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Infrared Active Species of Hydrogen Adsorbed by Alumina-Supported Platinum

L. T. DIXON,[1] ROGER BARTH AND J. W. GRYDER

Department of Chemistry, The Johns Hopkins University,
Baltimore, Maryland 21218

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Two infrared active hydrogen species adsorbed on alumina-supported platinum with bands at 2120 and 2060 cm^{-1} are reported. Corresponding bands are observed for deuterium at 1520 and 1480 cm^{-1}. Both species are removed from the surface by pumping at room temperature and neither is adsorbed at 77°K on a surface cooled in helium from 573°K. The species responsible for the 2120 cm^{-1} band does adsorb at 77°K on a surface which has been exposed to hydrogen at room temperature, evacuated, and cooled to 77°K in helium. The 2060 cm^{-1} band is markedly enhanced on a surface containing water, either intentionally added or formed *in situ* by reaction of hydrogen with oxygen. The 2060 cm^{-1} band is easily obscured by an intense CO band at the same frequency. Neither species is necessary for the catalysis of the isotopic exchange reaction at 77°K and only the species responsible for the 2060 cm^{-1} band exchanges at this temperature.

INTRODUCTION

Hydrogen adsorbed by platinum on various supports has been studied by numerous investigators with the goal of establishing the nature of the active form in the catalysis of exchange and hydrogenation reactions.

Conductivity and surface potential measurements suggest that hydrogen adsorbs on platinum in two forms, one strongly adsorbed and one weakly adsorbed species (*1–3*). The heats of adsorption for these forms have been reported as 21 to 23 kcal and 9 to 10 kcal, respectively (*4*). Up to five forms of hydrogen adsorption have been detected by temperature programmed desorption studies from 77 to 573°K (*5,6*). Three forms have been observed on platinum electrodes in solution (*16,17*).

Two infrared bands have been ascribed to adsorbed hydrogen (*7,8*) at about 2120 and 2060 cm^{-1}. While the 2120 cm^{-1} band is generally accepted as being due to a Pt–H stretching vibration, some workers assign the 2060 cm^{-1} band to a carbonyl contaminant (*9–11*). It has been recognized that not all of the hydrogen adsorbed on platinum can be accounted for in the infrared (*12*). Some previous studies have found that the 2120 cm^{-1} band disappears after brief evacuation at room temperature, while the 2060 cm^{-1} band cannot be removed by evacuation at room temperature (*8–10*).

Treatment of supported platinum with oxygen prior to hydrogen adsorption causes an increase in the intensity of the infrared bands (*8,11*). This observation has been ascribed to incomplete reduction of the surface (*8*) and to an increase in active surface area (*11*).

This study has been undertaken in an attempt to resolve some of the conflicts in the literature and to shed more light on the nature of hydrogen adsorbed on platinum.

EXPERIMENTAL PROCEDURES

The alumina-supported platinum was prepared by impregnation of Degussa Alu-

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[1] Present address: Scientific Research Division, Ford Motor Co., P. O. Box 2053, Dearborn, MI 48121.

minum Oxide C (a gift of Degussa, Inc.) with a sufficient amount of a 10% solution of chloroplatinic acid (Fisher Scientific Co.) to give 10% platinum by weight after drying. Enough water was used to give a pasty consistency. The mixture was pumped overnight in a vacuum desiccator, crushed, and passed through a 180 mesh sieve. The resulting powder was pressed at an applied pressure of 1.0×10^7 N m^{-2} between mica sheets in a stainless steel die of $^{13}/_{16}$ in. diameter.

The 0.1 g pellet was mounted in a stainless steel cell (*13*) with NaCl windows. The cell was wrapped with Nichrome wire for heating and had a jacket to contain cooling baths. The cell could be mounted on a conventional Pyrex gas handling system or on a portable system which could be used while the sample was in the spectrometer. Both systems could attain a vacuum of about 10^{-6} Torr.

The sample was activated by evacuation at 393°K for 1 hr, evacuation at 573°K for 1 hr, treatment with unpurified tank hydrogen at 573°K for 4 hr, and treatment with purified hydrogen circulating via a liquid nitrogen trap for 4 hr. The sample was always cooled in hydrogen or helium to avoid carbonyl contamination.

