52), but it will also be remembered that if 100×10^{-6} mole Zn(II) was present this slowing effect of 7 per cent water in acetic acid was not observed.

Not all the experiments in Table 12 were followed to completion. It appeared they all would absorb the theoretical amount of H_2 if sufficient time was allowed. The times required for completion of reaction seemed to be considerably longer than those in Table 11 where 0.012 mole cinnamaldehyde was used. In experiment C 24 the tendency for H_2 to be absorbed beyond the theoretical amount was again noted. The repeated observation of this tendency when "Fe(II)" is used may very well be due to consumption of H_2 in reducing Fe(III) to Fe(II) in addition to possible hydrogenation of the phenyl group.

Since Fe(II) is rather easily oxidized to Fe(III) it was of interest to obtain direct evidence on the effect added Fe(III) ions would show on the rate and H_2 absorption in these reactions. Several experiments which noted the effects of added Fe(III) on cinnamaldehyde hydrogenation using Adams' catalyst were carried out. The results of these experiments are shown in Table 13.

The first three experiments in Table 13 are triplicate runs showing the agreement in the rate constants found. The average value of k'_{30} is 326×10^{-4} for these experiments. This value is 17 per cent greater than that found for B 118 in Table 12. The tendency for 7 percent water content to show a reduced initial rate in acetic acid is evidenced again in experiment B 148. It does not seem likely the effect of added water is due to a solvent volume increase of 8 per cent. Calculations show that the magnitude and direction of the effect cannot be accounted for in terms of an effective change in concentration of

Table 13. Effect of Added Fe(III) on the Initial Rate and Hydrogen Absorption

Conditions: 0.020 mole cinnamaldehyde; 0.200 g. PtO_2 ; 64.7 ± 0.2 p.s.i.a. initial H_2 pressure; and 50 ml. acetic acid solvent.

Experiment Number	Moles H_2 , Absorbed @ Time, Minutes	Moles Fe(III) as FeCl_3 Added $\times 10^6$	k'_{30} g. ⁻¹ min. ⁻¹ $\times 10^4$
B 114	0.037 @ 70	100	330
B 144	0.030 @ 60	100	325
B 146	0.030 @ 62	100	322
B 148 ^a	0.045 @ 389	100	258

(a) This experiment contained an additional four ml. of H_2O to make the solvent volume 54 ml. of 93 per cent acetic acid.

either cinnamaldehyde or Fe ions. Furthermore, it has already been shown in cases using reaction bottles of five ml. difference in volume (see above, page 43) that this change in the effective hydrogen volume had no noticeable effect on the initial rates of hydrogenation of cinnamaldehyde.

Relation Between the Amount of Fe(II) Added and the Amount of Fe(II) Adsorbed on the Isolated Catalyst

The use of Fe(II) as a modifier of Adams' catalyst made it desirable to obtain information on its adsorption on the isolated catalyst. This was accomplished in a manner exactly analogous to that described for Zn(II) but using radioactive Fe solutions containing Fe^{59} . The variables in the isolation procedure were not investigated

as was done in the Zn(II) case, but a single wash was used and the time before catalyst isolation was 44.0 to 44.5 hours. Two series of experiments were carried out: one series used 0.012 mole cinnamaldehyde, the other series used 0.020 mole of the same material. The results obtained in both series are shown in Table 14.

A plot of the data obtained in the first series of experiments in Table 14 is shown in Figure 5 from which it was observed that the amount of adsorbed Fe(II) increased as the amount of added Fe(II) increased, approaching a limiting value asymptotically. The limiting value of adsorbed Fe(II) was apparently not reached in the range of added Fe(II) ions studied. Comparison of Figure 3 with Figure 5 indicates the Zn(II) curve might cross the Fe(II) curve near 250×10^{-6} mole of added ions. However, the amount of adsorbed Fe(II) is considerably greater than Zn(II) at the lower levels of added ions.

Comparison of the adsorption data for the two series in Table 14 indicated the lesser amount of cinnamaldehyde favored higher adsorbed Fe(II). This difference though, decreased as added Fe(II) increased and became negligible at about 5×10^{-5} mole added Fe(II).

Effect of Adsorbed Fe(II) on the Initial Rate and H₂ Absorption

An examination of the values obtained for adsorbed Fe(II) and the corresponding rate constants showed no simple relationship. The form of this dependence was of the shape as that found between the initial rate and the amount of added Fe(II). This had also been noted for the Zn(II) case. Figure 6 shows a plot of k'_{30} vs. adsorbed Fe(II) and added Fe(II) ions to illustrate graphically these results for the first series of experiments in Table 14.

Table 14. Comparison of Added Fe(II) With Adsorbed Fe(II)
on the Isolated Catalyst

Conditions: 0.012 or 0.020 mole cinnamaldehyde; 0.200 g. PtO_2 ; and 50 ml. glacial acetic acid solvent.

Experiment Number	Moles Fe(II), Added $\times 10^6$	Moles Fe(II) Adsorbed $\times 10^6$	Per Cent Adsorbed
C 32 ^a	1.00	0.68	68
C 34	5.00	2.15	43
C 36	10.0	2.73	27
C 38	25.0	6.71	27
C 40	50.0	9.89	20
C 42	75.0	11.71	16
C 44	100	12.89	13
C 46	175	14.81	8
C 48	250	15.94	6
C 16 ^b	1.00	0.48	48
C 18	5.00	1.63	33
C 20	25.0	6.23	25
C 22	50.0	9.42	19
C 24	125	13.27	11

(a) This series of runs used 0.012 mole cinnamaldehyde.

(b) This series of experiments used 0.020 mole cinnamaldehyde.

