TABLE II

DENSITY, SQUARE OF REFRACTIVE INDEX, DIELECTRIC CONSTANT OF GASOLINE AT 35°

Temp., °C.	d	n^2_D	E	$E - n^2_D$
Original sample of gasoline	0.7349	2.002	2.012	0.010
Boiling fraction: 60–90	.6782	1.909	1.909	0
90–100	.6933	1.937	1.937	0
100–120	.7164	1.960	1.960	0
120–140	.7257	1.987	1.990	0.007
140–160	.7449	2.008	2.021	.013
160–180	.7619	2.033	2.050	.017
Above 180	.7910	2.074	2.097	.023

that the highest boiling fraction has relatively the highest dipole moment of all fractions, namely, 0.31×10^{-18}. Benzene and carbon tetrachloride have frequently been used as non-polar solvents in dipole moment determinations. The difference in n^2_D and E for benzene and carbon tetrachloride at 25° are, however, 0.037 and 0.114, respectively. According to this criterion, gasoline should be more non-polar than benzene or carbon tetrachloride.

Table III lists the dipole moment values which have been obtained using gasoline and similar solvents of indefinite molecular weights and the values obtained for the same compounds using solvents of known molecular weights.

TABLE III

DIPOLE MOMENT AT 25°[a]

Castor oil	in gasoline 3.62×10^{-18}	in benzene 3.7×10^{-18}
Tung oil	kerosene 2.92	benzene 2.9
Di-*n*-butyl ether	kerosene 1.17	benzene 1.22 toluene 1.13
Ethyl-*n*-butyl ether	kerosene 1.19	benzene 1.24
Acetone	gasoline 2.8	benzene 2.72
Chloroform	gasoline 1.16	benzene 1.15
Acetonitrile	gasoline 3.33 kerosene 3.35 petroleum ether 3.35	benzene 3.37 toluene 3.38

[a] The values for castor oil and tung oil are taken from Li, *J. Chinese Chem. Soc.*, 13, 8 (1946); the values for the ethers from Li and Hsü, *ibid.*, 13, 11 (1946); the other values are from Ref. 1 of this paper.

Summary

Dipole moment can be measured using gasoline as solvent, a substance which has no definite molecular weight and whose physical properties may vary greatly with different samples. Experimental results indicate that gasoline and its fractions are essentially non-polar. A summary of the dipole moment values obtained using gasoline and similar solvents of indefinite molecular weights is given and shown to be in close agreement with values obtained using non-polar solvents of known molecular weights.

ST. LOUIS, MO. RECEIVED AUGUST 18, 1947

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Catalytic Decomposition of Ethane and Ethane–Hydrogen Mixtures

BY CHARLES KEMBALL[1] AND HUGH STOTT TAYLOR

The work of Morikawa, Benedict and Taylor[2,3] and of Morikawa, Trenner and Taylor[4] showed that the exchange reactions between the lower hydrocarbons and deuterium on supported nickel catalysts could be brought about at lower temperatures than the decomposition reactions. The energy of activation for the breaking of the carbon–hydrogen bond was some 15 kcal./mole less in the case of propane, than that for the breaking of the carbon–carbon bond. There is little doubt that the exchange reaction involves dissociative adsorption of the hydrocarbon, *e. g.*, as ethyl radical and hydrogen atom, and re-evaporation of the ethyl with a deuterium atom. Much less can be conjectured about the decomposition reaction and it was considered worthy of further study. Morikawa and his co-workers showed that, over a certain range of composition, the rate of production of methane from ethane and hydrogen depended inversely on the 2.5 power of the hydrogen pressure. This point required further investigation because it is difficult to see the kinetic interpretation of such a dependence. Accordingly it was decided to extend their investigation to a wider range of composition for the reacting mixture and further to study the decomposition of ethane in the absence of hydrogen.

Experimental

Analysis.—The reaction was followed by the withdrawal of a sample of gas and analysis by means of a mass spectrometer. The height of the mass 30 peak was determined solely by the ethane concentration and the mass 16 peak was almost entirely due to the methane. A small correction was made for the mass 16 in the ethane pattern; this amounted to 0.004 of the height of the "30 peak." In order to allow for fluctuations in the behavior of the instrument and to avoid the difficulty of using a constant pressure behind the leak of the spectrometer, the ratio of the "16 peak" to the "30 peak" was always measured. A series of known mixtures of ethane, methane and hydrogen were used to obtain calibration curves giving the ratio methane/ethane in terms of the ratio "16 peak"/"30 peak." The curve was linear up to 0.7 for methane/ethane, and was not greatly affected by the presence of hydrogen in the mixture. It was possible to estimate the amount of methane in a mixture to closer than 2% in this manner. A static system was used to follow the reaction and checks were made that the samples withdrawn were representative of the whole reacting gas.

