

*t*-butylbenzene and cyclohexene were reagent grade samples obtained from Phillips Petroleum Co. All were found to be well over 99.5% pure by gas chromatography. Redistilled phenol (Dow Chemical Co.) was a colorless crystalline solid with no impurities detectable by gas chromatography. Cobalt naphthenate was Nuodex Product Co. Nuodex Co 6. 2,2'-Azobis(isobutyronitrile) (ABIN) was obtained from E. I. du Pont de Nemours Co., stored under refrigeration, and used without further purification. Standard solutions were prepared containing phenol in substrate, ABIN in inert diluent, and cobalt soap in

inert diluent; these were stored in a light-shielded, purged, argon-padded system from which portions were withdrawn and combined volumetrically for each run. Oxidations were carried out in a constant-volume semistatic apparatus described previously.<sup>31</sup>

**Acknowledgment.**—We wish to thank one of the referees for valuable criticism of the original manuscript.

(31) W. G. Lloyd, *J. Am. Chem. Soc.*, **78**, 72 (1956); *J. Chem. Eng. Data*, **6**, 541 (1961).

[CONTRIBUTION FROM THE PROCESS RESEARCH DIVISION, ESSO RESEARCH AND ENGINEERING CO., LINDEN, N. J.]

## Chemisorption and Surface Chemistry of Ethylene on Supported Platinum Catalysts

By P. J. LUCCHESI, J. L. CARTER, AND J. H. SINFELT

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The chemisorption and surface chemistry of ethylene on Pt-Al<sub>2</sub>O<sub>3</sub> catalysts have been studied and compared with previously reported results on ethylene over Al<sub>2</sub>O<sub>3</sub>. The same types of species are formed on the Pt-Al<sub>2</sub>O<sub>3</sub> catalysts as are formed on the Al<sub>2</sub>O<sub>3</sub> alone, but the reactivities of the adsorbed species are greatly different. On treatment with H<sub>2</sub>, the adsorbed species were removed much more readily from the Pt-Al<sub>2</sub>O<sub>3</sub> catalysts than from the Al<sub>2</sub>O<sub>3</sub> alone. The desorption products resulting from the H<sub>2</sub> treatment consist largely of ethane and *n*-butane at the lower temperatures investigated (100–150°), but increasing amounts of methane and propane are formed at the higher temperatures, where rupture of C–C bonds becomes important. The much greater ease of removal of the adsorbed species from Pt-Al<sub>2</sub>O<sub>3</sub> catalysts on H<sub>2</sub> treatment suggests that migration of reactive species between Pt and Al<sub>2</sub>O<sub>3</sub> centers may be important.

Supported platinum catalysts are of great technical interest for a variety of hydrocarbon reactions. When the platinum is supported on an acidic oxide such as alumina or silica-alumina, the catalyst is termed bifunctional, *i.e.*, the catalyst has the properties of both a hydrogenation-dehydrogenation catalyst and an acidic catalyst. It has been amply demonstrated that certain reactions over these bifunctional catalysts, including the isomerization of alkanes<sup>1</sup> and the dehydroisomerization of methylcyclopentane,<sup>2,3</sup> involve the cooperative action of the platinum centers and the acidic centers of the catalyst. Furthermore, recent studies suggest that the hydrogenation of ethylene over mixtures of Pt-SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> catalysts may involve a cooperative action of separate centers on the two catalysts.<sup>4</sup>

In view of the well established bifunctional nature of Pt-Al<sub>2</sub>O<sub>3</sub> in the catalysis of certain hydrocarbon reactions, the question arose whether the presence of a small amount of platinum could significantly affect the nature of chemisorption of a molecule such as ethylene on Al<sub>2</sub>O<sub>3</sub>, or alter the subsequent reactivity of the chemisorbed species on the Al<sub>2</sub>O<sub>3</sub>. Consequently, in the present work it was decided to investigate the chemisorption and surface chemistry of ethylene on Al<sub>2</sub>O<sub>3</sub> containing small amounts of platinum. The chemisorption of ethylene on alumina itself has previously been studied with the use of infrared spectroscopy, and the reactivity of the chemisorbed species with hydrogen determined.<sup>5</sup> The results of the present paper represent an extension of this work. The main emphasis in the present study, however, has been on the reactivity of the chemisorbed species rather than

with infrared measurements of the nature of the chemisorption process.