On occasion it was necessary to remove carbonyl impurity. Removal was accomplished by a 2 hr treatment with circulating oxygen at 573°K, a 15 min evacuation at about 533°K, and a 4 hr treatment with circulating hydrogen at 573°K. Liquid nitrogen traps were used near the cell during this procedure. The stainless steel cell could not be evacuated for more than 15 min at elevated temperatures without a noticeable carbonyl impurity adsorbing on the sample.

A similar sample was placed in a quartz cell and was reduced by the same procedure, followed by a 2.5 hr evacuation and cooling in helium.

The surface area was determined for a 2 g sample pressed in 0.1 g lots, crushed, sieved, and pressed as described above. The surface area measured with nitrogen by the BET method was 113 m^2 g^{-1}. The platinum dispersion of the fresh sample was measured by adsorption at room temperature, using the value extrapolated to zero pressure and assuming 1 adsorbed atom/surface platinum atom. The result was 56% measured by hydrogen adsorption and 35% measured by oxygen adsorption.

All spectra were taken on a Perkin-Elmer 521 double-beam grating infrared spectrometer. A scale expansion of 1 to 5 times was used. The spectral slit width varied from 2 to 5 cm^{-1}. The quartz cell was used in the reference beam. Temperatures were measured on both samples with Chromel–Alumel thermocouples in contact with the pellets. Dynamic pressures in the cell were determined with a National Research Corp. type 516 Pirani gauge calibrated for hydrogen. Before and after each series of runs, the reference cell was checked against an evacuated glass cell with no sample to insure against contamination of the reference. When necessary the reference sample was purified by the procedure outlined above.

Hydrogen–deuterium exchange kinetics were investigated on a 0.05 g sample which had been part of a previously used ir pellet. This sample was placed in a Pyrex reactor with a precooling coil and installed in the recirculating loop of the gas handling system. Activation was the same as for the samples used for infrared studies. Samples were withdrawn and analyzed by gas chromatography.

Deuterium was supplied by Matheson Scientific Co.; all other gases except water were supplied by Baltimore Oxygen Co. Deuterium was purified with a palladium purifier. Hydrogen was passed through an activated charcoal trap at 77°K or through a palladium purifier. Helium was passed through an activated charcoal trap at 77°K. Oxygen and nitrogen were condensed in cold traps and the middle third was used. Barium chloride dihydrate used in wetting experiments was supplied by J. T. Baker Chemical Co., and was pumped for several minutes prior to use.

Evacuation of the infrared cell at low temperature required a special technique. The cell could only be pumped for about 1 min before the temperature began to rise due to decreased conduction to the cold jacket. The cell was therefore pumped in 1 min cycles and helium ($p = 30$ Torr) was replaced in the cell. In this way the temperature was kept below 87°K.

RESULTS

Hydrogen Studies

Because of the disagreement mentioned above concerning the 2060 cm^{-1} band, it was necessary to verify whether or not this band is due to adsorbed hydrogen. A reduced sample was exposed to air, then evacuated at 573°K for 1 hr with no precautions taken to prevent carbonyl contamination. After cooling in vacuum spectrum a in Fig. 1 was recorded, using an empty cell in the reference beam. Addition of oxygen at room temperature decreased the intensity of the 2060 cm^{-1} band, shifted it closer to 2100 cm^{-1}, and increased the intensities of the bands below 1900 cm^{-1}. When the sample was purified by the oxygen–hydrogen treatment outlined above, cooled in hydrogen, and evacuated for 15 min at room temperature, it displayed spectrum b in Fig. 1. These spectra show that a sample free of water and of carbonate and related impurities can be obtained.

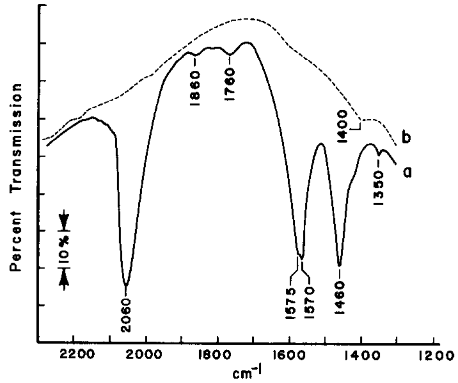

FIG. 1. Infrared spectra of alumina-supported platinum: (a) after activation at 573°K, exposure to air at room temperature, and evacuation at 573°K (1 hr); (b) after oxygen treatment at 573°K (2 hr), hydrogen treatment at 573°K and evacuation at room temperature.

