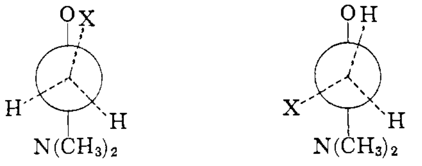
small K. When X is a chloro group interaction between the donor chlorine atom and the iodine appears to occur in addition to interaction with the carbonyl. This interaction is probably best described as London dispersion and dipole-induced dipole interactions. Since the interaction is weak, it has a negligible effect on ΔH, but ring formation leads to a favorable entropy term enhancing the stability of the complex. The favorable entropy term is in part cancelled by the entropy of rearrangement. Coördination can also occur to a lesser extent with isomer II. As a result of all of these effects, $ClCH_2\overset{O}{\overset{/\!\!/}{C}}—N(CH_3)_2$ falls on the σ^* plot. In the case of DMTCA, a chloro group most probably is always *cis* to the carbonyl. Fischer–Hirschfelder models indicate a pronounced steric effect between the Cl and $—N(CH_3)_2$ groups when they are both in the same plane. This steric effect requires the chloro group to be *cis* to the carbonyl. This chloro group interacts with the iodine and the equilibrium constant for the iodine complex of DMTCA is larger than that expected from the σ^* number. Since all molecules have a chloro-group *cis* to the carbonyl, rearrangement is not necessary and the absence of the unfavorable entropy term for complexation produces a large deviation from the σ^*–log K line. The interaction of the chloro group with the iodine is not manifested in the heats of association for this effect is smaller than the experimental error in the ΔH.



I II

Fig. 4.—Possible isomers in $XCH_2\overset{O}{\overset{/\!\!/}{C}}—N(CH_3)_2$ compounds.

Acknowledgment.—The authors gladly acknowledge the generous support of this research by the Chemistry Branch of the Atomic Energy Commission through Contract No. AT(11-1)-758.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY, SCHENECTADY, NEW YORK]

The Chemisorption and Catalytic Decomposition of Ethylene on Nickel

BY DOUGLAS W. MCKEE

RECEIVED SEPTEMBER 20, 1961

The chemisorption and dissociation of ethylene on unsupported nickel catalysts has been studied by a volumetric technique over the temperature range −78 to 200°. The formation of ethane by self-hydrogenation was measureable even at the lowest temperature and the kinetics of the reaction were studied between −78° and 0°. The rate of ethane evolution was found to be proportional to the initial concentration of chemisorbed ethylene and the apparent activation energy for the self-hydrogenation reaction was 3 kcal./mole. Above 60°, methane began to appear in the gas phase and at 200° was the sole gaseous product. The mechanism of catalytic dissociation of ethylene and the nature of the adsorbed residues on the metal surface are discussed.

Introduction

In spite of the very considerable literature that exists on the catalytic addition reactions of olefins, there is still little general agreement as to the detailed mechanisms of these processes. The hydrogenation of ethylene on nickel has been studied intensively since the days of Sabatier, but the reaction kinetics and structure of the adsorbed complex on the surface remain highly controversial.[1] Almost every possible mechanism has been proposed for the hydrogenation reaction at one time or another and the activation energy has been assigned values ranging from 1.8 kcal./mole to 11 kcal./mole. However, a value of about 10.7 kcal./mole, based on Beeck's work on evaporated films,[2] is generally considered the most reliable.

Of crucial importance to the whole problem is the nature of the surface complex which is formed when ethylene is chemisorbed on a clean metal surface. Surprisingly, studies of the chemisorption and dissociation of ethylene on metals, in the absence of hydrogen, are rather sparse and often contradictory. Early exchange experiments by Horiuti and Polanyi[3] and by Twigg and Rideal,[4] suggested that adsorption of ethylene takes place by the "associative" mechanism in which opening of the double bond occurs, whereas, more recent work on ethylene chemisorption on evaporated nickel films by Jenkins and Rideal[5] and by Stephens[6] have supported the alternative "dissociative" mechanism involving fission of the carbon–hydrogen bond. It is probable that both mechanisms have some validity under different conditions and the infrared spectra of adsorbed ethylene on nickel, as determined by Eischens,[7] showed that adsorption could take place by either mechanism depending on the temperature and presence or absence of a pre-adsorbed hydrogen layer.