### Experimental

**Apparatus and Procedure.**—The experiments were carried out in a cell specially designed for use with a Beckman IR-7 double-beam grating spectrometer. A detailed description of the apparatus, along with the sample preparation procedure, has been reported previously.<sup>5</sup> Although the details of the infrared spectra were of secondary interest in the present work, it was convenient to do the experiments in this apparatus. Furthermore, the spectra were of use in giving information about the extent of removal of adsorbed species after treatment with hydrogen.

The Pt-Al<sub>2</sub>O<sub>3</sub> catalysts used in the present work were pretreated as follows, prior to adsorption of the ethylene: The catalysts were slowly heated to 500° while they were being evacuated. When the pressure was  $5 \times 10^{-6}$  mm., hydrogen was admitted to the sample cell. The sample was then reduced for 0.5 hr. at 500°, and was subsequently evacuated to  $5 \times 10^{-6}$  mm. at 500°. This pretreating procedure is similar to that described by Spenadel and Boudart.<sup>6</sup>

After the cell was cooled to room temperature under vacuum, the background spectrum of the sample was recorded. The ethylene was then admitted to the sample cell and the spectrum again recorded. The spectra were also recorded after various intervals of time up to several days. At certain times the unadsorbed ethylene was removed from the sample cell by evacuation at room temperature and the spectrum of the adsorbed species recorded.

After the adsorption part of the experiment was completed, the hydrogenation of the adsorbed species was investigated. This was done by heating the sample to the desired hydrogenation temperature and then admitting hydrogen to the cell at a pressure of 18 cm. The hydrogenation temperatures varied from 150 to 450° and the reaction times from 20 min. to 2 days. At the end of the hydrogenation period, the gaseous material containing the desorbed products was drawn into a liquid nitrogen trap. The contents of the trap were then analyzed with a capillary gas chromatographic column employing a flame ionization detector. This technique can detect hydrocarbons in the parts per million range, and was necessary because of the very small amount of product available for the analysis. After the desorbed products were removed from the cell, the sample was cooled to room temperature and the infrared spectrum recorded.

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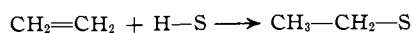
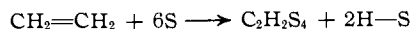
**Materials.**—The  $\text{Al}_2\text{O}_3$  used in preparing the Pt- $\text{Al}_2\text{O}_3$  samples was the same as that designated (A)  $\text{Al}_2\text{O}_3$  in the previously reported study<sup>5</sup> of the chemisorption of ethylene on  $\text{Al}_2\text{O}_3$ . It was prepared by heating  $\beta$ -alumina trihydrate, obtained from Davison Chemical Co., for 4 hr. at  $600^\circ$ . After heating, the B.E.T. surface area was  $295 \text{ m}^2/\text{g.}$ , and an X-ray diffraction measurement showed the  $\text{Al}_2\text{O}_3$  to be  $\eta$ -alumina.

The platinum catalysts were prepared by impregnation of (A)  $\text{Al}_2\text{O}_3$  with aqueous chloroplatinic acid, followed by drying at  $120^\circ$  and subsequent heating for 1 hr. at  $500^\circ$ . This preparation procedure, when coupled with the previously described reduction procedure, gives a surface with a high degree of dispersion of the platinum.<sup>6</sup>

The ethylene used in this work was supplied by the Matheson Co. and was stated to be at least 99.5% pure. The hydrogen used was obtained from the Linde Co. and was dried by passing through a liquid nitrogen trap prior to use.

### Results

The previously reported infrared study of the chemisorption of ethylene on alumina presented evidence for the formation of two different surface species,  $\text{CH}_3\text{-CH}_2\text{-S}$  and  $\text{S-CH}_2\text{-CH}_2\text{-S}$ , where S represents a surface site.<sup>5</sup> The relative amounts of the two species on the surface varied with the source of the alumina. In the case of the adsorbed ethyl radical,  $\text{CH}_3\text{-CH}_2\text{-S}$ , evidence was presented showing that this species was formed by a self-hydrogenation reaction; *i.e.*, the hydrogen required in the formation of a particular ethyl group came from another molecule of ethylene rather than from the alumina, as was shown by experiments with deuterated aluminas. The self-hydrogenation reaction might simply be represented as



The first step involves dissociative adsorption of ethylene. This serves as a source of hydrogen atoms which can combine with the ethylene in the second step.