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[1] Commonwealth Fund Fellow, Princeton University, 1946–1947.

[2] Morikawa, Benedict and Taylor, THIS JOURNAL, 58, 1445 (1936).

[3] Morikawa, Benedict and Taylor, *ibid.*, 58, 1795 (1936).

[4] Morikawa, Trenner and Taylor, *ibid.*, 59, 1103 (1937).

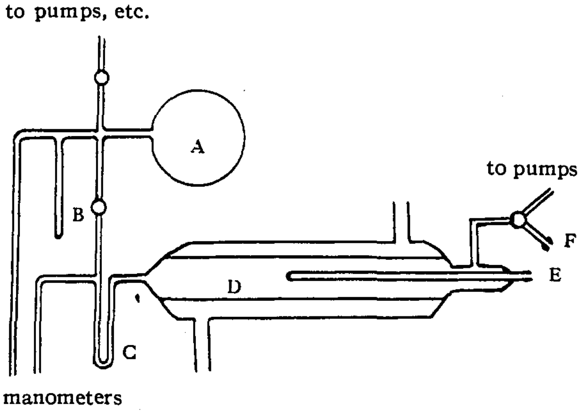

Fig. 1.—The apparatus.

Apparatus.—The essential part of the apparatus is shown in Fig. 1. The gases were allowed to mix in the bulb A. B could be cooled in liquid air to condense ethane during the admission of hydrogen. The trap C, maintained at −80°, prevented mercury out of the manometer from poisoning the catalyst, which was placed in the vessel D. The tube E was large enough to hold a thermometer. Sample bulbs could be fitted on to the ground joint F. The total volume of the reaction vessel was some 100 cc.; it was thermostated by means of the vapor jacket shown. Aniline, and, in the later experiments, naphthalene boiling under reduced pressure, were used for this purpose. The outside of the vapor jacket was wound with resistance wire and well lagged. The resistance unit served as an auxiliary heater and could also be used to bring the catalyst up to a high temperature for reduction or cleaning.

Preparation of Gases.—Cylinder hydrogen was purified by passing over heated copper at 400° and then dried over calcium chloride, Ascarite and finally phosphorus pentoxide. Cylinder ethane was passed over phosphorus pentoxide, condensed in liquid air and after two distillations the middle fraction was stored. Ethylene, which was required in some of the later experiments, was treated like ethane.

Catalyst.—The catalyst contained 15% Ni supported on kieselguhr. It was a specimen no. 330 prepared by the E. I. du Pont de Nemours Co., many years ago and was from the same batch of catalyst that was used by Morikawa[2,3,4]; 2.4 g. was used, being reduced in a stream of hydrogen at 430° and then evacuated. Between each experiment the catalyst was merely evacuated at the reaction temperature.

Experimental Results

Decomposition of Ethane–Hydrogen Mixtures.

A. Normal Kinetics.—The kinetic expression for the rate of production of methane from ethane and hydrogen depended on the composition of the reacting gases. At 182°, provided there was an excess of hydrogen (ratio > 1:1), the rate of reaction depended on $p_{C_2H_6}{}^{0.7} \times p_{H_2}{}^{-1.2}$ and the behavior of the catalyst was reproducible. The results of experiments of this type are given in Table I. Whenever the reacting gases were introduced into the reaction vessel there was a decrease in pressure of some 2 mm., taking place mainly in the first fifteen minutes. This was assumed to be due to adsorption of hydrogen but the correction it involved in the calculation of the mean pressures was small. In the last column of Table I the calculated rates of reaction for a given mixture (10 cm. ethane, 15 cm. hydrogen) based on the kinetic expression mentioned above, are listed. The constancy of these figures was the evidence for the expression $p_{C_2H_6}{}^{0.7} \times p_{H_2}{}^{-1.2}$. The reactions at 214° followed similar kinetics provided the hydrogen/ethane ratio was maintained at 2 or greater, see Table II. Neglecting the change in density of the gas between the two temperatures the mean rates gave an energy of activation of 52 kcal./mole.

