

upper pressure limit, while the accuracy in the analysis and the pressure measurement determined the lower limit. The results which are plotted in Fig. 2 show a definite decrease in the first-order rate constants below 1 mm.

### Discussion

Reaction 1 is analogous to the thermal decomposition of cyclobutane to two molecules of ethylene.<sup>6</sup> The mechanism of the two processes may also be entirely similar since they are both homogeneous, unimolecular reactions and are unaffected by the addition of molecules which serve to trap free-radical species. Whether this mechanism is a concerted process or proceeds through a short-lived diradical species<sup>8</sup> is not of primary concern here provided it is the same mechanism that is operative in both reactions.

Walters and his co-workers have observed that the thermal decompositions of a variety of mono- and dialkyl-substituted cyclobutanes are homogeneous, unimolecular reactions. In cyclobutane itself<sup>6</sup> and in the cases in which the substituents are methyl, ethyl, and *n*-propyl groups,<sup>9</sup> it was observed that the activation energy falls within  $\pm 0.7$  kcal./mole of an average value of 61.8 kcal./mole and the pre-exponential factor within  $1 \times 10^{15}$  of the average value of  $3.4 \times 10^{15}$ . It would appear that alkyl substitution of the cyclobutane rings affects both the activation energy and the pre-exponential factor only slightly. The statement seems to be valid for the kinetics of the decomposition of dimethylcyclobutanes,<sup>10</sup> although in this instance the activation energies fall a little outside the limits stated previously.

In the case of bicyclohexane, the present study indicates that the pre-exponential factor is of the same order of magnitude as for the mono- and dialkyl-substituted cyclobutanes and only slightly smaller. But the activation energy is 6.8 kcal./mole lower when compared to an average value for the monocyclic compounds. It seems reasonable to interpret this lowering

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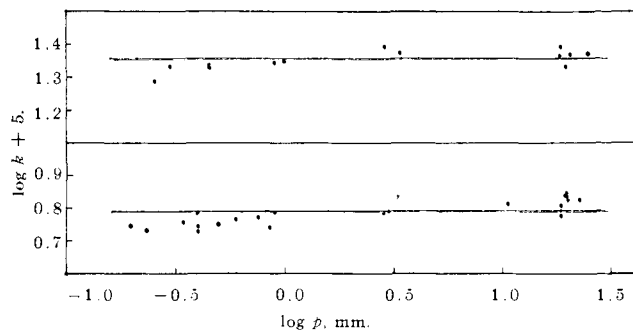


Fig. 2.—Plot of the first-order rate constants vs. initial pressure. The lines have been drawn parallel to the x-axis; top curve at 366.3°; lower curve at 347.4°.

in the activation energy as being due to the contribution of the extra strain energy in the bicyclic compound (compared to cyclobutane) to the activation energy for the break-up of the four-membered ring. Unfortunately, the strain energy in bicyclohexane has not been calculated as thermochemical data for this molecule are not yet available. From the present data, it would appear that this energy is probably not more than 7 kcal./mole relative to cyclobutane, if all of the strain energy is available for the rupture of the cyclobutane ring.<sup>11</sup>

Very little can be said about the dependence of the first-order rate constants on pressure, since the pressure range over which this was observed, and the magnitude of the effect, are quite small. The trend seems to fall in line with the commonly held view that the total number of atoms in a molecule is the chief factor which determines the initial observable part of the fall-off of rate constants in thermal unimolecular reactions of small hydrocarbons.

(11) In a parallel case in which both hydrogenation and pyrolysis data are available, an interesting correlation can be found. In the thermal isomerization of bicyclo[2.1.0]pentane to cyclopentene, the over-all reaction is analogous to the thermal isomerization of cyclopropane (T. S. Chambers and G. B. Kistiakowsky, *ibid.*, **56**, 399 (1934)). The preexponential factors for the two reactions are of the same order of magnitude. The activation energies for the two reactions differ by 18.4 kcal./mole. The difference between the heat of hydrogenation of bicyclo[2.1.0]pentane (R. B. Turner, "Kekulé Symposium on Theoretical Organic Chemistry," Butterworths, London, 1959, p. 67) and cyclopropane is 17.6 kcal./mole. The agreement between the two values may not be entirely fortuitous.