In view of the complexities of the published data on ethylene adsorption on nickel, it seemed desir-

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(1) *E.g.*, T. I. Taylor, "Catalysis," Vol. V, ed. P. H. Emmett, Reinhold Publishing Corp., New York, N. Y., 1957, p. 257.

(2) O. Beeck, *Rev. Mod. Phys.*, **17**, 61 (1945); *Discussions Faraday Soc.*, **8**, 118 (1950).

(3) J. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

(4) G. H. Twigg and E. Rideal, *Proc. Roy. Soc. (London)*, **A171**, 55 (1939).

(5) G. I. Jenkins and E. Rideal, *J. Chem. Soc.*, 2490 (1955).

(6) S. J. Stephens, *J. Phys. Chem.*, **62**, 714 (1958).

(7) R. P. Eischens, "Advances in Catalysis," Vol. X, Academic Press, Inc., New York, N. Y., 1958, p. 1.

able to study this system in detail over a wider range of temperature than had been used in previous work. It was hoped that information could be obtained on the relative importance of the self-hydrogenation and dissociation reactions, involving fission of carbon–hydrogen and carbon–carbon bonds respectively.

Experimental

(a) **Materials.**—High purity 325 mesh "Inco D" carbonyl nickel was used in this work. The powder was lightly pressed into 6.2 mm. diam. pellets before being sealed into the adsorption cell. Matheson "C.P. Grade" ethylene and ethane were passed through Dry-Ice traps to remove propane and water and then fractionally distilled from a liquid nitrogen trap before being admitted to the adsorption apparatus. "Research Grade," 99.9% pure krypton was used in the surface area determination. Hydrogen for reduction purposes was purified by diffusion through a palladium tube before passage over the metal.

(b) **Apparatus and Procedure.**—The adsorption apparatus was of the conventional volumetric type and included thermostated gas burets, storage bulbs and manometers for adsorbate storage and measurement. Gold foil traps protected the adsorbent cell and contents from mercury vapor and Silicone vacuum grease was generally used on stopcocks in contact with the hydrocarbon gases. Samples of the gas phase in contact with the metal could be condensed in a series of demountable traps cooled in liquid nitrogen; these could then be connected directly to the gas chromatograph for analysis. A McLeod gauge was used for pressure calibrations and for measuring the total pressure in the system while a thermistor was used to determine the composition of the gas in contact with the metal. The essential features of the thermistor gauge have been described by Rosenberg.[8] Thermistors (Type A-58) were obtained from the Victory Engineering Co., Union, N.J., and were calibrated against the McLeod for each of the gases used. The thermistor readings for ethylene–ethane mixtures varied linearly with gas composition and the calibration curves were used to measure changes in gas phase composition during the self-hydrogenation reaction described below. Thermistor readings were generally limited to measurements below 200 microns total pressure and above this value the pressure was measured to 0.01 mm. by means of a wide-bore mercury manometer and cathetometer. Corrections for thermal transpiration were made at the lower temperatures according to the method described by Liang.[9] Slush baths of melting ice (0°); bromobenzene (−31°); 1-hexanol (−49°); carbon tetrachloride (−22°); chloroform (−64°) and methanol–Dry-Ice (−78°) were used as constant temperature baths. Above room temperature a Honeywell controller and furnace were used to maintain the catalyst temperature constant to within ± 1° at the various temperatures studied. In the measurements above 0°, analyses of the gas phase in contact with the metal were carried out using a F and M "300" Linear Programmed Temperature Gas Chromatograph, with helium as carrier gas and a silica gel column.

Most of the results were obtained with samples of reduced nickel weighing 14.8 g. The metal was initially reduced in a stream of pure hydrogen at 400° for several days after being sealed into the vacuum system. At the conclusion of each measurement, the metal was evacuated at 400° for 2 hr., then reduced in a stream of pure hydrogen for 6 hr. at 400°, the pressure of the hydrogen over the metal being maintained at 2–3 cm. Finally, the reduced metal was evacuated for at least 12 hr. at 400°, at which time the residual gas pressure, as measured by the ionization gauge, was less than 2×10^{-6} mm. This treatment was found to remove adsorbed residues completely from the metal surface and no evidence for residual chemisorbed hydrogen was found as long as the evacuation time was longer than 4 hr. Unreproducible results were, however, obtained when the sample was evacuated for shorter periods. A similar treatment for activating metal catalysts has been found to be effective by Galwey and Kemball.[10] The surface area of the activated metal, as determined by krypton adsorption at −195°, was found to be 950 cm.^{2}/g. by the B.E.T. method.