B. Abnormal Kinetics.—With lower ratios of hydrogen to ethane (<1.0 at 182°, <2.0 at 214°) there was an increase in the rate of reaction above that expected from the kinetic expression. The results are tabulated in Table III which can be compared with Tables I and II. The behavior of the catalyst was not as reproducible for mixtures with low hydrogen content. Experiments 41, 42 and 43 showed unusually rapid reaction—this was attributed to the fact that the catalyst had been evacuated at a few degrees above the reaction temperature. Again while experiments 52 and 53 (ratio $H_2/C_2H_6 \approx 1$) showed normal kinetics, experiments 20, 21 and 22 were rapid. The deviation from normal behavior was greater the smaller the ratio of hydrogen to ethane and the smaller the total pressure. A kinetic expression for these reactions would have to contain a factor of the order $p_{H_2}{}^{-2}$ and it is interesting to note that it was in this region of composition that Morikawa, Benedict and Taylor found the factor $p_{H_2}{}^{-2.5}$. They worked with hydrogen/ethane ratios varying between 0.5 and 2.0 at 184°.

The Decomposition of Ethane Alone.—In experiments 22 and 24 a slight increase of pressure had been observed. This indicated that some of the ethane was decomposing to give carbon and methane. The rate of reaction of ethane in the absence of hydrogen was then examined. It was clear from the earlier work of Morikawa that the carbon so deposited might poison the surface; however, it was found that the carbon could be removed with hydrogen. The decomposition of ethane was followed by the increase of pressure, and the reaction was found to proceed to completion according to the equation $2C_2H_6 \rightarrow 3CH_4 + C$.

The data for three decompositions at 182° are shown in Fig. 2. Before each reaction the surface had been freed from carbon by hydrogenation as will be described in the next section. The small dip, experimentally observed, at the beginning of each curve was due to the adsorption of ethane. The experiments 27 and 29 were left overnight with little further change in pressure. The ratios of the final to initial pressure were, respectively, 1.49 and 1.51, indicating that the reaction $2C_2H_6 \rightarrow 3CH_4 + C$ was complete. A sample of the gas at the end of experiment 27 was analyzed on the mass spectrometer and the ratio of ethane to methane shown to be approximately 1/3,000. In experiment 31 there was a noticeable decrease in the rate of reaction after the pressure had increased by 2 cm. This was assumed to be due to the covering of surface with carbon and consequent lack of activity. It was found that the shape of the curves corresponded to an expression

$$dp/dt = k(p_\infty - p)^{0.7}$$

where p_∞ is the final pressure, *i. e.*, the rate of reaction depended on a fractional power of the unchanged ethane. The plots of $(p_\infty - p)^{0.3}$ *versus* t, the integrated form of the equation, are shown in Fig. 3 and the values of k are listed in Table IV. The poisoning in experiment 31 is easily seen in Fig. 3.

TABLE I

REACTIONS OF HYDROGEN AND ETHANE WITH NORMAL KINETICS AT 182°

Expt.	Time, hr.	Temp., °C.	Mean pressures, cm. Methane	Ethane	Hydrogen	Methane cm./hr.	Calcd. CH_4 cm./hr. for 10 cm. C_2H_6 15 cm. H_2
6	4	181.3	0.30	1.88	4.57	0.147	0.114
7	4	182.1	.06	2.09	15.27	.032	.098
8	4	182.6	.21	9.25	14.13	.104	.102
9	4	182.0	.45	1.95	2.94	.224	.099
10	4	181.8	.24	4.79	7.20	.122	.085
18	4	181.7	.16	3.75	10.92	.082	.111
19	4	181.8	.22	1.51	4.51	.109	.097
50	4	181.8	.23	5.42	10.57	.114	.115
51	4	181.1	.35	1.75	3.55	.176	.096
52	2	181.6	.14	9.96	9.75	.135	.081
53	2	181.5	.28	2.87	2.91	.279	.094
							Mean, 0.099

TABLE II

At 214 °C.