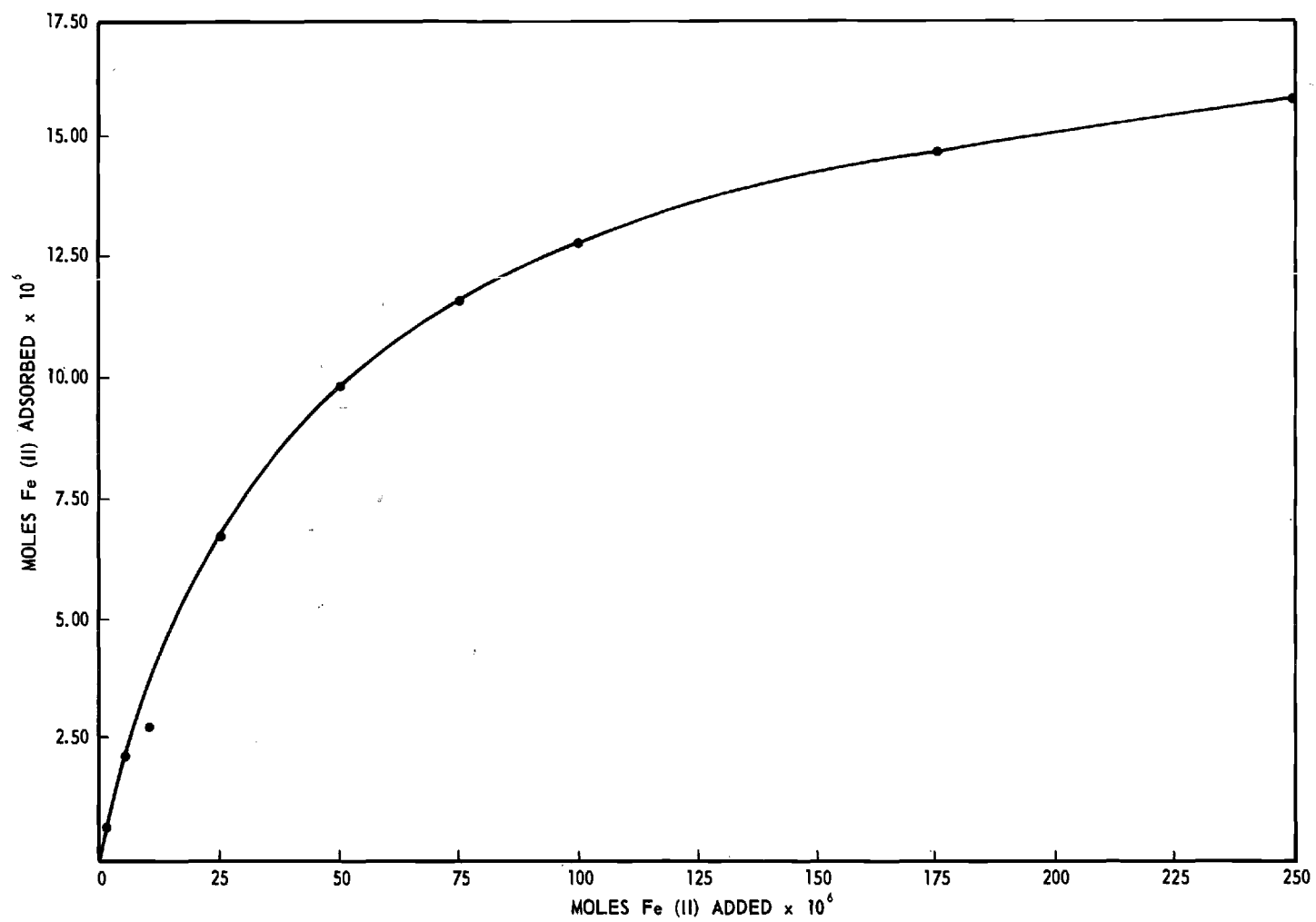


Figure 5. Amount of Fe(II) Adsorbed vs. Amount Added in the Range from 0 to 250 x 10⁻⁶ Mole Added.

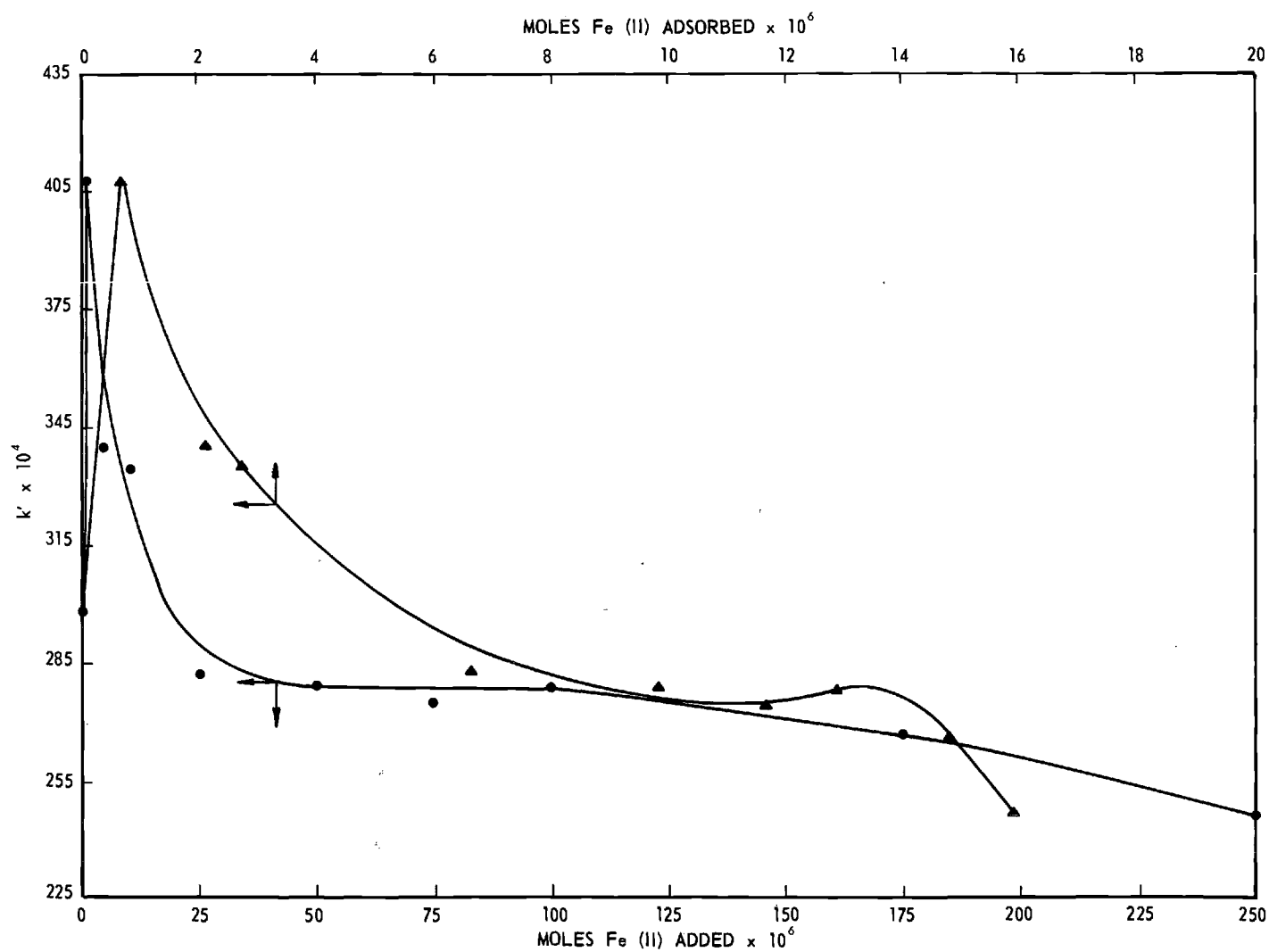


Figure 6. Dependence of k' on Amount of Fe(II) Added and Amount of Fe(II) Adsorbed.

Product Analysis for Hydrogenation of Cinnamaldehyde
to 50 and 83 Per Cent Completion

The apparent selective hydrogenation of the carbonyl group in cinnamaldehyde using Adams' catalyst in the presence of Zn(II) or Fe(II) or mixtures of these two ions has already been noted from the work of Tuley and Adams (11). It was important then, to see if selective hydrogenation could be observed under the conditions used in this work. It should be pointed out though, there are significant differences in the conditions used in this work from those used by Tuley and Adams. Foremost among these differences is the pre-reduction of the PtO_2 before reagents were added as part of the procedure used in the experiments of Tuley and Adams. These workers also did some work in which the PtO_2 was reduced in the presence of the reagents but no experimental data were given. However, it was stated the selectivity of hydrogenation was not affected by this change in terms of which group, ethylenic or carbonyl, was hydrogenated first. Another significant difference in conditions was the use of 0.2 or 0.4 mole cinnamaldehyde by Tuley and Adams, whereas in the area of work reported here, 0.024 or 0.040 mole of the same material was used. These differences in experimental conditions along with other differences which may not be so obvious prevent a strict comparison of the results obtained in this work with those found by Tuley and Adams. In this same connection one should recall the conflicting results obtained by Skita (23) and Straus and Grindel (22) when both used a colloidal palladium catalyst to hydrogenate cinnamaldehyde. The reversal of selectivity in cinnamaldehyde hydrogenation due to the use of different amounts of catalyst as observed

by Csürös (18) should add a further note of caution if comparison of results is attempted.

Recent years have seen the widespread use of vapor phase chromatography (V.P.C.) as an analytical tool in determining the composition of complex mixtures of chemical compounds. Its application to the problem of reaction mixture analysis at various stages of cinnamaldehyde hydrogenation seemed particularly desirable. After the catalyst had been filtered from such reaction mixtures and the solvent had been stripped off under reduced pressure, such mixtures could contain traces of water and solvent, cinnamaldehyde ($\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$, I), cinnamyl alcohol ($\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{OH}$, II), 3-phenylpropanal ($\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CHO}$, III), and 3-phenyl-1-propanol ($\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, IV).

Under optimum conditions of operation, V.P.C. analyses can give quantitative results for the composition of mixtures. It was not felt in this work that optimum conditions were found for the V.P.C. analyses reported here. This was true in spite of the use of a variety of V.P.C. columns under a variety of operating conditions. Keeping this in mind, the V.P.C. results reported here can be considered as semi-quantitative.