In the low temperature adsorption studies, small increments of ethylene were admitted from the gas burettes and the thermistor gauge was used to measure the gas composition over the catalyst as a function of time. In most runs the total pressure in the system was checked independently with the McLeod gauge throughout the course of the adsorption. This total pressure fell rapidly after the addition of each increment of ethylene but levelled off 4–5 min. after the injection and subsequently remained constant for a further 10 min. before beginning to increase slightly. The thermistor gauge current, however, reached a minimum value after about 5 min. and then began to rise steadily due to the liberation of ethane from the metal surface. The rate of ethane evolution was calculated from the slope of the linearly rising portion of the thermistor current *vs.* time curve, the total pressure being measured directly with the McLeod gauge at this point. Before the addition of fresh ethylene, the bulk of the gas phase, but not the sample bulb, was evacuated to remove accumulated ethane. At the end of each run the metal was reduced and activated as described above.

For measurements above 0°, 6 mm. of ethylene were allowed to stand over the activated metal for a period of 4 hr. at each of the temperatures studied, the volume of the system being about 130 ml. At the end of this period, the contents of the gas phase were condensed in a trap cooled in liquid nitrogen. The non-condensable pressure was found to be due to methane, although small amounts of hydrogen were also found at the lower temperatures. The contents of the trap were analyzed with the gas chromatograph described above.

Results

(a) Measurements between −78 and 0°.—The first increments of ethylene added to the metal over this temperature range resulted in a rapid adsorption and corresponding fall in pressure. About 30 min. were required before adsorption equilibrium was attained after each addition of gas and the residual pressure over the metal was generally less than 1×10^{-2} mm. It was not found possible to remove this chemisorbed layer by prolonged pumping at this adsorption temperature. When a certain volume of ethylene had been adsorbed, evolution of ethane from the surface began, and the steady rate of gas evolution was calculated as described above from the thermistor calibration curves and total pressure. Figure 1 shows the rate of ethane evolution, $\mathrm{d}\, n_{C_2H_6}/\mathrm{d}t$ molecules/min., plotted against the total number of molecules of ethylene added $n_{C_2H_4}$ for the various temperatures used. In every case an initial amount of ethylene $n_{C_2H_4}{}^0$ was chemisorbed before the evolution of ethane began. From the volume of hydrogen adsorbed at −195° (see below (d)), the ratio $n_{C_2H_4}{}^0$: sites available varied from 1:34 at −22° to 1:6.9 at −78°. When the amount of ethylene present exceeded $n_{C_2H_4}{}^0$ at each temperature, the evolution of ethane commenced at a rate that was proportional to the amount of excess ethylene adsorbed. The self-hydrogenation reaction therefore followed the rate equation

$$\frac{\mathrm{d}n_{C_2H_6}}{\mathrm{d}t} = K(n_{C_2H_4} - n_{C_2H_4}{}^0)$$

The constancy of the total pressure in the system suggested that the rate of disappearance of ethylene was equal to the rate of evolution of ethane, as would be expected from a first order process.

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[8] A. J. Rosenberg, *J. Am. Chem. Soc.*, **78**, 2929 (1956).

[9] C. Liang, *J. Phys. Chem.*, **56**, 660 (1952); *J. Appl Phys.*, **22**, 148 (1951).

[10] A. K. Galwey and C. Kemball, *Trans. Faraday Soc.*, **55**, 1959 (1959).

The rate of ethane evolution increased 4.8 fold on raising the temperature from −78 to −22°. By plotting the values of K against $1/T$ according to the Arrhenius equation, the apparent activation energy for the self-hydrogenation was calculated to be 3 ± 0.5 kcal./mole.