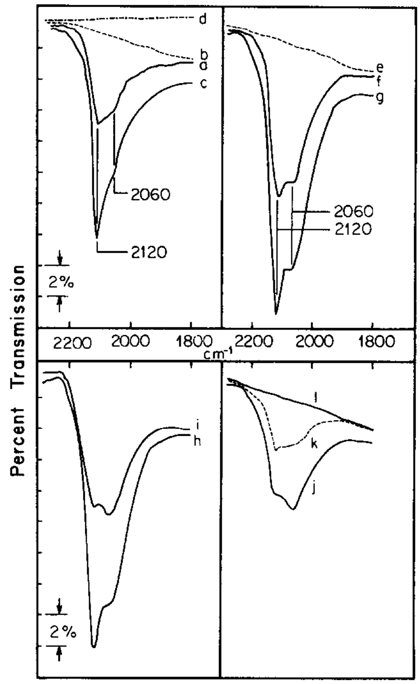

FIG. 2. Infrared spectra of hydrogen adsorbed on supported platinum: (a) at 295°K; (b) after 15 min evacuation; (c) at 77°K cooled in hydrogen; (d) at 77°K after addition of oxygen at 77°K; (e) at 295°K after evacuation; (f) after reexposure to hydrogen at 295°K; (g) cooled to 77°K in hydrogen; (h) after evacuation (5 min) at 77°K; (i) after evacuation (11 min) at temperatures below 123°K; (j) after evacuation (17 min) at temperatures below 123°K; (k) after allowing to warm to 295°K and standing overnight; (l) after evacuation (15 min) at 295°K.

The spectrum obtained when hydrogen at 100 Torr was adsorbed at room temperature is shown in Fig. 2a. This band (2120 cm^{-1} with a slight shoulder at 2060 cm^{-1}) was completely removed by 15 min evacuation (Fig. 2b). If the sample was again exposed to hydrogen at room temperature and cooled in hydrogen to 77°K, spectrum c in Fig. 2 was obtained, showing a sharp band at 2120 cm^{-1} and only a hint of a shoulder at 2060 cm^{-1}. Evacuation at 77°K by the special technique mentioned above caused no detectable change in the intensity of these bands. Introduction of oxygen at 77°K caused these bands to disappear, as shown in Fig. 2d, and one band at 1630 cm^{-1} appeared, indicating the presence of water.

After the sample was warmed to room temperature in vacuum, spectrum e was obtained. Exposure to hydrogen at room temperature gave a spectrum with a sharp peak at 2120 cm^{-1} and a prominent shoulder at 2060 cm^{-1} as shown in spectrum 2f. After the sample was cooled in hydrogen to 77°K, the shape of the bands remained the same, but the intensity increased (spectrum 2g). At 77°K these bands showed no pressure dependence, and evacuation as mentioned above caused no significant change in intensity or shape, spectrum 2h. If, however, the sample was allowed to pump for 10 min ($p = 0.5$ μm) and the temperature rose as high as 123°K, the spectrum 2i was obtained, showing more decrease in the intensity of the 2120 cm^{-1} band than of the 2060 cm^{-1} band. Spectrum 2j resulted after 17 min of evacuation ($p = 0$ μm), showing the 2120 cm^{-1} band reduced to a shoulder on the remaining 2060 cm^{-1} band. When the sample was allowed to warm to room temperature overnight, spectrum 2k resulted. Here the 2120 cm^{-1} band once again predominates. Evacuation for 15 min at room temperature removed both bands giving spectrum 1 similar to background spectra 2b and 2e.

A reactivated sample, evacuated at 573°K, cooled in helium to 77°K, and then exposed to hydrogen at 77°K showed no bands in the 2300 to 1800 cm^{-1} region. On warming a broad band first appeared at a temperature above 133°K. The spectra in

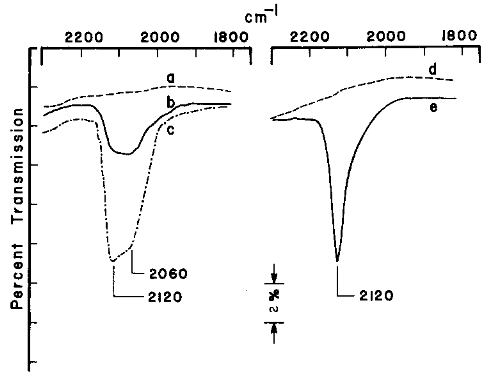

FIG. 3. Infrared spectra of hydrogen on supported platinum: (a) at 77°K after reactivation and cooling in helium; (b) at 223 to 243°K after allowing to warm from 77°K in hydrogen; (c) at room temperature after warming from 77°K in hydrogen; (d) at 77°K after room temperature evacuation and cooling in helium; (e) at 77°K after (d) upon exposure to hydrogen.