Measurements of the infrared spectra of ethylene adsorbed on the form of alumina designated (A)  $\text{Al}_2\text{O}_3$ , prepared by heating  $\beta$ -alumina trihydrate at  $600^\circ$  for 4 hr., show absorption bands at 2970, 2932, and 2880  $\text{cm.}^{-1}$ ,<sup>5</sup> as shown in Fig. 1. These bands are assigned, respectively, to the asymmetrical C-H stretching mode in alkane  $\text{CH}_3$  groups, the corresponding mode in alkane  $\text{CH}_2$  groups, and the symmetrical C-H stretching mode in alkane  $\text{CH}_3$  groups.<sup>5</sup> Spectra of ethylene adsorbed on Pt- $\text{Al}_2\text{O}_3$  catalysts prepared by impregnating Pt on (A)  $\text{Al}_2\text{O}_3$  show bands at the same frequencies, as indicated in Fig. 2 for a sample containing 0.6 wt. % Pt. However, the relative absorbances at the different frequencies are somewhat different from that observed for ethylene adsorbed on (A)  $\text{Al}_2\text{O}_3$  alone. In the case of the (A)  $\text{Al}_2\text{O}_3$  alone, after exposure to ethylene at 15 cm. pressure for 3 days at room temperature, the ratio of absorbance ( $\log 1/\text{transmission}$ ) at 2970  $\text{cm.}^{-1}$  ( $\text{CH}_3$ ) to the absorbance at 2932  $\text{cm.}^{-1}$  ( $\text{CH}_2$ ) was found to be 1.33, corresponding to a 1:1 ratio of  $\text{CH}_2$  to  $\text{CH}_3$ . Hence, in this case it is concluded that the predominant species on the surface is  $\text{CH}_3\text{-CH}_2\text{-S}$ .<sup>5</sup> In the case of the 0.6% Pt on (A)  $\text{Al}_2\text{O}_3$  catalyst, after exposure to ethylene at 20 cm. pressure for 23 hr. at room temperature, the ratio of absorbance at 2970 to that at 2932  $\text{cm.}^{-1}$  was 0.82. This value corresponds to a  $\text{CH}_2/\text{CH}_3$  ratio greater than one, and it is suggested that the surface contains a mixture of the species,  $\text{CH}_3\text{-CH}_2\text{-S}$  and  $\text{S-CH}_2\text{-CH}_2\text{-S}$ . It is conceivable