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

## Kinetic Evidence for the Migration of Reactive Intermediates in Surface Catalysis

BY J. H. SINFELT AND P. J. LUCCHESI

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Rates of ethylene hydrogenation were measured on Pt/SiO<sub>2</sub> catalyst mixed with Al<sub>2</sub>O<sub>3</sub> and with SiO<sub>2</sub>. The rate of ethylene hydrogenation, at comparable conditions, was much greater when the Pt/SiO<sub>2</sub> catalyst was mixed with Al<sub>2</sub>O<sub>3</sub>. These results cannot be explained simply on the basis of additivity of separate catalytic contributions of the individual components of the mixtures. The data clearly show that a cooperative effect of the components of the mixtures is involved, at least in the case of the mixture of Pt/SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. It is concluded that this cooperative effect of the individual components involves migration of reactive intermediates from one component to the other. It is suggested that Pt centers on the Pt/SiO<sub>2</sub> catalyst activate hydrogen in some manner, and that the active hydrogen can migrate to other centers to react with chemisorbed ethylene. The fact that Al<sub>2</sub>O<sub>3</sub> chemisorbs ethylene to a much greater degree than does SiO<sub>2</sub> then offers a reasonable explanation for the much higher activity of the mixture of Pt/SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.

### Introduction

Supported metal catalysts are important industrially, and they have also received considerable attention from workers interested in the fundamental aspects of surface catalysis. For example, there have been several theories concerning the presence of two distinct types of sites *vs.* single or "complex sites" on supported metal

catalysts.<sup>1,2</sup> The presence of two separate functions, one a hydrogenation-dehydrogenation function due to the metal, and the other an acidic function due to the

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(2) K. W. McHenry, R. J. Bertolacini, H. M. Brennan, J. L. Wilson, and H. S. Seelig, Proceedings of the Second International Congress on Catalysis, Section II, Paper 117, Paris, 1960.

support, has been postulated to explain the experimental results in the isomerization of alkanes and the dehydroisomerization of methylcyclopentane.<sup>3,4</sup> These experiments were done with mixtures of the metal component on an inert support and an acidic oxide containing no metal. Kinetic experiments by one of us also led to the conclusion that the two site picture is valid in these reactions on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>5</sup>

The action of bifunctional catalysts such as Pt/Al<sub>2</sub>O<sub>3</sub> in reactions of the type mentioned above involves migration of intermediates between Pt and acidic centers on the catalyst. We present in this paper some kinetic evidence that migration of reactive intermediates may also be important in the hydrogenation of ethylene over mixtures of Pt/SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. The approach was based on the following line of reasoning: It was known from previous work on the infrared spectrum of adsorbed ethylene<sup>6</sup> that ethylene is adsorbed on Al<sub>2</sub>O<sub>3</sub>. Therefore, on a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst containing only 0.05 wt. % Pt, in which Pt centers occupy a very small extent of the surface (of the order of 0.05%), it seemed probable that much of the adsorbed ethylene on such a catalyst would be present on the Al<sub>2</sub>O<sub>3</sub>. Although Al<sub>2</sub>O<sub>3</sub> itself is not an active catalyst for ethylene hydrogenation when compared with 0.050% Pt on Al<sub>2</sub>O<sub>3</sub>, it seemed possible that in the presence of Pt the sites on the Al<sub>2</sub>O<sub>3</sub> could become important catalytically. This might happen, for example, if hydrogen had to be activated in some manner before it could react with ethylene chemisorbed on Al<sub>2</sub>O<sub>3</sub>, and if Pt served to accomplish this activation of hydrogen. Thus, a possible path for ethylene hydrogenation would involve activation of hydrogen by Pt, followed by migration of the active hydrogen to Al<sub>2</sub>O<sub>3</sub> centers to react with chemisorbed ethylene.

To check out the above hypothesis, it was decided to measure the rate of hydrogenation of ethylene over Pt supported on an inert carrier and compare this with the rate obtained over the same catalyst when mixed intimately with Al<sub>2</sub>O<sub>3</sub>. SiO<sub>2</sub> was chosen as the inert carrier for the Pt, since previous work had shown it to be inactive for chemisorption of ethylene<sup>6</sup> and additional work in this Laboratory has shown it to be inactive for hydrogen chemisorption. If the rate per unit amount of Pt was significantly higher in the presence of Al<sub>2</sub>O<sub>3</sub>, this would be taken as evidence for migration of reactive intermediates from the Pt catalyst to the Al<sub>2</sub>O<sub>3</sub>. The results of such experiments are presented herein.