Fig. 3a–c were taken as the temperature increased. Spectrum 3a was taken after 15 min exposure to hydrogen ($p = 100$ Torr) at 77°K. In spectrum 3b, which was taken over the range 223 to 243°K, the 2060 cm^{-1} band seems larger than the 2120 cm^{-1} band. Spectrum 3c was taken at room temperature and shows the 2120 cm^{-1} band with a shoulder at 2060 cm^{-1}. After evacuation the spectrum was identical to 3a. Spectrum 3d was taken after evacuation and cooling in helium to 77°K. When hydrogen was admitted to the cell, spectrum 3e resulted, showing only one sharp band at 2120 cm^{-1}.

Deuterium Studies

Hydrogen was adsorbed at room temperature on a sample which did not contain water as evidenced by the absence of the 1630 cm^{-1} band. The sample was cooled in hydrogen to 77°K and yielded spectrum 4a. Twenty-five minutes after the addition of D_2 at 50 Torr the spectrum 4b was obtained. In similar experiments the intensity of the band after 5 min was the same as that after 1 hr. A new band also appears at 1520 cm^{-1} shown in Fig. 4c.

More dramatic changes occur in a

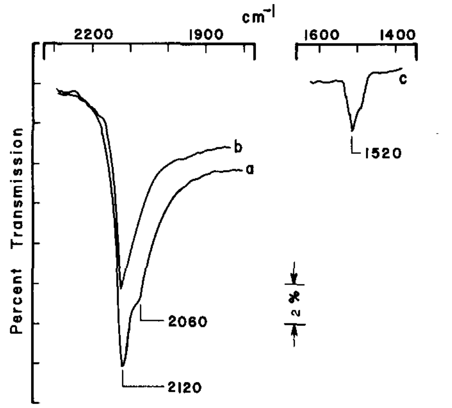

FIG. 4. The effect of deuterium on the bands due to hydrogen at 77°K in the absence of molecularly adsorbed water: (a) before D_2 addition, sample cooled to 77°K in hydrogen; (b) after addition of deuterium at 77°K; (c) deuterium band after addition of deuterium.

sample for which the 1630 cm^{-1} water band is prominent due to oxygen pretreatment. Spectrum 5a was taken for such a sample after cooling in hydrogen to 77°K and evacuating for 15 min. Under these conditions the temperature rises to 150°K and the 2120 cm^{-1} band is almost eliminated. Spectrum 5b was taken after exposure to D_2 at 50 Torr for 25 minutes at 77°K. The 2060 cm^{-1} band has almost disappeared but the 2120 cm^{-1} band remains. A band appears at 1520 cm^{-1} with a shoulder at 1480 cm^{-1} as shown in spectrum 5c. After evacuation for 15 min with an increase in temperature to 150°K followed by cooling to 77°K, spectrum 5d was observed, showing a band at 1480 cm^{-1} and an intense band at 1425 cm^{-1}.

Water Studies

A freshly regenerated sample cooled in helium to 77°K yielded spectrum 6a. After exposure to hydrogen at room temperature and cooling in hydrogen to 77°K, spectrum 6b was obtained similar to previous results. The spectrum is not as sharp or intense because the sample was 1 yr old by the time these experiments were performed.

The sample was then evacuated at room temperature for 15 min and exposed to water vapor from $BaCl_2 \cdot 2H_2O$ at 297.8°K for 10 min followed by 10 min pumping at room temperature. The vapor pressure of $BaCl_2 \cdot 2H_2O$ at this temperature is 20.1 Torr (*14*). After cooling to 77°K in He, spectrum 6c was obtained. This background spectrum is now sloped and has weak bands in the hydrogen region. Spectrum 6d results when hydrogen is admitted to the cell at room temperature and cooled in hydrogen to 77°K. There is a marked enhancement of the 2060 cm^{-1} band. After 15 min evacuation at room temperature, the background spectrum is obtained.