(b) **Measurements above 0°.**—The production of ethane at 0° and above was too rapid to be measured accurately with the thermistor gauge. In addition, the metal surface was rapidly covered with non-volatile residues which inhibited the self-hydrogenation reaction. For these reasons a different technique was used to study the products of ethylene dissociation above 0°, the metal being contacted with a constant initial pressure of the gas for the same length of time at each temperature. The results are shown in Fig. 2, in which the composition of the gas phase after 4 hr. contact with the metal is plotted against the temperature of the catalyst. At each temperature it was possible to determine the average composition of the surface residues in the form $(\mathrm{CH_n})_x$, where n was calculated from the relation

$$n = \frac{2(2n_{\mathrm{C_2H_4}}' - 2n_{\mathrm{C_2H_4}} - 3n_{\mathrm{C_2H_6}} - 2n_{\mathrm{CH_4}})}{2n_{\mathrm{C_2H_4}}' - 2n_{\mathrm{C_2H_4}} - 2n_{\mathrm{C_2H_6}} - n_{\mathrm{CH_4}}}$$

where $n_{\mathrm{C_2H_4}}'$ is the number of moles of ethylene introduced initially and the other molar quantities refer to the amounts of the various gases in the gas phase at the end of the run. The over-all composition of the adsorbed residues on the metal surface is shown by the dotted curve in Fig. 2 as a function of temperature.

(c) **Dissociation of Ethane.**—A few experiments on the catalytic dissociation of ethane were made for comparison purposes, using the same conditions as those employed for ethylene. In this case no gaseous products were detected below 100°. Above this temperature, methane was the only product, as shown by the dashed curve in Fig. 2.

(d) **Adsorption of Hydrogen.**—A determination was also made of the adsorption of hydrogen on the nickel sample at −195°. The total volume adsorbed was found to be 0.172 ml. S.T.P. on the 14.8 g. metal. Assuming that two lattice points were occupied per hydrogen molecule and that the specific surface of the metal was 950 m.²/g., the effective area per site was then 15 Å.², approximately, in reasonable agreement with the Ni–Ni lattice spacing.

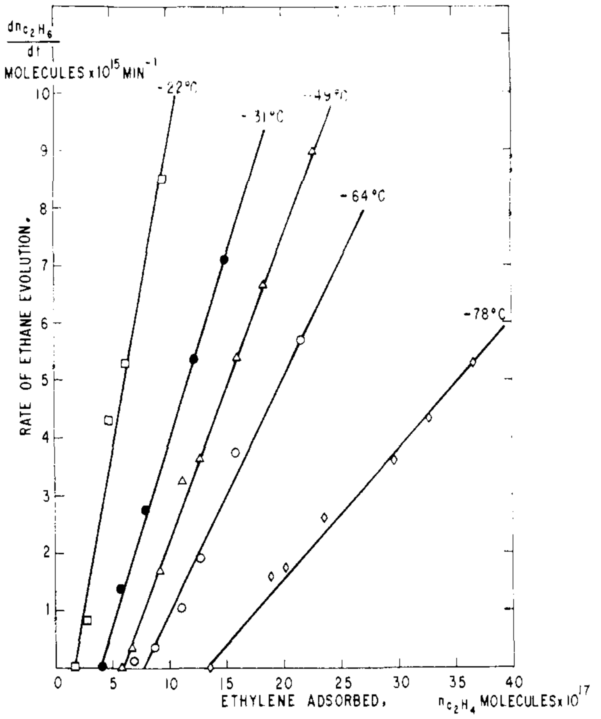

Fig. 1.—Rate of ethane evolution from ethylene on nickel.

Discussion

(a) **Low Temperature Measurements.**—An interpretation of the low temperature results involves a description of the process of self-hydrogenation. This arises from the dissociation of ethylene on the surface of the metal into hydrogen atoms and a non-volatile residue, subsequent reaction giving rise to ethane in the gas phase. This effect has been observed before and the reaction has been assumed to play a part in the catalytic hydrogenation process, where both hydrogen and ethylene are present in the gas phase. A detailed study of the mechanism of self-hydrogenation does not, however, appear to have been made and the information available is somewhat contradictory, as is to be expected from the wide differences in sample preparation, morphology and activation techniques used by different workers. Beeck[2] observed the evolution of ethane from nickel films at room temperature but failed to notice the effect at −38°. In discussing the mechanism of ethylene hydrogenation on nickel, he suggested that dissociative chemisorption of ethylene was the initial step

$$\mathrm{CH_2{=}CH_2\,(g)} \longrightarrow \underset{*}{\mathrm{C}}\mathrm{H{=}}\underset{*}{\mathrm{C}}\mathrm{H} + \underset{*}{\mathrm{H}} + \underset{*}{\mathrm{H}} \quad \ldots \quad (1)$$