Usual procedures in V.P.C. analysis first involve the determination of retention times* of known compounds which may be present in the mixture. These retention times are characteristic for specific compounds, though it is possible for a number of compounds to show the

* Retention time may be defined as the time required, after sample injection, for a peak to appear on the time scale of chart paper in a recorder connected to the detecting device of the V.P.C. instrument.

same retention times under a given set of operating conditions. If the known compounds in question show retention times that are suitably different, it is usually possible to identify components of the V.P.C. analyzed mixture by the retention times of the peaks that appear. This procedure then, represents a qualitative analysis of the mixture. The next step in V.P.C. analysis is to determine the composition of the mixture on a quantitative basis. This can be accomplished because the area under a given peak is proportional to the amount of that substance which is detected by the instrument. One general procedure involves taking the product of the peak height times its width at half its height as being proportional to the area under the peak. The percentage composition of the mixture is thus related to the relative magnitudes of the various peak areas found for the mixture.

V.P.C. analysis of mixtures may sometimes be complicated by interaction of the components to form new compounds or to cause a change in retention times from those observed for the separate components of the mixture. Such complications are usually easily detected and in some cases may not affect the analysis at all. The correction of the more serious complications may require the use of special techniques such as multistage separation.

In the following discussion of V.P.C. results it will be convenient to present the information on conditions of the hydrogenation runs first, followed by results of preliminary V.P.C. experiments on known samples of the four possible reaction mixture components. This will then be followed by the results obtained in V.P.C. analyses of the hydrogenation mixtures according to the column used.

It will be noted in this discussion that the term "retention time" is not used. But an analogous term, "elution time" i.e., the time at which a component began to eluted from the column as indicated by the inception of a peak on the chart paper, was used. Such elution times were reproducible under a given set of operating conditions in this work.

The conditions used in the hydrogenation runs analyzed by V.P.C. are shown in Table 15. At the conclusion of the reactions the catalyst was filtered from the reaction mixture using a fine porosity sintered glass funnel in a suction flask. The solvent was evaporated on a steam bath by use of a Rinco Rotary Film Evaporator attached to water-aspirator pump.

Table 16 shows the preliminary V.P.C. results with a number of different columns used to analyze separately each of the four components possible in a hydrogenation run stopped short of completion.

From the results in Table 16 it appeared each of the columns might be useful in the V.P.C. analysis of the hydrogenation mixtures obtained. Accordingly, each was tried in this work under a variety of operating conditions, but, as will be seen later, the V.P.C. results on the mixtures ranged from qualitative to semi-quantitative.

In all the columns used, the alcohols, II and IV, gave the poorest peaks in terms of sharpness and especially symmetry. This was a prime factor in the failure to obtain quantitative data on the composition of the reaction mixtures. Nevertheless, it should be emphasized that even qualitative results could demonstrate the degree of selectivity present if either of the half-hydrogenated materials

Table 15. Hydrogenation Runs for V.P.C. Analysis

Conditions: 0.400 g. PtO_2 ; 100 ml. total solvent; initial H_2 pressure 64.30 to 65.00 p.s.i.a.; temperature $22^\circ - 28^\circ \text{C}$.

Experiment Number	Moles, Cinnamaldehyde	Moles H_2 , Absorbed	Solvent	Moles Zn(II) Added $\times 10^6$	Moles Fe(II) Added $\times 10^6$
B 51 ^a	0.024	0.040	ethanol	None	None
B 53 ^a	0.024	0.040	ethanol	None	None
B 54 ^a	0.024	0.040	ethanol	20	None
B 56 ^a	0.024	0.040	ethanol	20	None
B 62 ^a	0.024	0.040	ethanol	None	None
B 64 ^a	0.024	0.040	ethanol	2	None
B 66 ^a	0.024	0.040	ethanol	20	None
B 70 ^a	0.024	0.040	ethanol	None	20
B 71 ^a	0.024	0.040	ethanol	None	20
B 79 ^a	0.024	0.040	ethanol	None	2
B 80 ^a	0.024	0.040	ethanol	None	5
B 81 ^a	0.024	0.040	acetic acid	None	50
B 83 ^a	0.024	0.040	acetic acid	50	None
B 84 ^a	0.024	0.040	acetic acid	None	5
B 85 ^a	0.024	0.040	acetic acid	5	None
B 98 ^b	0.040	0.040	acetic acid	50	None
B 100 ^b	0.040	0.040	acetic acid	None	50
B 102 ^b	0.040	0.040	ethanol	50	None

(a) These runs were stopped at 83 per cent completion.

(b) These runs were stopped at 50 per cent completion.

Table 16. V.P.C. Results on Known Samples

Column Type	Column Temperature ° C.	Elution Time, Minutes			
		I ^a	II ^b	III ^c	IV ^d
"O" Perkin Elmer	176	4.4	4.8	2.7	4.2
"O" Perkin Elmer	199	2.7	2.9	1.8	2.6
"R" Perkin Elmer	176	28.7	79.8	14.2	31.2
B 132 A	126	11.0	13.6	6.3	9.1
B 132 A	148	5.3	6.1	3.4	4.6
B 59	174	2.2	>30 ^e	1.6	2.0

(a) Compound I is $C_6H_5CH=CHCHO$.

(b) Compound II is $C_6H_5CH=CHCH_2OH$.

(c) Compound III is $C_6H_5CH_2CH_2CHO$.

(d) Compound IV is $C_6H_5CH_2CH_2CH_2OH$.

(e) Compound II was not eluted in this time period. Its actual elution time was not found.

(II or III) is absent from these mixtures. This statement, however, requires the assumption that neither II nor III would be completely transformed to IV as soon as they are formed.

V.P.C. Results Using Column B 132 A

The descriptions of typical chromatograms obtained using this column for the analysis of mixtures from experiments B 51, B 53, B 54, and B 56 are shown in Table 17.

In these chromatogram descriptions the solvent and water peaks are not listed since in every case these materials were eluted much

Table 17. V.P.C. Results Using Column B 132 A

Hydrogenation Run Number	Column Temperature ° C.	(All Runs Stopped at 83 Per Cent Completion) Chromatogram Description (1.0 µl. Samples)
B 51	151	Large peak at 3.4 min.; broad peak from 4.7 to 5.8 min.
B 53	151	Large sharp peak at 3.4 min.; broad peak 4.7 to 5.6 min.; with slight shoulder at 4.9 min.; small broad peak 10.1 to 10.6 min.
B 54	151	Large sharp peak at 3.4 min., broad peak 4.7 to 5.7 min.; no shoulder observable.
B 56	151	Same peaks at B 54.
Equavolume mixture of I, II, III, and IV	151	Relatively sharp peak at 3.4 min.; broad peak with shoulders at 4.9 and 6.2 min.
B 51	174	Sharp peak at 2.3 min., relatively sharp peak 2.9 to 3.3 min.; with shoulders.
B 53	174	Sharp peak at 2.3 min.; relatively sharp peak at 3.0 to 3.3 min.; a third peak 5.4 to 5.7 min.
B 54	174	Same peaks as for sample B 51.
B 56	174	Same peaks as for sample B 51.
Equavolume mixture of I, II, III, and IV	174	Sharp peak at 2.3 min. with shoulders at 3.4 and 4.3 min.

more rapidly than the other mixture components and were thus readily identified. The results in Table 17 show poor resolution of all components except for III which appears to be a major constituent of all the hydrogenation mixtures. Comparison of the synthetic mixture chromatogram with those from the hydrogenation runs show differences in the

shoulder positions of the unresolved peak. This indicated that if II were present in the hydrogenation mixtures it must have been in small amounts. This observation was based on the order of elution for these compounds shown in Table 16 for column B 132 A. It was evident from Table 17 this column was not completely suitable for the V.P.C. analyses under the conditions used.

V.P.C. Results Using Column B 59

This column, like B 132 A, was a specially prepared column but three feet longer. It was felt this greater length should aid the resolution of the mixture components. The results obtained using this column on hydrogenation runs B 62, B 64, and B 66 are shown in Table 18. These results again show compound III to be a major constituent in the hydrogenation mixture. Compounds I and IV were detected in runs B 64 and B 66. In the case of run B 62 which contained no added Zn(II) the presence of a small amount of II may be indicated by the "hump" at 2.8 min. In the other runs appreciable amounts of II could not be detected. Column B 59 was also used in some analyses at 150° C. but the results were poorer than those shown in Table 18 in terms of resolution of components. From these results it was concluded column B 59 was also not suitable for quantitative V.P.C. analysis.