11	1	214.3	3.05	3.70	6.48	6.10	4.47
12	1	214.3	0.56	4.83	30.29	1.11	4.27
13	1	214.3	0.92	0.92	7.81	1.84	4.45
16	1	214.0	1.60	3.27	11.04	3.21	4.84
17	1	214.0	1.65	3.40	11.51	3.29	5.10
							Mean, 4.63

TABLE III

REACTIONS OF HYDROGEN AND ETHANE WITH ABNORMAL KINETICS

Expt.	Time, hr.	Temp., °C.	Mean pressures, cm. Methane	Ethane	Hydrogen	Methane cm./hr.	Calcd. CH_4 cm./hr. for 10 cm. C_2H_6 15 cm. H_2
14	1	215.0	3.60	18.10	25.76	7.14	9.38
15	1	215.0	5.03	2.74	5.22	10.06	7.03
20	2	182.0	0.18	12.25	12.23	0.181	0.123
21	2	182.0	.67	4.09	4.12	0.333	.132
22	2	181.9	.74	1.70	1.86	0.743	.264
23	1	182.1	.65	7.91	3.99	1.30	.313
24	1	182.1	1.29	1.53	1.26	2.58	.491
41	1	182.0	0.87	24.30	11.75	1.74	.697
42	1	182.0	1.13	18.31	8.73	2.25	.769
43	1	182.5	1.95	11.21	5.11	3.90	.714
44	1	182.0	0.50	9.61	4.61	1.00	.250
45	1	182.2	.64	6.58	3.11	1.28	.260
46	1	181.9	.26	25.98	12.78	0.51	.216
47	1	181.9	.26	19.96	9.80	.51	.189
48	1	182.4	.31	14.93	7.28	.62	.196
49	1	182.9	.33	10.72	5.26	.66	.179
54	1	181.8	.29	10.44	4.97	.57	.148

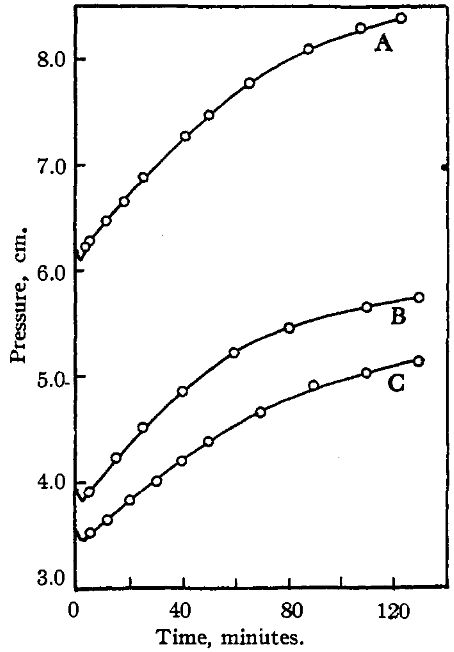

Fig. 2.—Ethane decompositions at 182°: A, Expt. 31, 182.8°; B, Expt. 29, 182.1°; C, Expt. 27, 182.0°.

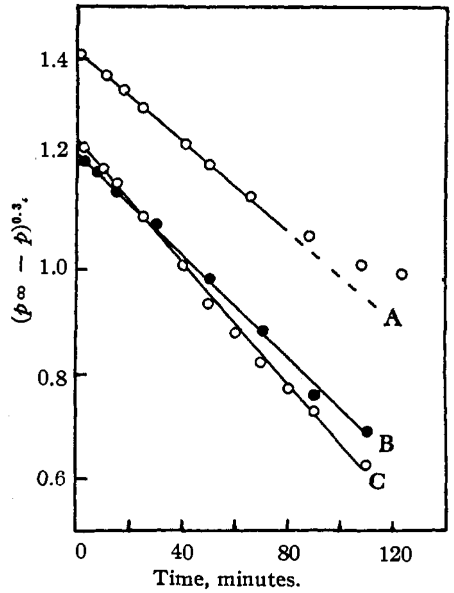

Fig. 3.—Ethane decompositions at 182°: A, Expt. 31, 182.8°; B, Expt. 27, 182.0°; C, Expt. 29, 182.1°.