## Experimental

**Apparatus and Procedure.**—The reaction rate measurements were carried out in a flow system. The reactor was a 3/8-in. stainless steel tube approximately 3 in. long. In use, the reactor was held in a vertical position and was surrounded by a small electrical oven. The catalyst occupied a space about 0.5 in. long and was centered with respect to the two ends of the reactor. A fritted stainless steel disk was used to support the catalyst in the reactor, and quartz wool was pressed down on top of the catalyst to keep it in place. The reaction gases were passed downflow through the catalyst bed, and the products were analyzed by a chromatographic unit connected directly to the outlet of the reactor. The chromatographic column was 1.0 m. long with a diameter of 0.25 in. and was packed with 100-mesh silica gel. The column was operated at 40° and gave excellent resolution of the ethane and ethylene.

The reactant gases, ethylene and hydrogen, were passed over the catalyst in the presence of helium diluent. The gas flow rates were determined using orifice type flow meters with manometers. A total gas flow rate of 1.0 l. per min. was used through-

out. In a typical run, the reactant gases were passed over the catalyst for a period of 3 min., at which time a sample of the product was taken for chromatographic analysis. The ethylene was then cut out and the catalyst was treated with hydrogen for a period of 10 min. at the reaction temperature prior to another run. In this way it was possible to obtain reproducible catalyst activity for extended periods. Before any reaction studies were made, the catalyst was pretreated in flowing hydrogen for 3 hr. at 500°.

**Materials.**—The ethylene used in this work was C.P. grade obtained from the Matheson Co. A chromatographic analysis of the ethylene showed no detectable impurities, and we would estimate the level of impurities to be less than 0.10 wt. %. High purity hydrogen was obtained from the Linde Co. and was further purified by passing it through a Deoxo unit to remove traces of oxygen, prior to passage through a molecular sieve dryer.

The Pt/SiO<sub>2</sub> catalyst used in these experiments contained 0.050 wt. % Pt and was prepared by impregnating Davison silica gel, previously calcined at 538°, with aqueous chloroplatinic acid, followed by calcination in air for an additional hour at 538°. The B.E.T. surface area of the calcined silica gel was 388 m.<sup>2</sup>/g. The alumina was prepared by calcining β-alumina trihydrate, obtained from Davison Chemical Co., for 4 hr. at 593°. X-Ray diffraction measurements obtained in these laboratories indicated the alumina to be η-alumina. The B.E.T. surface area of the alumina was 296 m.<sup>2</sup>/g.

## Results

Mixtures of Pt/SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were prepared in two different ways: (1) by grinding Pt/SiO<sub>2</sub> catalyst with η-Al<sub>2</sub>O<sub>3</sub>, pelleting, regrinding, and finally screening to 45–60 mesh and (2) by simply mixing the Pt/SiO<sub>2</sub> catalyst with the Al<sub>2</sub>O<sub>3</sub>, both of which were previously screened to 45–60 mesh. The first mixing procedure obviously gives a more intimate mixture and should therefore magnify any effect of the Al<sub>2</sub>O<sub>3</sub>. However, it is possible that the grinding in the first procedure could lead to very high localized temperatures with resultant transport of platinum from the silica to the Al<sub>2</sub>O<sub>3</sub>. Consequently, it was considered important to prepare an additional mixture by the second procedure described above, so that any complication due to grinding would be ruled out. However, since the intimacy of mixing would be poorer in the second mixing procedure, it was expected that any effect resulting from transport of intermediates between active sites would be smaller.