Gas phase hydrogen was also chemisorbed as hydrogen atoms

$$\mathrm{H_2\,(g)} + {*}{-}{*} \longrightarrow 2\underset{*}{\mathrm{H}} \ldots \qquad (2)$$

and the rate-controlling step in the hydrogenation reaction was the slow surface recombination

$$\underset{*}{\mathrm{C}}\mathrm{H{=}}\underset{*}{\mathrm{C}}\mathrm{H} + 4\underset{*}{\mathrm{H}} \longrightarrow \mathrm{C_2H_6\,(g)} + {*}{-}{*} \ldots \quad (3)$$

This gave rise to an activation energy for the reaction of 10.7 kcal./mole. The reaction between chemisorbed hydrogen atoms and gaseous ethylene

$$\mathrm{CH_2{=}CH_2\,(g)} + \underset{*}{\mathrm{H}}\;\underset{*}{\mathrm{H}} \longrightarrow \mathrm{C_2H_6\,(g)} + {*}{-}{*} \ldots \quad (4)$$

was believed by Beeck to be too fast to be rate-controlling. However, tungsten gave a much lower activation energy (2.5 kcal./mole) and in this case it was suggested that the slow reaction 3 did not occur, reaction 4 then being rate determining.

In the present work the kinetics of the self-hydrogenation reaction yield an apparent activation energy of 3 kcal./mole. It seems likely that the rate-controlling step in this reaction is (4), involving chemisorbed hydrogen atoms and gaseous ethylene, rather than the surface reaction 3 and subsequent desorption of the ethane. It is interesting that the photochemical combination of

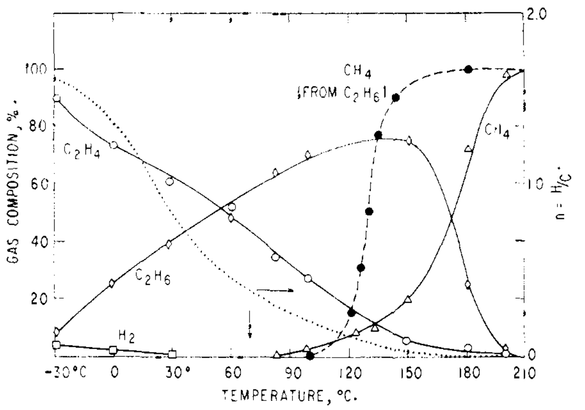

Fig. 2.—Product composition *vs.* temperature after 4 hr. contact with nickel; initial gas pressure was 6 mm. Solid curves refer to products from ethylene, dashed curve was obtained from ethane. Dotted curve gives temperature dependence of over-all composition of surface residues $(CH_n)_x$ from ethylene decomposition.

hydrogen atoms with ethylene has been found to have an activation energy of 4.1 kcal./mole at room temperature,[11] lending support to the proposed mechanism.

Schissler, *et al.*,[12] recently studied the behavior of ethylene on a reduced nickel–kieselguhr catalyst, by allowing 3 mm. of gas to contact the catalyst for 30 min. at −132, −90 and −78°. No ethane was found at the end of this time but, at the latter temperature, the residual gas consisted of 95% ethylene and 5% of a product believed to contain benzene and cyclohexane. On the basis of these results, it was proposed by these authors that self-hydrogenation is not a necessary step in the gaseous hydrogenation reaction, as suggested by Beeck. However, the present results indicate that the evolution of ethane is so slow at −78° that the concentration in the gas phase after 30 mins. would probably not have been detectable. Also no polymers of higher molecular weight products were found.