V.P.C. Results Using Perkin Elmer "O" Column

V.P.C. analyses with this column at 175° C. were carried out for a number of hydrogenation mixtures but there was essentially no resolution of compounds I and IV at this temperature. This meant a lower temperature would be required thus sacrificing sharpness of peaks for

Table 18. V.P.C. Results Using Column B 59 at 174° C.

Experiment Number	Volume of Sample, μ l.	(All Runs Stopped at 83 Per Cent Completion) Chromatogram Description
B 62	1.0	Sharp peak at 1.6 min., shoulder on far side of peak; two small "humps" poorly resolved at 2.5 and 2.8 min.
B 64	1.0	Large sharp peak at 1.6 min., shoulder on far side at 1.9 min., very small peak at 2.1 min., larger peak at 2.2 min.
B 66	1.0	Sharp peak 1.6 min.; very small peak at 2.1 min. on tail of previous peak; larger peak at 2.2 min., tailing to 9.0 min.
$C_6H_5CH = CHCHO(I)$	0.8	Sharp peak at 2.2 min. with some tailing.
$C_6H_5CH_2CH_2CHO(III)$	0.8	Very sharp peak at 1.6 min., with no tailing.
$C_6H_5CH_2CH_2CH_2OH(IV)$	0.8	Sharp peak at 2.0 min., some tailing.
Equavolume Mixture of I, II, III, and IV	0.6	Essentially no resolution.

better resolution. Table 19 shows the results obtained at 152° C. with this column. As in previous V.P.C. results the use of column "O" showed some displacement of elution times for the components in the mixtures from the times observed for single components. If some peaks appeared as shoulders or on the tail section of a previous peak, the elution time for such peaks could only be estimated. In these cases it was more convenient to note the time at which the peak maximum occurred for identification purposes. From Table 19 it is again qualitatively apparent that III is a major component of the hydrogenation mixtures analyzed.

Table 19. V.P.C. Results Using Perkin Elmer "O" Column at 152° C.

Experiment Number	Volume of Sample, μ l.	(All Runs Stopped at 83 Per Cent Completion) Chromatogram Description
B 62	1.0	Large, sharp peak at 3.4 min.; small peak at 5.0 min.; medium peak at 6.1 min.
B 66	1.0	Large, sharp peak at 3.4 min.; medium large peak at 5.4 min. with tailing; broad shoulder peak appears at 6.7 min.
B 70	1.0	Small peak at 3.6 min.; large peak at 4.9 min.; small hump at 5.9 min.; small peak at 6.3 min.
$C_6H_5CH = CHCHO(I)$	0.6	Large sharp peak at 5.7 min., little tailing.
$C_6H_5CH_2CH_2CHO(III)$	0.8	Large, sharp peak at 3.5 min., little tailing.
$C_6C_5CH_2CH_2CH_2OH(IV)$	0.6	Medium broad peak at 5.4 min., considerable tailing.

V.P.C. Results Using Perkin Elmer "R" Column

The use of column "R" in the V.P.C. analysis permitted the analyses to be expressed in semi-quantitative terms, but the use of this column had the obvious disadvantage of not eluting compound II except at very long times (Table 16). The calibration of this column in terms of compound III was accomplished by measuring peak areas for various sample sizes of this compound. The use of this calibration in conjunction with an internal normalization of all peaks observed permitted some approximate percentage composition data to be obtained. These procedures also showed the total volume of the sample analyzed could be accounted for within a few per cent in terms of the peaks observed.

Since these procedures give only approximate results, the presence of a few per cent of compound II cannot be definitely ruled out. Table 20 shows some of the results obtained at 183° C. using the calibration and internal normalization procedures just described. Similar results were obtained at 173° C. column temperature though peak areas of compounds I and IV appeared to be less reproducible.

From Table 20 the approximate percentages of III in the hydrogenation mixtures can be estimated as 25 to 30 per cent in runs B 62 (no Zn(II) or Fe(II) present), B 64, and B 66 (both with Zn(II) present). But, in runs B 70 and B 71 the amount of III in the mixture was found to be about 40 per cent. These runs contained Fe(II) as the catalyst modifier. The increase in III for B 70 and B 71, over that found for B 62, B 64, and B 66, was accompanied by a decrease in the amounts of I and especially IV found in the mixtures. This result seemed to indicate the Fe(II) ions in ethanol hinder the transformation of III to IV or the Fe(II) ions aid the transformation of I to III while at the same time not affecting the transformation of III to IV or alternatively, the result could be a combination of both these effects. Table 20 also shows the sample of IV had become contaminated. This was shown by a double peak observed when a supposedly "pure" sample of IV was analyzed. This fact did not prevent the identification of the major components in the hydrogenation mixtures.

Column "R" was used to analyze other hydrogenation mixtures at 183° C. but with a greater flow rate of carrier gas. The results of these analyses are shown in Table 21. The higher flow rate displaced the peaks (except solvent) to slightly shorter elution times so the peak identifications remained the same in terms of order of elution from the column.

Table 20. V.P.C. Results Using Perkin Elmer "R" Column at 183° C.
for Runs B 62, B 64, B 66, B 70, and B 71

Experiment Number	Volume of Sample, μ l.	Peak Areas	(All Runs Stopped at 83 Per Cent Completion) Chromatogram Description
B 62	2.0	- 55.4 12.8 53.4	Solvent peak at 0.7 (off scale). Peak at 10.5 min. Peak at 17.6 min. Peak at 21.2 min.
B 64	2.0	6.6 58.1 14.7 64.4	Solvent peak at 0.7 min. Peak at 10.5 min. Peak at 17.6 min. Peak at 21.2 min.
B 66	2.0	8.2 51.0 21.6 85.1	Solvent peak at 0.7 min. Peak at 10.5 min. Peak at 17.7 min. Peak at 21.2 min.
B 70	2.0	11.1 62.8 7.0 44.1	Solvent peak at 0.7 min. Peak at 10.5 min. Peak at 17.7 min. Peak at 20.6 min.
B 71	2.0	19.7 64.0 6.0 39.1	Solvent peak at 0.7 min. Peak at 10.5 min. Peak at 17.6 min. Peak at 20.6 min.
$C_6H_5CH = CHCHO(I)$	1.0	104	Peak at 20.6 min.
$C_6H_5CH_2CH_2CH_2OH(IV)$	1.0	9.6 39.9	Peak at 17.7 min. Peak at 21.2 min.
C_2H_5OH	0.1	18.8	Peak at 0.7 min.
$C_6H_5CH_2CH_2CHO(III)$	0.2 0.4 0.6 0.8	22.2 40.1 58.6 79.4	Peak at 10.5 min. Peak at 10.5 min. Peak at 10.5 min. Peak at 10.5 min.

Table 21. V.P.C. Results Using Perkin Elmer "R" Column at 183° C.
for Runs B 79, B 80, B 81, B 83, B 84, and B 85

Experiment Number	Volume of Sample, μ l.	Peak Areas	(All Runs Stopped at 83 Per Cent Completion) Chromatogram Description
B 79	2.0	20.0 62.5 14.9 51.1	Solvent peak at 0.7 min. Peak at 10.1 min. Peak at 17.0 min. Peak at 19.8 min.
B 80	2.0	10.8 33.0 16.0 26.4 76.4	Solvent peak at 0.7 min. Peak at 10.1 min. Peak at 17.0 min. Peak at 18.3 min. Peak at 19.8 min.
B 81	2.0	13.2 35.5 13.2 95.2	Solvent peak at 0.7 min. Peak at 10.0 min. Peak at 17.0 min. Peak at 19.8 min.
B 83	2.0	10.7 39.5 17.9 120.	Solvent peak at 0.7 min. Peak at 10.0 min. Peak at 17.0 min. Peak at 20.0 min.
B 84	2.0	1.5 43.9 19.8 105.	Solvent peak at 0.7 min. Peak at 10.1 min. Peak at 17.0 min. Peak at 19.8 min.
B 85	2.0	1.0 60.0 15.3 100.	Solvent peak at 0.7 min. Peak at 10.1 min. Peak at 17.0 min. Peak at 19.8 min.
$C_6H_5CH = CHCHO(I)$	1.0	100.	Peak at 19.8 min.
$C_6H_5CH_2CH_2CHO(III)$	1.0	110.	Peak at 10.1 min.
$C_6H_5CH_2CH_2CH_2OH(IV)$	1.0	19.6 112.	Peak at 18.0 min. and at 21.3 min.