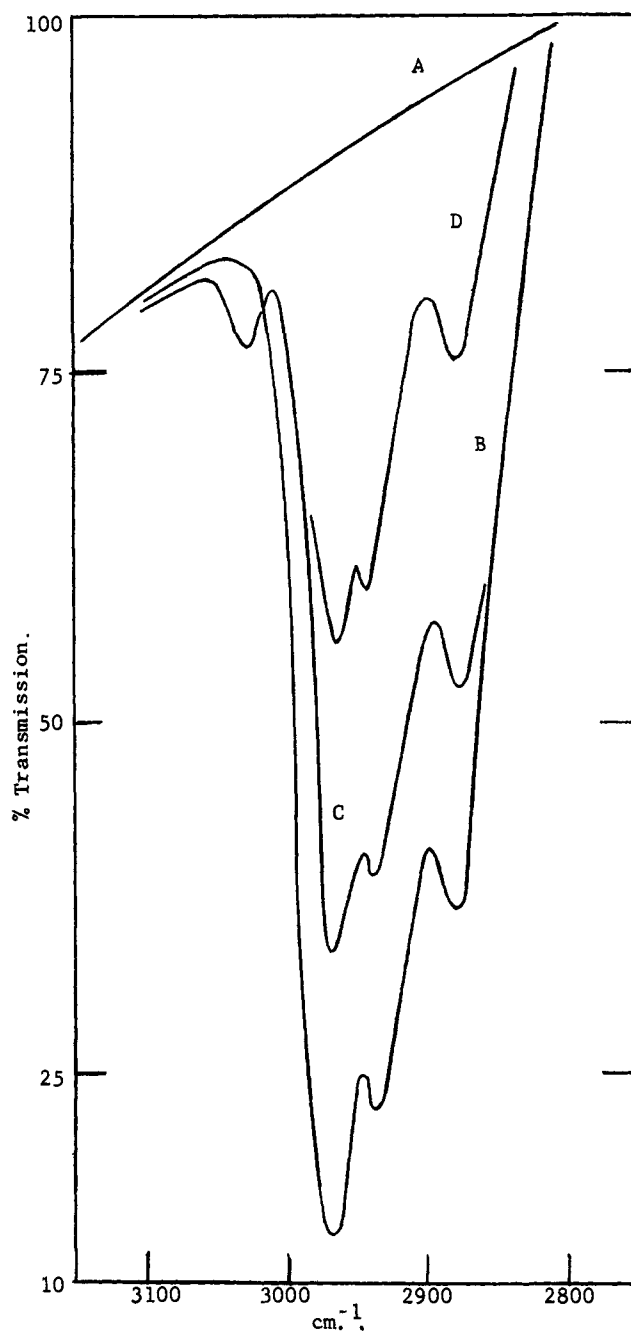


Fig. 1.—(A) Background spectrum of (A)  $\text{Al}_2\text{O}_3$  after evacuation at  $600^\circ$ ; (B) spectrum of adsorbed species (after evacuation of gaseous ethylene from the cell at room temperature for 5 min.) formed from ethylene (15 cm.) at room temperature after 3 days; (C) after hydrogen treatment (37 cm.) for 1.5 hr. at  $450^\circ$ ; (D) after hydrogen treatment for 18 hr. at  $450^\circ$ .

that the surface might also contain species such as  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-S}$  and  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-S}$ , but it seems unlikely that still longer chain species are present, since no band was observed near  $720 \text{ cm.}^{-1}$ . A strong absorption band would have been expected in this region for any hydrocarbon chain containing 4 or more directly linked  $\text{CH}_2$  groups.<sup>5</sup>

The chemical reactivity of the adsorbed species with hydrogen shows some pronounced differences between the  $\text{Al}_2\text{O}_3$  and the Pt- $\text{Al}_2\text{O}_3$  catalyst. Treatment of the chemisorbed species on (A)  $\text{Al}_2\text{O}_3$  with 37 cm.  $\text{H}_2$  at  $350^\circ$  for 90 min. resulted in no change in the intensity of the bands at 2970, 2932, and 2880  $\text{cm.}^{-1}$ . Additional treatment with 37 cm.  $\text{H}_2$  at  $450^\circ$  showed