Rate Studies

A preliminary study of the kinetics of hydrogen–deuterium exchange was undertaken. The results show that exchange takes place on a sample which had been cooled in helium from 573 to 77°K at which temperature an equimolar mixture of H_2 and D_2 was admitted. The half-life is about 10 min.

DISCUSSION

The results of this work, in contradiction to previous reports (*9,10*), show that two infrared active bands are observed for hydrogen adsorbed on alumina-supported platinum. One of these bands at 2120 cm^{-1} has been observed by all investigators. The other occurs at 2060 cm^{-1} and, unlike the band at this position reported by others (*8–10*) or the band at the same position observed for CO, is completely removed by evacuation for 15 min at room temperature. Considerable care is required to obtain samples free of the 2060 cm^{-1} band attributable to CO. For example, prolonged evacuation at high temperature or exposure to water containing traces of CO_2 yields the carbonyl band. We conclude, in agreement with others (*9–11*), that a band around 2060 cm^{-1} previously reported is attributable to CO. However, a weak, broad band at this same position also arises from a hydrogen species. These results are in general agreement with the original report of Pliskin and Eischens (*7*). Although they did not remove the 2060 cm^{-1} band by their pumping procedure, they did not pump as long or to as low a pressure as in the work reported here.

Both hydrogen bands result from species which are reversibly bound at room temperature, and neither is adsorbed at 77°K on a sample cooled in helium from 573°K. Hence, both bands arise from activated adsorption.

That the two bands do not result from the same type of adsorption is clearly shown by the spectra in Fig. 2 and 3. The spectrum in 3e shows that only the 2120 band is observed when hydrogen is adsorbed at 77°K on a sample previously saturated with irreversibly bound hydrogen at room temperature and cooled in helium. Under these conditions the energy of activation for adsorption of the species responsible for the 2120 cm^{-1} band has been reduced to the point that it can now be adsorbed at 77°K while the energy of activation for adsorption of the species responsible for the 2060 cm^{-1} band has not been similarly changed. On the other hand, the spectra in Fig. 3b and c show that for a sample which has not been previously exposed to hydrogen, the energy of activation for adsorption for the species responsible for the 2060 cm^{-1} is lower than that for the species giving rise to the 2120 cm^{-1} band. These data suggest that the 2120 cm^{-1} band can only appear when a type of infrared inactive hydrogen is also adsorbed on the sample or that a rearrangement of surface occurs when hydrogen is adsorbed at room temperature. Finally, the spectra in Fig. 2h, i, and j show that when both bands are present the species responsible for the 2120 cm^{-1} band pumps off more quickly than that responsible for the 2060 cm^{-1} band; and, hence, the species giving rise to the 2120 cm^{-1} band is less strongly bound than the other infrared active species.

Other differences between the two bands are observed when the spectra of dry samples are compared with samples containing water, either formed *in situ* by oxygen titration or added in the form of H_2O. Comparison of Fig. 2a and f or 2c and g shows enhancement of the peaks after oxygen titration in agreement with past work (*8,11*). We note, however, that the 2060 cm^{-1} band is much more prominent on the wet surface, which agrees with the volumetric measurements found in the next paper (*18*). The same qualitative enhancement of the 2060 cm^{-1} band occurs when water is added to a dry sample as shown by a comparison of Fig. 6b and d.

That the 2060 cm^{-1} band is associated with hydrogen is further substantiated by the results obtained when deuterium is added at 77°K to a surface which had been pretreated with oxygen, exposed to hydrogen, and evacuated at temperatures below 150°K. Comparison of Fig. 5a and b shows that the 2060 cm^{-1} band disappears on the addition of D_2 and Fig. 5c shows

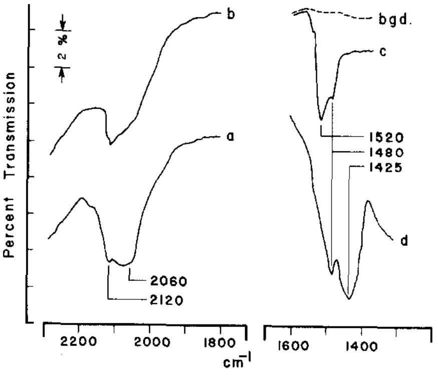

FIG. 5. The effect of deuterium on the bands due to hydrogen in the presence of molecularly adsorbed water: (a) before addition, at 77°K after evacuation at temperatures below 165°K; (b) after addition of deuterium at 77°K; (c) deuterium band after addition; (d) at 77°K after allowing sample to warm to 150°K with evacuation.