The results in Table 21 permit the determination of percentages of compound III in the mixtures, but, again the poor resolution of the other peaks prevented clear cut estimations of their percentages. Runs B 79 and B 80 gave essentially the same results in terms of III content as earlier runs using ethanol solvent with added Fe(II). The runs in acetic acid with either Zn(II) (B 83, B 85) or Fe(II) (B 81, B 84) present showed the III content of these mixtures to be about 25 per cent with the remainder accounted for by I and IV. Calculations from H_2 absorption show IV is present at about the 70 per cent level and I at 5 per cent.

The peak at 17.6 min. in runs shown in Table 20 and at 17.0 min. in Table 21 represented a puzzling result. In Table 20 the impurity peak in a sample of IV appeared at about the same time. However, this may have been merely coincidental since under the conditions used in Table 21 the impurity peak in IV appeared at 18 min., whereas the unknown peak consistently appeared at 17.0 min. in the hydrogenation mixtures. Although, in any case the unknown peak was small and rather broad, it consistently appeared largest when the solvent content of the hydrogenation mixture was smallest regardless of whether the solvent was ethanol or acetic acid. However, it should be pointed out in cases using acetic acid as the hydrogenation solvent, the mixture was finally isolated from a solution composed primarily of ethanol. All of these observations seemed to point to a reaction product of ethanol with some component of the mixture as the substance responsible for the "unknown" peak. One good possibility in this connection is the formation of acetals and/or hemiacetals by reaction of ethanol with an aldehyde component of the

reaction mixture. An ester of acetic acid is also a possibility in accounting for the unknown peak in some runs.

It was of some importance in the area of V.P.C. analysis of hydrogenation mixtures to obtain information on the composition of mixtures from experiments in which the reaction had been stopped after one mole-equivalent of hydrogen had been absorbed, i.e., 50 per cent completion. The analysis results of such mixtures is shown in Table 22. A duplicate analysis of one run is included to give an indication of the reproducibility found in the V.P.C. analyses. Poor resolution was again observed for peaks of I and IV, but the peak due to III was easily found and measured. In acetic acid, runs B 98 (Zn(II) present) or B 100 (Fe(II) present) showed the composition in terms of III to be 25 per cent. In ethanol, run B 102 (Zn(II) present) showed a III content of 35 per cent. If, as appears to be the case, little or no II is present, calculations readily show the compositions to be 25 per cent III, 37.5 per cent I, and 37.5 per cent IV for runs B 98 and B 100. For B 102 the composition would be 35 per cent III, 32.5 per cent I and 32.5 per cent IV.

A brief summary of the V.P.C. results might be helpful at this stage. First, under none of the conditions used was it possible to identify positively cinnamyl alcohol (II) as a component of either the 83 per cent or 50 per cent completion reaction mixtures. It may have been present in some cases to the extent of a few per cent. Second, 3-phenylpropanal (III) was clearly identified as a major component of the 83 per cent and 50 per cent completion reaction mixtures. Third, in ethanol the presence or absence of Zn(II) appeared to have little

Table 22. V.P.C. Results Using Perkin Elmer "R" Column at 183° C.
for Runs B 98, B 100, and B 102

Experiment Number	Volume of Sample, μ l.	Peak Areas	(All Runs Stopped at 50 Per Cent Completion) Chromatogram Description
B 98	2.0	2.9 30.5 127.	Solvent peak at 0.7 min. Peak at 9.1 min. Peak at 17.8 min.
B 100	2.0	2.5 30.4 135.	Solvent peak at 0.7 min. Peak at 9.1 min. Peak at 17.8 min.
B 100	2.0	2.6 28.1 130.	Solvent peak at 0.7 min. Peak at 9.1 min. Peak at 17.8 min.
B 102	2.0	5.8 45.3 83.0	Solvent peak at 0.7 min. Peak at 9.1 min. Peak at 17.8 min.
$C_6H_5CH = CHCHO(I)$	1.0	125.	Peak at 17.7 min.
$C_6H_6CH_2CH_2CHO(III)$	1.0	120.	Peak at 9.0 min.
$C_6H_5CH_2CH_2CH_2OH(IV)$	1.0	17.0 87.5	Peak at 15.2 min. and peak at 18.1 min.

effect on the composition at 83 per cent completion but Fe(II) caused a significantly greater amount of III to be found at the same degree of completion. Fourth, in acetic acid Fe(II) showed no differences in effects on composition from Zn(II) at either 83 or 50 per cent completion.

These V.P.C. results tend to show that if any selectivity of hydrogenation was achieved under the conditions used, it was to a great degree the hydrogenation of the ethylenic group rather than the carbonyl group

of cinnamaldehyde. This selectivity, in terms of III content, appeared to be greatest when Fe(II) was present in ethanol solvent for the hydrogenation. It was also noted that significant differences in composition were not found in varying the amounts of added Zn(II) or Fe(II) in the range from 2 to 50×10^{-6} mole used.

If one supposes the previously made assumption, i.e., II is not rapidly and completely transformed to IV as soon as it is formed, is not valid then the V.P.C. results do not clearly define the reaction path from I to IV. Since II contains an isolated ethylenic group, it should be susceptible to rapid hydrogenation. Thus, its apparent absence in significant amounts could be explained by a rapid transformation of II to IV. From these statements, it can be seen that further work is needed to determine the reaction path from I to IV.

The results of Tuley and Adams (11) are quite different from those presented here. It doesn't seem likely that the products in their work or this work were mistakenly identified. In their work cinnamyl alcohol (II) was isolated by distillation and identified by its melting point. In this work 3-phenylpropanal (III) was clearly identified as a major component in the hydrogenation mixtures by V.P.C. analysis. Since the present work made no attempt to duplicate the experimental conditions used by Tuley and Adams (11), it cannot be said that these results contradict their findings. It is suggested the larger amounts of catalyst (PtO_2) used by Tuley and Adams and the pre-reduction of this catalyst constitute significantly different conditions from those used in this work. These factors alone may account for the striking difference of results. However, it would certainly be desirable for additional work to be done to clarify this situation.

Surface Coverage of the Catalyst by Zn(II) and Fe(II)

Surface Area of PtO₂ and Reduced PtO₂

In connection with the ion adsorption data obtained in this work, it was desirable to obtain information on the amount of catalyst surface covered by the added ions. This was particularly true since the curves showing adsorbed vs. added ions appeared to be approaching a limiting value of adsorbed ions at about 250×10^{-6} mole of added ions. The limiting adsorbed amount seemed to be the same for both Zn(II) and Fe(II) and was apparently close to 16×10^{-6} mole.

In order to determine if these apparent limiting values represented saturation of the catalyst surface, it was necessary to obtain information on the surface area of a catalyst sample used in these studies. Surface area measurements were made on a 2.00 g. sample of PtO₂ and a 1.48 g. sample of Pt (PtO₂ reduced in glacial acetic acid to Pt). These measurements were performed by Mrs. M. B. Gandy of the Engineering Experiment Station at this institution. The method employed was the standard B.E.T. (Brunauer, Emmett, and Teller) nitrogen adsorption procedure. The results showed PtO₂ had a surface area of 34.9 m.² per g. (one determination) while the Pt sample had a surface area of 8.3 m.² per g. This value is an average of two determinations, one showing 8.6 m.²/g., the other 8.0 m.²/g. The value of 8.3 m.²/g. was surprisingly low and is worthy of some comment.