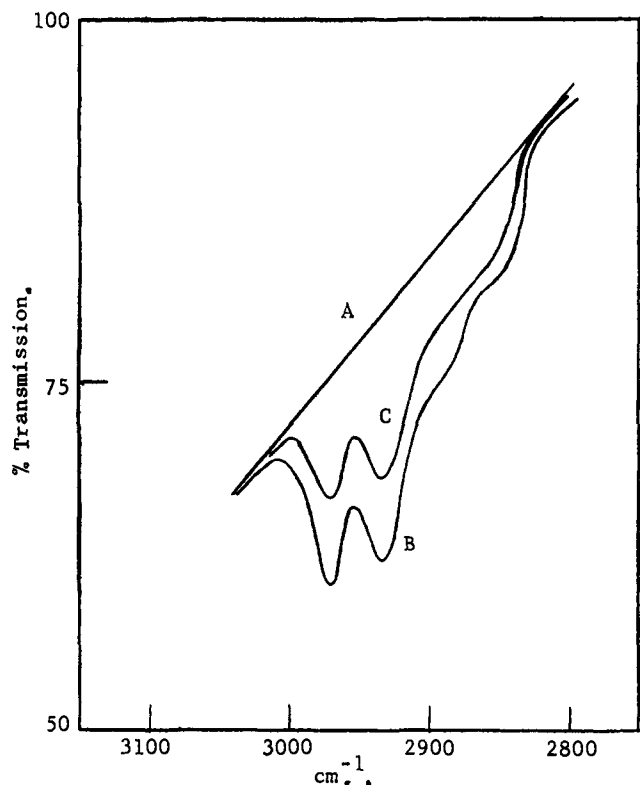


Fig. 2.—(A) Background spectrum of 0.6% Pt on (A)  $\text{Al}_2\text{O}_3$  after evacuation at  $500^\circ$ ; (B) spectrum of adsorbed species (after evacuation of gaseous ethylene from the cell at room temperature for 5 min.) formed from ethylene (20 cm.) at room temperature after 23 hr.; (C) after hydrogen treatment (18 cm.) for 30 min. at  $150^\circ$ .

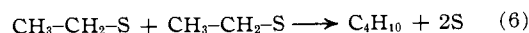
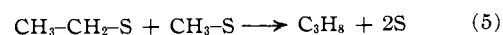
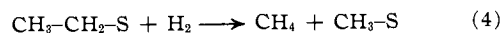
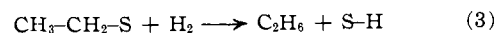
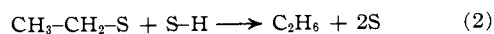
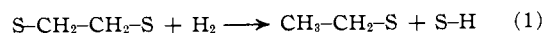
some effect after 90 min., and after 18 hr. the bands were substantially reduced in intensity, as shown in spectra C and D of Fig. 1.<sup>5</sup> Analysis of the gaseous hydrocarbons removed from the surface after 18 hr. gave the composition (mole %): 48%  $\text{CH}_4$ , 34%  $\text{C}_2\text{H}_6$ , 16%  $\text{C}_3\text{H}_8$ , and 2%  $n\text{-C}_4\text{H}_{10}$ . In contrast with the observations on the (A)  $\text{Al}_2\text{O}_3$ ,  $\text{H}_2$  treatment in the case of the 0.6% Pt on (A)  $\text{Al}_2\text{O}_3$  catalyst removed the adsorbed species much more readily. Thus, treatment of the adsorbed species with hydrogen at a pressure of 18 cm. for 30 min. at  $150^\circ$  removed a significant fraction of the adsorbed hydrocarbons from the surface, as shown in spectrum C of Fig. 2. Analysis of the hydrocarbons desorbed from the surface showed 90 mole %  $\text{C}_2\text{H}_6$  and 10 mole %  $n\text{-C}_4\text{H}_{10}$ . Further treatment with hydrogen (17 cm. pressure) at  $350^\circ$  for 30 min. removed all of the adsorbed species, so that the spectrum was indistinguishable from the background spectrum. The composition (mole %) of the desorbed product was 35%  $\text{CH}_4$ , 58%  $\text{C}_2\text{H}_6$ , 5%  $\text{C}_3\text{H}_8$ , and 2%  $n\text{-C}_4\text{H}_{10}$ . No isobutane was detected in the products resulting from the  $150^\circ$  hydrogenation. However, trace amounts of isobutane were observed in the products desorbed from the surface during the hydrogen treatment at  $350^\circ$ . The adsorption of ethylene and subsequent hydrogenation of the adsorbed species have also been studied on a catalyst containing 1.0 wt. % Pt on (A)  $\text{Al}_2\text{O}_3$ . After contacting a sample of this catalyst with ethylene at 28 cm. pressure for 22 hr. at room temperature, and subsequently treating the adsorbed species with hydrogen (17 cm. pressure) for 20 min. at  $150^\circ$ , the analysis of the gaseous hydrocarbons desorbed from the surface

gave the composition (mole %): 83%  $\text{C}_2\text{H}_6$  and 17%  $n\text{-C}_4\text{H}_{10}$ .