Very recently, Selwood[13] has used magnetization measurements to study the adsorption of ethylene on nickel-silica between 0 and 130°. His results appear to lend support to the associative mechanism. Self-hydrogenation was found to be negligible at 0° but became important with increasing temperature. The reasons for the discrepancies between these results and those of the present investigation are not obvious, and it is possible that the specific nature of the catalyst surface and support plays the decisive role in determining the adsorption mechanism. However, it may be noted that Selwood evacuated his sample for only 2 hr. at 360° after reduction. It is the experience of the present author that this period is insufficient for the removal of the last traces of chemisorbed hydrogen from the metal, and it seems feasible that a small amount of hydrogen can modify the mechanism of the subsequent adsorption of ethylene.

(b) **Measurements above 0°.**—The results shown in Fig. 2 indicate that the evolution of ethane continued above 0°. By varying the evacuation time of the metal after reduction from 4 to over 60 hr., it was established that this ethane could only have originated from the self-hydrogenation reaction and not as a result of hydrogenation by trace amounts of hydrogen occluded in the metal. A small amount of hydrogen was found in the products at the lower temperatures, but its concentration was always less than 5% of the total gas phase and undoubtedly arose from the self-hydrogenation and subsequent desorption. These small amounts of hydrogen were apparently consumed in the catalytic hydrogenation reaction as no hydrogen could be detected above 30°. Methane began to appear in the gas phase above 60°, and its concentration increased rapidly until at 200° it was the sole product of reaction. At the latter temperature, the pressure over the metal remaining constant during the reaction, which therefore followed the equation

$$C_2H_4 \longrightarrow CH_4 + C$$

The residual carbon may, however, exist in the form of a surface carbide.

If the cracking process involves an initial self-hydrogenation step, it would be expected that the dissociation of ethane and ethylene would show similar characteristics. Actually the two gases behaved differently, as is shown in Fig. 2. At temperatures above 100°, methane was the sole product of ethane cracking, the evolution of methane being attended by a pressure increase according to the equation

$$2C_2H_6 \longrightarrow 3CH_4 + C$$

A similar result was also obtained by Kemball and Taylor.[14] Only a trace of methane was produced from ethane at 100°, whereas ethylene gave nearly 2% methane under the same conditions. The activation energy for the dissociation of ethane appears to be greater than that for ethylene and the results are consistent with the idea that the residues produced from the initial self-hydrogenation step may partially poison the surface. In the experiments with ethane, no trace of hydrogen was found in the products. This result is in conflict with those of Wright, Ashmore and Kemball[15] who claim to have measured the evolution of hydrogen from ethane adsorbed on nickel films between 0 and 100°. However, no definitive analysis of the reaction products was made by these authors who assumed that the non-condensable gas evolved was hydrogen. It seems entirely possible that methane was the sole gaseous product, as has been demonstrated conclusively for ethane dissociation on rhodium films by Roberts.[16]

The over-all composition of the adsorbed residues from ethylene decomposition changed regularly with temperature, as shown by the dotted curve in Fig. 2. At 0°, a value of n approaching 1.5 was

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[12] D. O. Schissler, S. O. Thompson and J. Turkevich, "Advances in Catalysis," Vol. IX, Academic Press, Inc., New York, N. Y., 1957, p. 37.

[13] P. W. Selwood, *J. Am. Chem. Soc.*, **83**, 2853 (1961).

[14] C. Kemball and H. S. Taylor, *ibid.*, **70**, 345 (1948).

[15] P. G. Wright, P. G. Ashmore and C. Kemball. *Trans. Faraday Soc.*, **54**, 1692 (1958).

[16] R. W. Roberts, *Nature*, **191**, 170 (1961).

obtained, suggesting that the complex had an average composition intermediate between $\underset{*}{C}H{=}\underset{*}{C}H$ and $\underset{*}{C}H_2\underset{*}{C}H_2$, or alternatively $\underset{*}{C}H{=}\underset{*}{C}H_2$. At about 20°, the value of *n* had fallen to 1, in agreement with the result of Jenkins and Rideal[5] whose work on films at this temperature yielded a H/C ratio of unity in the surface residues. On this basis these authors, and also Beeck,[2] suggested the presence of acetylenic residues $\underset{*}{C}H{=}\underset{*}{C}H$ and hence evidence for the dissociative mechanism of ethylene chemisorption. However, as Eischens[7] has pointed out, it is perfectly possible for the surface complex to have an average composition of about (C_1H_1) and still be almost completely saturated if each carbon is bonded to more than one nickel atom. Infrared evidence has added support to the dissociative mechanism on a bare nickel surface, but the present work indicates that the resultant surface complex probably did not have a specific stoichiometric composition, the value of *n* falling continuously with increasing temperature as hydrogen was progressively removed from the surface.