Three experiments at 192° are recorded in Figs. 4 and 5 and the values of k are given in Table IV. The higher rate of reaction levelled out the dips

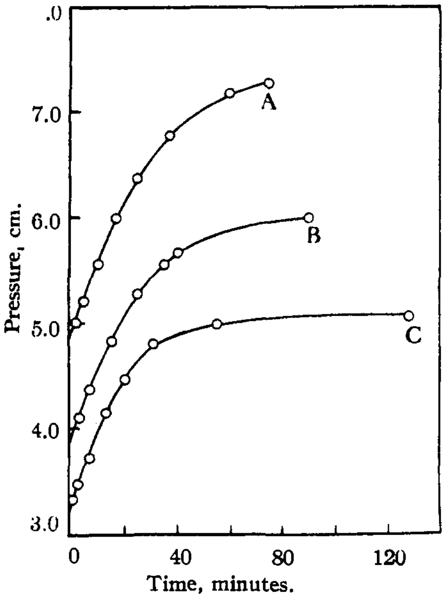

Fig. 4.—Ethane decompositions at 192°: A, Expt. 33, 194.2°; B, Expt. 35, 192.2°; C, Expt. 39, 192.0°.

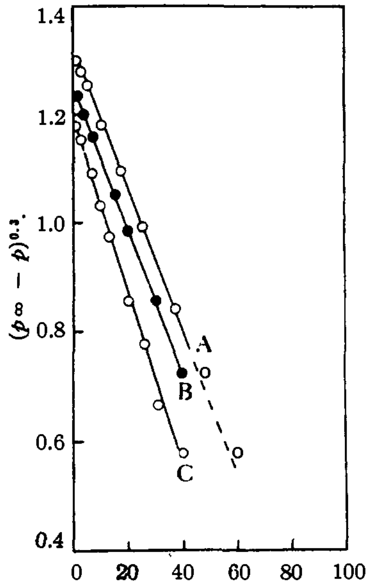

Fig. 5.—Ethane decompsitions at 192°: A, Expt. 33, 194.2°; B, Expt. 35, 192.2°; C, Expt. 39, 192.0°.

due to adsorption which were now only visible as smaller initial gradients. The energy of activation from the mean values of k was 40 kcal./mole.

The Removal of Deposited Carbon by Hydrogenation.—The ethane decompositions were alternated with carbon removal reactions according to the equation $C + 2H_2 \rightarrow CH_4$. The decrease in pressure observed on allowing hydrogen access to the catalyst (subject to a correction for adsorption) was therefore equivalent to the carbon removed and was found to correspond in each case to the rise in pressure in the previous ethane decomposition within the experimental error. This indicated that the carbon deposition was reversible, which was confirmed by the absence of any progressive poisoning. Two reactions are shown in Fig. 6. The decrease in rate of reaction with time was marked and it was not possible to fit a kinetic expression to the curves. The initial part could be fitted to a rate given by $-dp/dt = k(p - p_\infty)^3$, where $(p - p_\infty)$ represents the carbon still to be removed. However, a dependence of rate on the third power of the carbon to be removed is meaningless as regards a physical picture of the mechanism. The plot of $(p - p_\infty)^{-2}$ *versus* t enabled the initial·rates of reaction to be estimated. Attempts were made to use rate expressions of the type

$$-dp/dt = k(p - p_\infty)(2p - p_0)^2$$

and

$$-dp/dt = k(p - p_\infty)(2p - p_0)^3$$

but without success; the term $(2p - p_0)$ is a measure of the hydrogen available. The rapid decrease in rate was more likely to be connected with the ease of removal of carbon from a heterogeneous surface.

TABLE IV

DECOMPOSITION OF ETHANE

Expt.	Temp., °C.	Initial pressure, cm.	k	
27	182.0	3.56	0.0160	0.0173
29	182.1	3.90	.0200	
31	182.8	6.22	.0159	
33	194.2	4.89	.043	0.047
35	192.2	4.01	.044	
39	192.0	3.32	.054	

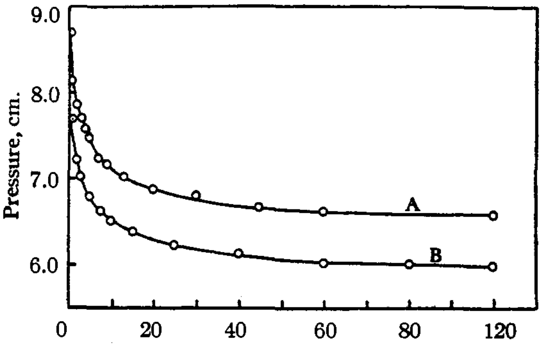

Fig. 6.—The reaction of hydrogen with adsorbed carbon to form methane: A, Expt. 32, 192.0°; B, Expt. 38, 182.1°.