### Discussion

Pt- $\text{Al}_2\text{O}_3$  catalysts prepared by the technique discussed in this paper are characterized by extremely high dispersion of the platinum, the platinum surface areas approaching that of atomically dispersed platinum, namely, 273  $\text{m}^2/\text{g}$ . of Pt.<sup>6</sup> However, since the surface area of (A)  $\text{Al}_2\text{O}_3$  is 295  $\text{m}^2/\text{g}$ ., the platinum sites cover less than 1% of the alumina surface in the low platinum content catalysts used in the present study. Consequently, it would be expected that most of the ethylene chemisorbed on these catalysts would be present on the  $\text{Al}_2\text{O}_3$  rather than on the Pt sites. Unpublished data obtained in this laboratory<sup>7</sup> indicate that the equilibrium coverage of the alumina by ethylene at  $250^\circ$  would be greater than 25% at the ethylene adsorption pressures used in the current work (15–30 cm.). The equilibrium coverage would be expected to be still higher at room temperature. However, it did not appear that equilibrium was attained in the room temperature adsorption studies described in this paper, since the rate of adsorption was quite low. However, even if the coverage of the  $\text{Al}_2\text{O}_3$  by ethylene were as low as 5% and the platinum was completely covered with ethylene, the number of  $\text{Al}_2\text{O}_3$  sites covered by ethylene in the case of the 0.6% Pt on  $\text{Al}_2\text{O}_3$  catalyst would amount to about 90% of the total number of surface sites covered. Consequently, it is reasonable that the same infrared absorption bands which were originally observed on the  $\text{Al}_2\text{O}_3$  were also observed on the Pt- $\text{Al}_2\text{O}_3$  catalysts after adsorption of ethylene. It is possible that the same types of species are present on the platinum as are present on the  $\text{Al}_2\text{O}_3$ , but it is also possible that other species are present which were not detected in these studies. For example, it might occur that the main species on the platinum sites is an acetylenic residue, *i.e.*,  $\text{C}_2\text{H}_2\text{S}_2$  or  $\text{C}_2\text{H}_2\text{S}_4$ , arising from dissociative adsorption of the ethylene. However, no band corresponding to the C-H stretching frequency ( $3010\text{--}3040\text{ cm}^{-1}$ ) for the first species was observed, and a similar band for the second species ( $2890 \pm 10\text{ cm}^{-1}$ ) would be overlapped by the  $2880\text{ cm}^{-1}$  band previously mentioned.

The results of the experiments on treating the adsorbed species with hydrogen give us information on the nature of the chemical transformations which take place on the surfaces of the  $\text{Al}_2\text{O}_3$  and Pt- $\text{Al}_2\text{O}_3$  catalysts. The following reactions can account for the nature of the products formed



Reactions 1 through 3 account for the formation of  $\text{C}_2\text{H}_6$  from either of the adsorbed species,  $\text{S-CH}_2\text{-CH}_2\text{-S}$  or  $\text{CH}_3\text{-CH}_2\text{-S}$ , while reactions 4 through 6 account for the formation of  $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ , and  $n\text{-C}_4\text{H}_{10}$ . Reactions such as 1, 2, 3, and 6 evidently occur on the Pt- $\text{Al}_2\text{O}_3$

(7) V. Kevorkian, unpublished data, 1962.

catalysts at temperatures of 100–150°, at which temperatures reactions such as 4 and 5 are of minor importance. However, reactions like 4 and 5 become increasingly more important as the temperature is increased, indicating that the higher temperatures are necessary to accomplish the rupture of C–C bonds by a step such as 4. In an earlier part of the paper it was remarked that the surface species resulting from the chemisorption of ethylene could conceivably contain propyl and butyl groups as well as the dicarbon species. However, the fact that propane is not formed in the low temperature treatments with hydrogen, but instead requires higher temperatures, tends to cast doubt on the possibility that significant amounts of the propyl group are initially present, since the hydrogenation of such a group should be relatively easy.

It is of interest that the C<sub>4</sub> product resulting during the hydrogenation experiments is *n*-butane, with relatively little formation of isobutane. This casts some doubt on the possibility that the adsorbed species leading to the formation of the butane are similar to carbonium ions in their properties, since isobutane would then be expected to be a major product.