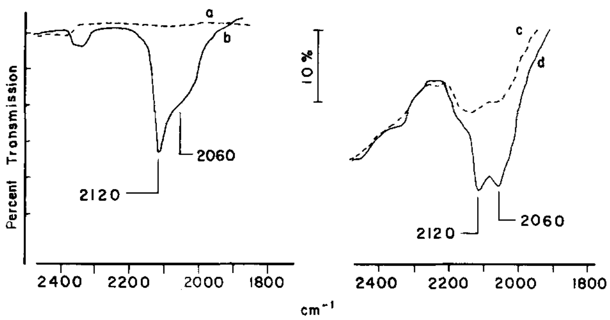

FIG. 6. Effect of water on hydrogen bands: (a) dry sample at 77°K before addition of H_2; (b) at 77°K after addition of H_2; (c) wet sample at 77°K before addition of H_2; (d) at 77°K after addition of H_2.

that new peaks appear at 1520 and 1480 cm^{-1}. The latter frequencies are reasonable for Pt–D bands analogous to Pt–H bands at 2120 and 2060 cm^{-1} and agree with those found previously (*7,11*). For a dry sample which shows only a weak shoulder at 2060 cm^{-1}, only the 1520 cm^{-1} band appears after addition of D_2 (spectrum 4c). As the wet sample is allowed to warm, the 1480 cm^{-1} band increases in intensity (spectrum 5d) analogous to the increase in the 2060 cm^{-1} band under similar circumstances for hydrogen shown in Fig. 3b and c. The intense band at 1425 cm^{-1} in spectrum 5d corresponds to the observed value for HDO (*15*). Further evidence that the 2060 cm^{-1} band is associated with a hydrogen species is found in the fact that this band disappears when D_2 is introduced. The carbonyl species at approximately the same frequency does not react with hydrogen.

Neither infrared active species is necessary for the isotopic exchange reaction as shown by the fact that the half time for exchange is about 10 min at 77°K on a surface which has been cooled in helium from 573°K. Figure 3a shows that neither infrared active species is formed under these conditions. Furthermore, the 2120 cm^{-1} band does not exchange with D_2 at 77°K after 1 hr.

We conclude that two infrared active species of adsorbed hydrogen exist on alumina-supported platinum. Both species are reversibly bound at room temperature. The species with an infrared band at 2060 cm^{-1} is the more strongly bound form, is markedly increased in intensity by the presence of water, and is an activated adsorption which occurs at a reasonable rate only above 130°K. The other species with a band at 2120 cm^{-1} adsorbs irreversibly at 77°K, but only if the sample has previously been exposed to hydrogen at 300°K.

We agree with the conclusions of other workers (*9–11*) that the hydrogen band at 2045 cm^{-1} observed by Eley *et al.* (*8*) is probably caused by a carbonyl species. However, our results agree with Eley and co-workers in finding that water enhances the intensities of the infrared bands. Although surface rearrangement and change in surface area may well occur when adsorptions and reactions take place on supported platinum, we do not believe that the work of Darensbourg and Eischens (*11*) with CO proves that an increase in surface area occurs during the oxygen titration because, although the total quantity of irreversibly bound hydrogen remains constant, the relative amounts of different types of irreversible adsorption differ markedly on dry and wet samples as shown in the following paper (*18*). We do, however, agree with Darensbourg and Eischens on the positions of the infrared bands for both adsorbed hydrogen and deuterium.

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Professor Richard J. Kokes, as thesis advisor for Louis Dixon, suggested that this study be undertaken. His sudden death occurred before the experimental design was completed. We are saddened by the loss of a good friend and invaluable colleague. Professors D. W. Robinson, Joe Hightower and Paul H. Emmett participated in helpful discussions. Financial support was provided by the donors of the Petroleum Research Fund administered by the American Chemical Society and by the National Science Foundation under Grant GP 34034.

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