Three experiments were carried out at 182° and four at 192°. There was always some difficulty in obtaining the value for the initial pressure especially at the higher temperature. The estimated initial rates of reaction are shown in Table V. They yielded an activation energy of 18 kcal./mole. However, a graphical comparison of the rates after five minutes indicated zero energy of activation which was further evidence for variation in the ease of carbon removal, *i. e.*, heterogeneity of the surface. These reactions with hydrogen were always left overnight and check experiments over a second night showed no further change in pressure.

TABLE V

REMOVAL OF CARBON BY HYDROGEN

Expt.	Temp., °C.	Initial pressure, cm.	Initial rate of reaction, cm./min.	
26	181.8	10.4	0.50	0.50
28	182.1	7.7	.67	
30	182.2	4.4	.32	
32	192.5	8.7	.87	0.76
34	192.0	10.2	.59	
36	192.0	11.5	.93	
38	191.7	10.5	.67	

Decomposition of Ethylene.—For reasons which will emerge from the subsequent discussion it was decided to study the formation of methane from pure ethylene. Preliminary experiments indicated that some methane was formed from ethylene, but that a similar amount of ethane would give more methane; the time of these experiments was either thirty or sixty minutes. Analysis with the mass spectrometer showed that the ethylene was converted to saturated hydrocarbons, probably quantitatively. It was difficult to detect traces of ethylene because the "28 peak" of ethane was large. However, by examination of the ratio "28 peak"/"30 peak" it was possible to show that there was little ethylene remaining. The carbon deposited in the early stages of the reaction of ethylene

$$3C_2H_4 \longrightarrow 2C_2H_6 + 2C$$
$$C_2H_4 \longrightarrow CH_4 + C$$

had a considerable poisoning action. Thus, the ethane formed would not decompose to methane nearly as rapidly as in the reactions described in a previous section. Once again the carbon was readily removable by hydrogenation to form methane. It became clear that if there was to be a fair comparison between the reactions with the two gases, the reaction time would have to be short. With longer times, the less poisoned surface under the ethane would lead to a greater yield of methane. The rapid formation of ethane from ethylene might have been accelerated by the hydrogen present on the surface (the surface was not normally pumped out above the reaction temperature and therefore was partially covered with hydrogen). An attempt was made to run some reactions on the catalyst relatively free from hydrogen. Before each of the six reactions in Table VI and Fig. 7 the catalyst was decarbonized overnight with hydrogen and then evacuated for two hours at 425° to remove the majority of the adsorbed hydrogen. The ratio "28 peak"/"30 peak" appeared to vary from day to day for ethane; part of this variation may have been due to the presence of differing amounts of methane. However, it will be observed that, in all three cases, the ratio, "28 peak"/"30 peak," is less for the mixture from ethylene than for the corresponding mixture from ethane. It was therefore most unlikely that there was any unchanged ethylene in the final product. Figure 7 shows clearly how the initial production of methane is faster from ethylene than from ethane. The slight induction period was presumably due to the time taken for the gas to come to reaction temperature and to permeate the catalyst. The greater poisoning of the surface with ethylene is also clear.

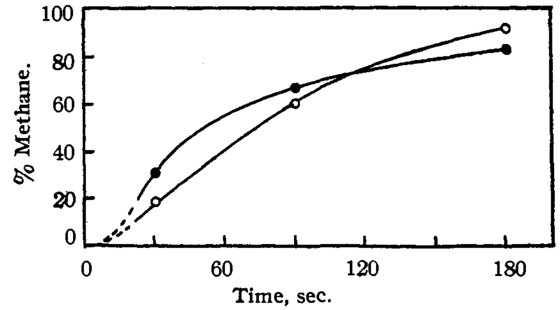

Fig. 7.—The formation of methane from ethane or ethylene: ○, ethane; ●, ethylene.