In the isolation of the reduced PtO₂ sample, ethanol was used to rinse acetic acid from the sample in order to facilitate degassing of the sample before N₂ adsorption was carried out. As the last portion of ethanol was removed under suction, the catalyst sample rapidly became

very hot. The suction was immediately turned off but it is very likely the heat evolved, even for such a short time, altered the catalyst surface area by sintering or fusing catalyst microparticles. The effects of such sintering on surface area are commonly encountered in catalytic work. For example, Maxted and co-workers (52) showed that sintering at 400° - 410° C. decreased the specific surface area of a Pt sample from $11.8 \text{ m}^2/\text{g.}$ to $8.0 \text{ m}^2/\text{g.}$ This represented a loss of about one-third of the original surface area by such a treatment.

Another point of interest occurs in comparing the surface areas of PtO_2 and reduced PtO_2 (Pt). In spite of the much greater surface area of PtO_2 , it was shown in Table 9 that Pt had a much greater adsorptive ability toward Zn(II) ions, although the adsorption was effected in the presence of H_2 , of course. From these results one might note that the nature of the catalyst surface, rather than only surface area, is a prime factor in determining the extent of ion adsorption on the catalyst surface.

Calculations of Catalyst Surface Coverage for Zn(II) and Fe(II)

Relatively simple calculations could be made on the area of catalyst covered by the adsorbed ions by assuming a spherical shape for the ions and using a plane projection of that sphere on the catalyst surface. The area of one such projected circle was multiplied by the number of ions found present to obtain the area covered by the adsorbed ions. But, this procedure is complicated by choice of an ionic radius or a covalent radius. The suitable choice would depend on the type of

(52) E. B. Maxted, K. L. Moon, and E. Overgag, Discussions Faraday Soc., 8, 135 (1950).

bond formed between the ion and Pt surface. The exact nature of such bonds is not clear; however, Maxted (53) has shown in a systematic study of many metal ions as poisons on Pt catalysts that the electronic structure of the ion was a factor in determining whether or not the ion would be a poison (strongly adsorbed). It was observed by Maxted that each orbital just under the s or p valency orbital must contain at least one electron for an ion to act as a poison. He then suggested the bonding may be of dative type with the ion as the donor to the Pt. Boudart (54), in more general terms, notes that the electron transfer in chemisorption on metals may take place in either direction and the resulting bonds may vary from ionic to covalent and all intermediate stages between the two. In view of these observations, the choice of an average between the ionic and covalent radii for Zn(II) and for Fe(II) seemed appropriate in giving a reasonable approximation of the desired value of surface coverage by these ions.

Calculations are shown in detail in Appendix E using these averages but the results may be stated here. For both Zn(II) and Fe(II) at an adsorbed level of 16×10^{-6} mole the surface covered by the ions is 20 per cent of the total surface if it is assumed that the $8.3 \text{ m}^2/\text{g.}$ value is true for the Pt in these experiments. If sintering took place on the measured sample of Pt, the surface covered by the ions would be less than 20 per cent. Calculations based on ionic radii show 10 per

(53) E. B. Maxted, in W. G. Frankenburg, E. K. Rideal, and V. I. Komarewsky, Eds., Advances in Catalysis, Vol. III, Academic Press, Inc., New York, 1951, p. 154.

(54) M. Boudart, J. Am. Chem. Soc., 74, 1531 (1952).

cent coverage by Zn(II) and 12 per cent coverage by Fe(II). Based on covalent radii the per cent surface coverages would be 29 for Fe(II) and 33 for Zn(II). It is seen from these approximate calculations that the surface coverages by the metal ions do not appear to be near to saturation even if the larger covalent radii are used in the calculations.

Calculations of Catalyst Surface Coverage by Zn(II) and Fe(II) with Adsorbed Counter Ions

Since the ion adsorption curves for Zn(II) and Fe(II) showed 16×10^{-6} mole was near the limit of adsorption on the Pt catalyst, it was evident from the calculations above that some factor other than the metal ions was limiting the adsorption. One such factor is the strong likelihood that negative counter ions are associated with the metal ions on the surface. In the acetic acid solutions these counter ions could be assumed to be acetate ions. If a 2/1 ratio of acetate ions to metal ion is assumed, an approximate calculation of surface coverage by Zn(II) and Fe(II) with the counter acetate ions can be made.

In order to perform this calculation, a value for the effective "radius" of an acetate ion was needed. Inspection of Dreiding scale models of acetic acid showed the "radius" of the ion would depend on whether the carbon-carbon bond axis was parallel or perpendicular to the catalyst surface or, of course, intermediate between these two extremes. In the absence of a literature value for this "radius" in acetic acid solutions, approximate calculations were made using the Dreiding models. If the C-C bond axis is parallel to the catalyst surface, the effective "radius" was calculated to be 1.77 \AA . Straight forward calculations (assuming tangential touching of acetate ions) based on this value showed the acetate ions associated with the metal ions

could cover 1.90 m.^2 of catalyst surface. On the other hand, if the C-C bond axis is perpendicular to the surface, the "radius" would be 1.36 \AA and the acetate ions could cover 1.12 m.^2 of catalyst surface. Since only 1.42 m.^2 of surface is available from 0.171 g. of reduced PtO_2 (based on B.E.T. measurements), the later value of 1.12 m.^2 is probably more realistic. This calculation showed that 79 per cent of the available catalyst surface could be covered by acetate ions associated with the metal ions. Since the hydrogenation reaction is still proceeding even at the highest levels of adsorbed ions, it appeared that the total surface was not completely covered during the reaction. This observation should tend to support the view that the C-C bond in acetate ion is more nearly perpendicular than parallel to the catalyst surface. These calculations also show that not much more metal ions with acetate counter ions could be adsorbed by the catalyst.

Relation Between Surface Coverage and Initial Rates of Hydrogenation

In view of the uncertainties involved in determining a realistic value for surface coverage by adsorbed ions, the relationship between initial rates and surface coverage was not investigated thoroughly. Yet, there is one case that deserves comment. The k'_{30} s found for the experiments having 250×10^{-6} mole Zn(II) present were relatively very small (average value 40). The amount of adsorbed Zn(II) in these experiments was close to 16×10^{-6} mole. On the other hand, a similar experiment having 250×10^{-6} mole Fe(II) present showed a rate constant nearly four times greater (246) than the Zn(II) case and yet the amount of adsorbed Fe(II) was also very close to 16×10^{-6} mole. The surface coverage by these ions at this level has been shown to be almost the

same. These results tend to indicate Zn(II) at this level has a much greater poisoning effect on the catalyst than does Fe(II). Apparently, this is due to its ability to alter the electronic structure of the catalyst in such a manner so as to hinder chemisorption and subsequent reaction of cinnamaldehyde and/or hydrogen on the surface or alternatively, Zn(II) may hinder desorption of products from the catalyst.

CHAPTER IV

CONCLUSIONS

The conclusions stated below are derived in the context of the experimental conditions used in this work. Therefore, they should be regarded with this context in mind.

The rates of cinnamaldehyde hydrogenation using Adams' catalyst in the presence or absence of added metal ions show a first order dependence on H_2 pressure over approximately the first five minutes of the reaction, but show a decreasing rate thereafter.

In the absence of added metal ions, glacial acetic acid is a better solvent than either 95 per cent ethanol or 93 per cent acetic acid in terms of higher initial rates. However, in terms of the extent of H_2 absorption at times after which the reaction stopped or became very slow, 95 per cent ethanol is the best solvent. Alkaline 95 per cent ethanol is better than neutral 95 per cent ethanol in terms of initial rates, but poorer than the same solvent in terms of extent of H_2 absorption. Increasing concentrations of cinnamaldehyde cause an increase in the initial rates in glacial acetic acid and in 95 per cent ethanol, but, this increase is greater in acetic acid than ethanol.

Added $Zn(II)$ ions in 95 per cent ethanol as solvent do not significantly affect the initial rate or extent of H_2 absorption when either 5×10^{-6} or 20×10^{-6} mole were present in the hydrogenation mixture. On the other hand, in 93 per cent ethanol, 100×10^{-6} mole $Zn(II)$ decreases the rate of reaction and H_2 absorption significantly.