Perhaps the most interesting result of the present study was the finding that the presence of a small amount of platinum on Al<sub>2</sub>O<sub>3</sub> greatly increased the ease of removal of the adsorbed species by hydrogen treatment. It was shown that the adsorbed species on the Pt–Al<sub>2</sub>O<sub>3</sub> catalysts could be completely removed at temperatures 100° below that at which even a part of the adsorbed species could be removed from the Al<sub>2</sub>O<sub>3</sub>. Since most of the adsorbed ethylene is in all probability

present on the Al<sub>2</sub>O<sub>3</sub>, this means that the platinum somehow aided the removal of adsorbed species from the Al<sub>2</sub>O<sub>3</sub> during hydrogen treatment, and that the greater ease of removal in the case of the Pt–Al<sub>2</sub>O<sub>3</sub> catalysts was not simply a matter of removal of adsorbed species originally present on Pt sites. Thus, there appears to be a cooperative effect of Pt and Al<sub>2</sub>O<sub>3</sub> sites involved in the process, similar to that mentioned in the Introduction for the reactions of hydrocarbons over bifunctional catalysts. This cooperative effect would seem to arise because the Pt centers activate certain species for further reaction and subsequent desorption from the surface, and indicates some type of migration of reactive intermediates between the Pt and Al<sub>2</sub>O<sub>3</sub> centers. This explanation has previously been advanced by two of the present authors<sup>4</sup> to account for the results of ethylene hydrogenation experiments over mixtures of Pt–SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> particles. The results of the present work thus lend additional support to the findings of the previous study.

While the results of this work suggest that migration of reactive species between Pt and Al<sub>2</sub>O<sub>3</sub> centers may be important, the nature of the migrating species is still open to question. In the previous work, it was suggested that hydrogen might be the species in question, but there is no direct evidence that this is the case. However, the possibility that hydrocarbon species might migrate from Al<sub>2</sub>O<sub>3</sub> centers to Pt to react with hydrogen and desorb from Pt centers has not been ruled out and would not seem too unreasonable in view of current ideas about the action of bifunctional catalysts in promoting certain hydrocarbon reactions.<sup>1–3</sup>

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RESEARCH LABORATORY OF ELECTRONICS, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASSACHUSETTS]

## A Study of Nickel(II) and Cobalt(II) Phosphate Complexes<sup>1</sup>

BY GORDON G. HAMMES AND M. LEE MORRELL

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The metal binding constants and rate constants have been measured for the formation of the Ni(II) and Co(II) complexes of pyrophosphate and tripolyphosphate. The binding constants were determined with a pH titration method at metal to ligand ratios of 1:1 and 2:1. The binding constants for the Co(II) complexes are slightly greater than the corresponding ones for Ni(II). The rate constants for complex formation and dissociation were measured for some of the complexes with the temperature jump method. The relaxation times measured ranged from 50 μsec. to 3 msec. The results suggest that the rate of dissociation of a water molecule from the inner hydration shell of the metal ion is rate determining for complex formation, but that the highly charged ligands can accelerate this rate somewhat in the case of Co(II).

### Introduction

The interaction of metal ions with phosphate compounds is of considerable importance in biological systems.<sup>2</sup> Although the equilibrium properties of metal–phosphate complexes have been studied to some extent,<sup>3</sup> very few kinetic studies have been carried out, primarily because the reactions of interest occur too rapidly to study by conventional methods. How-

ever, the recent application of relaxation techniques to metal complex reactions now permits such studies to be made.<sup>4</sup>

Since pyrophosphate and tripolyphosphate are used as sequestering agents, several equilibrium studies have been made on the Ca(II) and Mg(II) complexes of these two ligands.<sup>3,5</sup> Some data are also available for the Cu(II) complexes of these two polyphosphates.<sup>6</sup> Studies involving other metal ions have been quite incomplete.<sup>3</sup>

Kinetic studies have been made of the reactions of adenosine 5'-triphosphate (ATP) and adenosine 5'-

(1) This work was supported in part by the U. S. Army Signal Corps, Air Force Office of Scientific Research, and Office of Naval Research and in part by the National Institutes of Health (MG-07803).

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(3) See for example J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants of Metal Ion Complexes," The Chemical Society, London, 1957.

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(5) S. M. Lambert, *J. Am. Chem. Soc.*, **79**, 4262 (1957).

(6) P. E. Sturrock, *Dissertation Abstr.*, **21**, 2090 (1960).