Interpretation of the Experimental Results

It is assumed that the breaking of the carbon–carbon bond is the slow reaction. In support of this there is the evidence of Morikawa, Benedict and Taylor that the ethane and deuterium exchange reaction proceeds at a temperature of 120°. They also reported 28 and 19 kcal./mole as the energies of activation for the methane exchange and the propane exchange. Thus, the carbon–hydrogen bond is easily broken and reformed and the large energy of activation in the decomposition reaction must be related to the breaking of the carbon–carbon bond. The experiments described in the preceding sections indicate that the equilibrium between methane, adsorbed methyl and methylene groups, etc., on the surface is quickly established. It is unlikely that a van der Waals adsorbed ethane will be sufficiently perturbed by the surface to lead to splitting of the C–C bond. It is possible that an adsorbed ethyl radical might dissociate into a methyl and a methylene group. However, it is more probable that the molecule has to be attacked at both ends, *i. e.*, as an adsorbed ethylene before dissociation can occur. If it is assumed that there will be an equilibrium established between the various species—van der Waals adsorbed ethane, chemically adsorbed ethyls, ethylenes and hydrogen—it is possible to use the device introduced by Temkin and Pyzhev[5] in the ammonia decomposition, namely, the use of a virtual equilibrium pressure.

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(5) Temkin and Pyzhev, *Acta Physicochimica URSS*, **12**, 327 (1940).

$$\begin{tikzcd}
C_2H_6 \arrow[r, shift left, "\text{Virtual}"] \arrow[d, shift left] & C_2H_4 \arrow[l, shift left] \arrow[d, shift right, "\text{Virtual}"'] + H_2 \arrow[d, shift right] \\
C_2H_{5ads} + H_{ads} \arrow[u, shift left, "\text{Established}"] \arrow[r, shift left] & C_2H_{4ads} \arrow[u, shift right] + 2H_{ads} \arrow[u, shift right, "\text{Established}"'] \arrow[l, shift left, "\text{Established}"]
\end{tikzcd}$$

If $P^*_{C_2H_4}$ is the pressure of ethylene that would fulfil the gas phase equilibrium, then it would also be in equilibrium with the adsorbed ethylene. Let $\sigma_{C_2H_4}$ be the fraction of the surface covered by ethylene and let A be the fraction of the surface bare. Then

$$p^*_{C_2H_4}A = k_1\sigma_{C_2H_4}$$

Making an assumption similar to that of Temkin and Pyzhev, we write

$$p^*_{C_2H_4} = K\frac{p_{C_2H_6}}{p_{H_2}}$$

It is not possible to express A accurately in terms of the pressures of the gases. However, ignoring the dissociation of the ethane and the hydrogen and using Langmuirian equations of the type

$$p_{H_2}A = k_3\sigma_{H_2}$$
$$p_{C_2H_6}A = k_4\sigma_{C_2H_6}$$

then

$$A = \frac{1}{1 + ap_{C_2H_6} + bp_{H_2}}$$

Hence the rate of reaction, which is assumed proportional to $\sigma_{C_2H_4}$ but not fast enough to interfere with the equilibrium discussed above, is given by

$$\text{Rate} = \frac{kp_{C_2H_6}}{p_{H_2}\,(1 + ap_{C_2H_6} + bp_{H_2})}$$

This means that the rate will depend on some power slightly less than unity, of the ethane, and on some negative power of the hydrogen, slightly greater than unity. This is in good agreement with the observed ${p_{C_2H_6}}^{0.7}{p_{H_2}}^{-1.2}$.

In the decomposition of ethane alone the following equations will hold

$$p_{C_2H_6}(1 - \sigma_{C_2H_5} - \sigma_{C_2H_4} - \sigma_H) = k_1\sigma_{C_2H_6}\sigma_H$$
$$\sigma_{C_2H_4}\sigma_H = k_2\sigma_{C_4H_5}$$

Now there is evidence which will be discussed below to indicate that the surface is well covered with hydrogen and if it is assumed that σ_H is a constant it is possible to show that

$$\sigma_{C_2H_4} = k'p_{C_2H_6}/(1 + k''p_{C_2H_6})$$

which again would account for the rate of the decomposition being dependent on a fractional power of the ethane. It was in order to confirm the mechanism proposed, namely, the formation of methane through the breaking of the C–C bond in adsorbed ethylene that the reactions with ethylene were carried out.

The experiments with ethylene supported the possibility that the mechanism of the ethane–hydrogen and ethane decompositions involved adsorbed ethylene. It will be seen that the rates of reaction with a carefully cleaned surface, experiments 70, 78 and 80 were much faster than the decomposition rates on the "usual" surface, *i. e.*, experiments 27, 29 and 31. This was evidence that the "usual" surface, which was prepared by evacuation of the hydrogen and other gases at 182°, was greatly covered with hydrogen. This had two important results. First, it proved that the surface was definitely heterogeneous with respect to hydrogen adsorption, because the hydrogen could not all be removed by the standard evacuation at 182°. Consequently it is reasonable to suggest that the increase in the rate of reaction with ethane–hydrogen mixtures of low hydrogen content, described as "abnormal kinetics," was due to the uncovering of fresh areas of the surface as the hydrogen pressure was decreased. Second, the fact that the rate was so much faster on a clean surface provided justification for considering σ_H as a fixed quantity when examining the kinetics of the ethane decomposition by itself.