The experiments on ethylene hydrogenation were made with mixtures of Pt/SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> prepared in both ways and compared with results on Pt/SiO<sub>2</sub> diluted simply with SiO<sub>2</sub> to about the same reactor volume. All the catalytic experiments were made with the same amount of Pt/SiO<sub>2</sub> catalyst (0.050 g.) in the reactor. The weight ratio of diluent (SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>) to Pt/SiO<sub>2</sub> catalyst was about 9 to 1. Results of experiments employing 0.05% Pt on SiO<sub>2</sub> catalyst are shown in Table I. The conversions listed in Table I are con-

TABLE I  
DATA ON ETHYLENE HYDROGENATION OVER CATALYST MIXTURES

Catalyst <sup>b</sup>	—Conversion, <sup>a</sup> %—	
	153°	100°
Pt/SiO <sub>2</sub> + SiO <sub>2</sub>	2.1	0.10
Pt/SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub>		
(1) ground together	39	2.1
(2) simple mixture	14	0.50

<sup>a</sup> Conditions: H<sub>2</sub> pressure, 0.20 atm.; C<sub>2</sub>H<sub>4</sub> pressure, 0.030 atm.; He pressure, 0.77 atm.; C<sub>2</sub>H<sub>4</sub> flow rate, 30 cc. (STP) per min. <sup>b</sup> The Pt/SiO<sub>2</sub> catalyst contained 0.050% Pt by wt.; the weight of Pt/SiO<sub>2</sub> catalyst charged was 0.050 g. in all cases; the weight ratio of diluent (SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>) to Pt/SiO<sub>2</sub> catalyst was 9 to 1 throughout.

sidered reliable to within 10% of the actual value. The results clearly show that the presence of Al<sub>2</sub>O<sub>3</sub> greatly

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(5) J. H. Sinfelt, H. Hurwitz, and J. C. Rohrer, *ibid.*, **64**, 892 (1960).

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enhances the hydrogenation activity of the Pt/SiO<sub>2</sub> catalyst. At the conditions of the experiments, the activity of the Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> was small in comparison with that of any of the mixtures containing Pt/SiO<sub>2</sub> catalyst. Thus, at 153° and other conditions similar to those of Table I, the conversion of ethylene over 0.45 g. of Al<sub>2</sub>O<sub>3</sub>, the amount used in the Pt/SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> mixtures, was less than 0.10%. The conversion over SiO<sub>2</sub> was even lower. Therefore, the exceptionally high rate obtained on mixing Al<sub>2</sub>O<sub>3</sub> with Pt/SiO<sub>2</sub> cannot be simply a matter of adding the separate catalytic contributions of the Pt/SiO<sub>2</sub> and the Al<sub>2</sub>O<sub>3</sub>. For, if we assume that the conversion over the mixture of Pt/SiO<sub>2</sub> and SiO<sub>2</sub> is due to the Pt/SiO<sub>2</sub> alone, the conversion over a mixture of Pt/SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> based on simple additivity considerations would only be 2.1 + 0.1 = 2.2%, which is many-fold lower than actually observed for the mixtures. The data clearly indicate that a cooperative effect of the Pt/SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> is involved.

### Discussion

As indicated in the previous section, the results of the present study on ethylene hydrogenation over catalyst mixtures cannot be accounted for simply on the basis of additivity of separate catalytic contributions of the individual components of the mixtures. In the absence of a simpler explanation for the results, we conclude that the marked synergistic effect observed when Al<sub>2</sub>O<sub>3</sub> is mixed with Pt/SiO<sub>2</sub> is due to a migration of reactive intermediates from one component of the mixture to the other. It appears reasonable that Pt centers activate hydrogen in some manner, and that the active hydrogen migrates to Al<sub>2</sub>O<sub>3</sub> centers to react with chemisorbed ethylene. The fact that Al<sub>2</sub>O<sub>3</sub> chemisorbs ethylene to a much greater degree than does SiO<sub>2</sub> then offers a reasonable explanation for the higher activity of the mixture of Pt/SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> when compared with the mixture of Pt/SiO<sub>2</sub> and SiO<sub>2</sub>.