Acknowledgments.—The author is indebted to Drs. E. J. Cairns, J. L. Holman and W. T. Grubb for many helpful discussions during the course of this investigation.

[CONTRIBUTION FROM THE EVANS CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO]

The Mechanism of Methyl Hydroperoxide Formation in the Photooxidation of Azomethane at 25°

BY N. R. SUBBARATNAM AND J. G. CALVERT

RECEIVED SEPTEMBER 28, 1961

Long-path infrared spectrometry has been used to follow the rates of formation of methyl hydroperoxide in the photoöxidation of azomethane in oxygen-rich mixtures at 25°. The rates of formation of CH_3O_2H and/or CD_3O_2D were determined in a series of experiments with varied $[O_2]$, with added C_2F_6, with mixtures of $CD_3N_2CD_3$–O_2, $CH_3N_2CH_3$–$CD_3N_2CD_3$–O_2, and in azomethane–O_2 mixtures with formaldehyde and acetaldehyde. The data prove the unimportance of the H-abstraction reaction, $CH_3O_2 + RH \rightarrow CH_3O_2H + R$, in oxygen-rich atmospheres at 25°; they are consistent with the formation of methyl hydroperoxide in the disproportionation reaction, $CH_3O_2 + CH_3O \rightarrow CH_3O_2H + CH_2O$.

In recent years considerable interest has developed in the mechanism of the room temperature oxidation of alkyl free radicals. The reactions of free radicals in oxygen-rich atmospheres are of special concern to the air pollution area.[1] A number of quantitative studies of the reactions of the simplest alkyl free radical, methyl, with oxygen have been made, and even in this simplest system there is considerable uncertainty as to the mechanism which is operative. Data from many laboratories suggest that the first step in the reaction sequence is the formation of an energy-rich methylperoxyl radical.[2–4] The third-order kinetics

$$CH_3 + O_2 \rightleftarrows CH_3O_2^{\ddagger} \qquad (1)$$

of the reaction between the methyl radical and oxygen in the usual pressure region suggests the establishment of an equilibrium between the energy-rich radical, $CH_3O_2^{\ddagger}$, and its dissociation products in 1.

Although most researchers would agree that CH_3O_2 is the initial product of the methyl radical-oxygen interaction at room temperature, there is little agreement as to the fate of this radical.[5–17] Calvert and co-workers contend that the major primary products of the methyl radical reactions in oxygen-rich media at 25° are methanol and formaldehyde, formed in approximately equal amounts.[14] Kutschke and co-workers question this contention; they have recently detected (by mass spectrometry) methyl hydroperoxide among the products of the photoöxidation of azomethane under conditions similar to those used by Calvert and co-workers; they believe that methyl hydroperoxide may be the major primary product under certain conditions.[16] Subbaratnam and Calvert[17] have confirmed the identification of methyl hydroperoxide in these systems using long-path infrared techniques, but under their conditions, oxygen-rich atmosphere at 25°, it is a minor product. They

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[1] P. A. Leighton and W. A. Perkins, *Air Pollution Foundation Rept.* 14, Rept. 15, 1956; Rept. 24, 1958, San Marino, California.

[2] D. E. Hoare and A. D. Walsh, *Trans. Faraday Soc.*, **53**, 1102 (1957).

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[11] P. L. Hanst and J. G. Calvert, *J. Phys. Chem.*, **63**, 71 (1959).

[12] R. L. Strong and K. O. Kutschke, *Can. J. Chem.*, **37**, 1456 (1959).

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[16] M. Shahin and K. O. Kutschke, *J. Phys. Chem.*, **65**, 2277 (1961).

[17] N. R. Subbaratnam and J. G. Calvert, in "Chemical Reactions in the Upper and Lower Atmosphere," Interscience Publishers, New York, N. Y., 1961, pp. 109-128.