In glacial acetic acid solvent, the dependence of initial rate on the amount of Zn(II) added or adsorbed on the isolated catalyst is complex. At an added level of 0.05×10^{-6} mole Zn(II), the initial rate is increased but all other added levels give lower initial rates when compared to runs in which zinc is absent. The lowest rate is observed at the highest added level of 250×10^{-6} mole Zn(II). The extent of H_2 absorption is at first lower, then becomes greater at about 100×10^{-6} mole of added Zn(II), but is lowest at 250×10^{-6} mole of added Zn(II). In the presence of the same level (100×10^{-6} mole) of added Zn(II) ions, 93 per cent acetic acid as solvent shows the same rate as glacial acetic acid solvent.

Measurements of adsorbed Zn(II) on the isolated catalyst show the amount adsorbed increases with an increase the amount added, approaching asymptotically a limiting value near 16×10^{-6} mole adsorbed with no indication of multilayer Zn(II) adsorption. Several factors influence the quantity of Zn(II) adsorbed. For example, the amount of adsorbed Zn(II) decreases with increasing time periods between the end of reaction and time of isolation of the catalyst, approaching a limiting value in approximately 36 hours. Also the presence of H_2 aids the adsorption of Zn(II) on the catalyst. Apparently the Zn(II) ions adsorbed on the isolated catalyst are tightly held since additional washings fail to remove any of the material.

Addition of Fe(II) to reaction mixtures in 95 per cent ethanol not only gives an increase in initial rates, but also increases extent of H_2 absorption. The rate increase is highest for 25×10^{-6} and 100×10^{-6} mole of added Fe(II).

In glacial acetic acid solvent, the initial rate is dependent in a complex manner on both the amount of Fe(II) added and the amount adsorbed. Up to levels of about 10×10^{-6} mole of added Fe(II), the rates are higher than those in the absence of Fe(II). However, in presence of higher levels of added Fe(II) the rates are lower and reach their minimum at 250×10^{-6} mole added Fe(II). In the presence of the same level of added Fe(II) ions, 93 per cent acetic acid is a poorer solvent than glacial acetic acid in terms of initial rates.

The quantity of adsorbed Fe(II) increases with an increase in added Fe(II), approaching asymptotically a limiting value near 16×10^{-6} mole of adsorbed Fe(II). The amounts of Fe(II) adsorbed at lower levels of added Fe(II) are significantly greater than the amounts of Zn(II) adsorbed at the same added levels. However, the difference is negligible at the highest levels of added ions. Again, there is no evidence of multilayer metal ion adsorption on the isolated catalyst.

Addition of Fe(III) ions to reaction mixtures in glacial acetic acid gives higher initial rates than the same level of freshly prepared Fe(II) solutions or "aged" Fe(II) solutions. However, freshly prepared Fe(II) solutions gives higher rates than "aged" Fe(II) solutions. For reaction mixtures containing Fe(III) ions, 93 per cent acetic acid is again a poorer solvent than glacial acetic acid in terms of initial rates.

3-Phenylpropanal (III) is a major component in cinnamaldehyde hydrogenation mixtures stopped at either 83 or 50 per cent completion. Significant amounts of cinnamyl alcohol (II) could not be detected in these reaction mixtures; however, these results do not clearly

define the reaction path from cinnamaldehyde (I) to 3-phenylpropanol (IV).

At the highest levels of adsorbed Zn(II) and Fe(II), these ions cover only about 20 per cent of the available catalyst surface, yet acetate counter ions can effectively cover about 79 per cent of the total surface available. The difference in initial rates at the highest level of adsorbed Zn(II) and Fe(II) is attributed to the greater ability of Zn(II) to modify the electronic nature of the catalyst surface in a deleterious manner with respect to hydrogenation rates.

CHAPTER V

RECOMMENDATIONS

The procedure described in this work for measuring the amount of adsorbed metal ions on the catalyst surface through the use of radioactive isotopes could logically be extended to other metal ions besides Zn(II) and Fe(II). In this area of work, the correlation of hydrogenation rates with catalyst surface coverage by various metal ions might provide useful information on the nature of the metal ion-catalyst chemisorption bond. This information could in turn lead to explanations for the behavior of some metal ions as promoters and others as poisons in given catalytic reactions. For instance, the "mechanism" of the promoting effect of Fe(II) and other metal ions in aldehyde hydrogenations with Adams' catalyst does not appear to be firmly established. Additional studies of the type described in the present work, but with an aldehyde less complex than cinnamaldehyde, might be of value in elucidating such a "mechanism."

In connection with metal ion adsorption studies on the catalyst surface, additional work in the area of factors which influence the adsorption would be desirable. Furthermore, an extension of surface area measurements on catalyst samples used in these areas of work would prove valuable.

As previously indicated, further work is needed to define the reaction path from cinnamaldehyde to 3-phenylpropanol. Evidence on

this point might be obtainable in hydrogenation rate studies on the separate half-hydrogenated products and known mixtures of these two compounds.

The procedures in this work could be easily adapted to investigate methods of removal of metal ions from the catalyst surface. It is possible that a variety of metal ion chelating reagents would prove useful in such a study. The information gained in these studies might also provide relative measurements of the strengths of metal ion-catalyst bonds.

Results reported in this work differed significantly on occasion with those reported by other investigators. It would thus seem desirable either to attempt a duplication of their exact experimental conditions or else to make additional studies under a wide variety of experimental conditions.

APPENDIX A

PREPARATION OF V.P.C. COLUMN B 59

Since the possible components of cinnamaldehyde hydrogenation mixtures had rather high boiling points, it was felt that a column with suitable high temperature operating conditions was desirable. The successful V.P.C. separation of a number of steroids was reported by VandenHeuvel, Sweeley and Horning (55) using a methyl silicone gum (S. E.-30) as the liquid phase. The basic instructions for the preparation of a column similar to that used by these workers was obtained from a private communication from Dr. Sweeley to Dr. John R. Dyer of this institution.

One hundred grams of Chromasorb P (30-60 mesh) was stirred with 360 ml. conc. HCl for three hours. The HCl was decanted and the material was washed with distilled water until the wash liquid was neutral to pH paper. The acid-washed Chromasorb P was oven dried at 110° C. and then was permitted to soak in 50 ml. of 0.5 N KOH in methanol for three hours. The methanol was decanted and the material was then washed with distilled water until the wash liquid was neutral to pH paper. Again, the material was oven dried at 110° C. Following this drying, the acid, base-washed Chromasorb P was resieved with 30-60 mesh sieves. After the resieved material (25 g. portion) was stirred

(55) W. J. A. VandenHeuvel, C. C. Sweeley, and E. C. Horning, J. Am. Chem. Soc., 82, 3482 (1960).

with 100 ml. of a 3 per cent (wt./vol.) solution of S. E.-30 in toluene for five minutes, the excess solution was filtered through a medium porosity sintered glass filter tube. The prepared adsorbent then was permitted to remain on the filter for 10 minutes under water-aspirator vacuum after which it was removed from the funnel to a triple thickness of 25 cm. filter paper and spread in a thin layer for preliminary oven drying at 100° C. The partially dried material was transferred to a large casserole for further drying in the oven at 110° C. This last drying period lasted about four hours.

A nine-foot length of copper tubing (4mm. O.D.) was carefully packed with about 20 g. of the Chromasorb P coated with S. E.-30 and then bent in the shape necessary to fit the Perkin Elmer Vapor Fractometer.

APPENDIX B

FRACTIONAL DISTILLATION OF
CINNAMALDEHYDE UNDER REDUCED PRESSURE

The kinetic results indicated the cinnamaldehyde could be reproducibly purified by fractional distillation under reduced pressure. These distillations were carried out in the Todd apparatus under an atmosphere of nitrogen. A reflux ratio of about 15 to 1 was used for all fractions boiling near the correct temperature. Table 24 shows the data obtained in the first distillation of cinnamaldehyde performed during the course of this work.

Table 23. Distillation of Cinnamaldehyde

Conditions: Reflux ratio about 15 to 1, N₂ Atmosphere.