While the results of the present study suggest that migration of intermediates between different types of

catalytic centers may be important, not much can be said about the detailed nature of these intermediates or the mechanism of migration. Experiments by Khoobiar<sup>7</sup> in this Laboratory have shown that WO<sub>3</sub>, which is not reduced by hydrogen treatment at room temperature, can be readily reduced if a small amount of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst is mixed with it. The reduction of the WO<sub>3</sub> is accompanied by a color change from yellow to blue. It is known that hydrogen atoms will reduce WO<sub>3</sub>,<sup>8</sup> and it has been suggested by Khoobiar that the role of the Pt/Al<sub>2</sub>O<sub>3</sub> is to dissociate hydrogen molecules into atoms which can then migrate to WO<sub>3</sub>. Applying this type of reasoning to the data obtained in the present study, one might speculate that Pt centers on the Pt/SiO<sub>2</sub> serve as a source of hydrogen atoms which migrate over the surface to centers on the Al<sub>2</sub>O<sub>3</sub> to undergo further reaction. While this explanation appeals to us, there is some difficulty in reconciling the notion of migration of hydrogen atoms from Pt to Al<sub>2</sub>O<sub>3</sub> centers with the work of Spenadel and Boudart,<sup>9</sup> who showed that the adsorption of hydrogen on Pt dispersed on Al<sub>2</sub>O<sub>3</sub> corresponded to a 1:1 ratio of H to Pt atoms. If appreciable migration to Al<sub>2</sub>O<sub>3</sub> centers had occurred, then one might have expected the ratio to be significantly higher than 1:1. There is also the question in the present experiments whether the extent of grain to grain contact is high enough for the rate of transport of active species by surface migration to be sufficient to account for the results. However, it is conceivable that a chain mechanism may be involved on the alumina. As an alternative to a mechanism involving surface migration of hydrogen atoms, there is the possibility that reactive intermediates may migrate through the gas phase, but more experimentation would be required to determine the nature of the intermediate species if this turned out to be the case.

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(8) H. W. Melville and J. C. Robb, *Proc. Roy. Soc. (London)*, **A196**, 445 (1949).

(9) L. Spenadel and M. Boudart, *J. Phys. Chem.*, **64**, 204 (1960).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UTAH STATE UNIVERSITY, LOGAN, UTAH]

## The Photochemistry of Riboflavin. I. The Hydrogen Transfer Process in the Anaerobic Photobleaching of Flavins<sup>1</sup>

BY WILLIAM M. MOORE, JACK T. SPENCE, FLOYD A. RAYMOND,<sup>2</sup> AND STEVEN D. COLSON

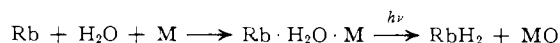
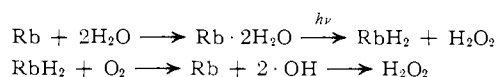
RECEIVED JULY 22, 1963

Several possible mechanisms for the anaerobic photobleaching of riboflavin have been eliminated on the basis of kinetic and polarographic studies. Simultaneous photolysis of solutions of riboflavin in deuterium oxide and water indicated no difference in the rate of photobleaching. Furthermore, polarographic studies of anaerobically photobleached solutions of riboflavin in the presence and absence of EDTA demonstrated that photoreduction does not occur in aqueous solutions in the absence of a hydrogen donor (such as EDTA) and that riboflavin is partially converted to lumichrome without the participation of oxygen. Rate studies on the anaerobic photolysis of the model flavins 9-(2'-hydroxyethyl)-isoalloxazine and 9-(2'-hydroxyethyl-2',2'-d<sub>2</sub>)-isoalloxazine showed a kinetic isotope effect of 2.5 for the ratio,  $k_H/k_D$ . This value agrees with that obtained for other photochemical hydrogen abstraction reactions. Spectrophotometric and polarographic data from the photolyzed solutions indicated that the products are alloxazine and an aldehyde, presumably acetaldehyde. A mechanism involving an intramolecular hydrogen transfer from the 2'-carbon to the 1-nitrogen is suggested as a pathway for the production of lumichrome and other photoproducts of the photobleaching of riboflavin.

### Introduction

In recent years two irreconcilable mechanisms have been proposed to explain the anaerobic photobleaching of riboflavin (6,7-dimethyl-9-[D-1'-ribityl]-isoalloxazine) in aqueous solutions.<sup>3,4</sup> Strauss and Nickerson<sup>3</sup> have

postulated that photoexcited riboflavin (Rb) can split water and abstract the equivalent of two hydrogen atoms to produce dihydroriboflavin (RbH<sub>2</sub>) and hydrogen peroxide. This transfer, they suggest, is facilitated by the presence of an activator (M), such as



(1) Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 8-13, 1963.

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