Fraction Number	Volume in ml.	Distillation Temperature, °C.	Pressure in mm. Hg	Index of Refraction @ °C., D Line
1	0- 40	120.2-129.8	24	-
2	41-120	129.8-131.4	27	-
3	121-190	131.4-132.2	27	1.6210 @ 22
4	191-290	132.2-132.7	27	1.6212 @ 22
5	291-390	130.6	15	1.6212 @ 22
6	391-430	130.6	15	1.6216 @ 22
7	431-510	130.4	15	1.6217 @ 21
8	511-550	130.0-129.0	15-14	1.6217 @ 21

APPENDIX C

PREPARATION OF 3-PHENYL-1-PROPANOL

A sample of this compound was needed for V.P.C. analyses since it is a possible component of hydrogenation mixtures of cinnamaldehyde. This material was not immediately available from other sources but it was prepared readily from the available cinnamyl alcohol by hydrogenation of the unsaturated alcohol in 95 per cent ethanol using Adams' catalyst at about 3 atmospheres of H_2 pressure. After a preliminary run using 50 ml. solvent, 0.200 g. PtO_2 , and 0.02 mole cinnamyl alcohol showed rapid and complete H_2 absorption, two preparative runs were carried out.

The first run used 0.06 mole cinnamyl alcohol, 0.200 g. PtO_2 , and 100 ml. solvent. In this run the H_2 absorption stopped at 0.064 mole and the reaction was complete in about 30 minutes. In the second preparative run, 0.08 mole of cinnamyl alcohol, 0.200 g. PtO_2 , and 100 ml. solvent were used. The H_2 absorption stopped at 0.088 mole and the reaction was complete in about 40 minutes. The catalyst was filtered from both reaction mixtures using a sintered glass filter tube and suction. The filtrates from the preparative runs were combined and the excess ethanol evaporated on a steam bath. Fractional distillation of the crude product under reduced pressure was then carried out using a 10-inch Vigreux column at a rate of about 30 drops per minute. The fraction boiling at $66-67^\circ C.$ under 0.9-1.0 mm. Hg pressure was chosen for use in the V.P.C. work.

APPENDIX D

ANALYSIS OF Zn(II) SOLUTIONS
BY E.D.T.A. TITRATIONS

In order to prepare "standard" radioactive solutions of Zn(II) ions of known concentrations, it was necessary that the Zn⁶⁵ solution from Oak Ridge (A.E.C. facility) be analyzed in terms of Zn(II) concentration. To avoid "wasting" the radioactive material, it was desirable that very small aliquots of the original Zn⁶⁵ solution diluted to 10 ml. in H₂O be used. An E.D.T.A. titration seemed feasible in this regard. The procedures developed in the present work were based on instructions given in a standard work on E.D.T.A. titrations (56). Zn(II) solutions can be titrated directly in solutions buffered to pH 10 or even at somewhat lower pH values. Erio T was the indicator for these titrations and showed a change from red to green-blue at the endpoint. The di-sodium salt of E.D.T.A. was used as the titrant. A number of preliminary experiments on prepared Zn(II) solutions of the acetate and chloride showed excellent reproducibility of endpoint detection when "normal" size aliquots were titrated. The next step involved titrations of very small aliquots (withdrawn by hypodermic syringes) of a Zn(II) solution of known concentration previously titrated by E.D.T.A. under usual conditions. The results obtained in these

(56) H. A. Flaschka, EDTA Titrations, Pergamon Press, Inc., New York, 1959, p. 75.

titrations and those obtained later for $\text{Zn}^{65}(\text{II})$ solutions are shown in Table 24.

Table 24. E.D.T.A. Titrations of Small Aliquots of $\text{Zn}(\text{II})$ Solutions

Conditions: Solutions buffered to pH 10 by $\text{NH}_4\text{Cl}-\text{NH}_3$; total volumes of titrated solutions, 75-100 ml.; Erio T indicator; 0.050 M E.D.T.A. (di-sodium salt) as titrant.

Experiment Number	0.028 M. ZnCl_2 , ml.	$\text{Zn}^{65}(\text{II})$ Sample Volume, ml.	E.D.T.A. Solution, ml.	$\text{Zn}(\text{II})$ M., Found
B 63 1	0.25	-	0.144	0.029
2	0.25	-	0.157	0.031
3	0.25	-	0.152	0.030
4	0.25	-	0.152	0.030
5	0.13	-	0.080	0.031
B 64 1	-	0.10	0.07	0.035
2	-	0.14	0.09	0.032
3	-	0.13	0.08	0.030
4	-	0.18	0.12	0.033

For titrations of such small samples, it was found that dilution of the sample in 75 to 100 ml. of H_2O and the use of a slightly larger than usual amount of indicator was necessary to obtain sharp reproducible endpoints. It can be seen from Table 25 that the results for B 63, 1 through 5, are good in terms of precision but all are consistently slightly higher in $\text{Zn}(\text{II})$ molarity than the previously found value. An estimation of this correction could be made for the titrations of $\text{Zn}^{65}(\text{II})$ solutions, but was probably not necessary since the amount of non-radioactive $\text{Zn}(\text{II})$ used in preparing a "standard" solution was so much larger than the amount of Zn^{65} solution used.

APPENDIX E

CALCULATIONS OF CATALYST
SURFACE COVERAGE BY ADSORBED IONS

In order to obtain information on the amount of catalyst surface that could be covered by the adsorbed ions, some straightforward calculations were made. From the radius of the ion, the area one such ion would cover was easily obtained. This area was multiplied by Avogadro's number and the number of moles of the ion found adsorbed on the isolated catalyst. The product of these three factors was the area covered by the ions adsorbed on the catalyst. The per cent surface covered was then obtainable since the total amount of surface available had been measured by the B.E.T. method. The following calculations at the highest levels of adsorbed ions are illustrative of the procedure just mentioned.

The values for ionic and covalent radii of Zn(II) and Fe(II) were taken from Gould (57). Zn has an ionic radius of 0.70 \AA^0 and a covalent radius of 1.25 \AA^0 . An average of these two is 0.98 \AA^0 . The average squared times pi gave $3.0 \times 10^{-20} \text{ m.}^2$ per ion. Avogadro's number, 6.02×10^{23} ions per mole, times the number of moles adsorbed, 16×10^{-6} , gave 96.3×10^{17} ions present on the surface. Now, $3.0 \times 10^{-20} \text{ m.}^2$ per ion times 96.3×10^{17} ions gave 0.289 m.^2 as the area covered

(57) E. S. Gould, Inorganic Reactions and Structure, Henry Holt and Company, New York, 1955, pp. 453, 455.

by this amount of Zn(II). The per cent coverage was 0.289 m.^2 divided by 1.42 m.^2 (the area of a 0.171 g. sample of reduced PtO_2), then this result multiplied by 100. This calculation showed 20 per cent of total surface available was covered by the Zn(II) ions adsorbed. This same procedure for Fe(II), whose ionic radius is 0.75 \AA° and covalent radius is 1.17 \AA° , gave the same result in terms of per cent coverage of the catalyst sample.

In calculations based on the acetate ion, the effective "radius" depends on the orientation of the ion toward the catalyst surface. The two extremes of possible modes of orientation are represented by 1., the C-C bond axis parallel to the surface and 2., the C-C bond axis perpendicular to the surface. The use of Dreiding scale models permitted an approximate calculation of these "radii." In case 1., the "radius" was 1.77 \AA° with the corresponding area being $1.025 \times 10^{-19} \text{ m.}^2/\text{ion}$. In case 2., the "radius" was found to be 1.36 \AA° and the area was $5.82 \times 10^{-20} \text{ m.}^2/\text{ion}$. Now, since two acetate ions were associated with each metal ion, there was 32×10^{-6} mole of acetate ions adsorbed for the highest levels of metal ion adsorption. Multiplication of 32×10^{-6} mole times 6.02×10^{23} ions/mole times $1.025 \times 10^{-19} \text{ m.}^2/\text{ion}$ gave 1.90 m.^2 as the surface covered by acetate ions from case 1. The same calculation for case 2. gave 1.12 m.^2 as the area covered by the acetate ions. Since B.E.T. measurements showed these catalyst samples (0.171 g.) from PtO_2 reduction (0.200 g.) would have only 1.42 m.^2 of surface, case 2. seemed to be more nearly realistic than case 1. The value of 1.12 m.^2 from case 2. represented 79 per cent surface coverage of the catalyst.

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VITA

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