TABLE VI

THE PRODUCTION OF METHANE FROM ETHYLENE AND ETHANE

Expt.	Substance	Pressure, cm.	Temp., °C.	Time. sec.	"16 peak" "30 peak"	"28 peak" "30 peak"	Methane, %
68	C_2H_4	0.87	181.9	90	3.09	3.78	67.0
70	C_2H_6	1.06	182.0	90	2.26	3.85	59.7
76	C_2H_4	1.05	181.0	30	0.663	4.04	30.3
78	C_2H_6	1.12	182.0	30	0.333	4.15	17.9
80	C_2H_6	1.10	181.0	180	17.3	3.98	91.9
82	C_2H_4	1.14	182.1	180	7.82	3.85	83.7

It would be interesting to extend the work of Morikawa in following the decomposition of propane with greater pressures of hydrogen to see if normal kinetics were obtained in that case. Morikawa, Trenner and Taylor reported a rate dependent on ${p_{C_3H_8}}^{0.92}$ ${p_{H_2}}^{-2.6}$ but this might turn over to a more normal expression with higher percentages of hydrogen present. If the mechanism was comparable to the present reaction, experiments with propylene would prove interesting.

The energy of activation found in the present work was 52 kcal./mole for the ethane–hydrogen reaction, which is slightly larger than the 43 kcal./mole given by Morikawa. The difference may be due to the region of composition in which the earlier work was done. As expected, the value for ethane decomposition in the absence of hydrogen was lower, being 40 kcal./mole. The decrease of 12 kcal./mole is reasonable when associated with a factor of ${p_{H_2}}^{-1.2}$.

It must be emphasized that little was known about the state of the catalyst except that its behavior was reproducible. It was certainly not yielding its maximum activity as shown by the later experiments with ethane and ethylene. The same sample of catalyst was used throughout and the reproducibility of the results is well illustrated in Table I where the experiments fall into three groups. The last group was carried out after the end of the ethane decomposition reactions and showed no loss in activity. A large fraction of the surface must have been permanently covered with hydrogen except in the last few experiments in which a carefully cleaned surface was used.

It would be interesting to try experiments with acetylene, to see whether it decomposed more readily than ethylene. It may well be that the breaking of the C–C bond would proceed through adsorbed ethylene rather than adsorbed acetylene. For, unless the latter was attached to four nickel atoms simultaneously there would be some double bond character in the C–C bond which should make it more difficult to break.

Acknowledgment.—One of us (C. K.) wishes to express his thanks to the Commonwealth Fund for the generous Fellowship which made this work possible.

Summary

1. The mass spectrometer can be used to follow the reaction of ethane and hydrogen producing methane using the ratio of the "16 peak" to the "30 peak."

2. The ethane–hydrogen decomposition on a supported nickel catalyst obeys the expression Rate = $kp_{C_2H_6}^{0.7}p_{H_2}^{-1.2}$ over a wide range of composition with an energy of activation of 52 kcal./mole.

3. At low ratios of hydrogen/ethane, abnormal kinetics, depending on a high inverse power of the hydrogen pressure, set in. This is ascribed to heterogeneity of the surface.

4. Ethane will decompose quantitatively over this catalyst to methane and carbon with a rate dependent on $p_{C_2H_6}^{0.7}$ and an energy of activation of 40 kcal./mole.

5. The carbon is reversibly deposited and can be converted to methane by hydrogen.

6. The rate-determining step of methane formation must be the breaking of the carbon–carbon bond. Both the ethane–hydrogen and the ethane decompositions can be interpreted by a mechanism involving the presence on the surface of adsorbed ethylene, in equilibrium with adsorbed ethyl radicals and hydrogen. This mechanism was supported directly by showing that the initial rate of production of methane is greater from ethylene than from ethane.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF SARAH LAWRENCE COLLEGE]

Vapor Pressure of Isobutene over Dioxane as Basis of Manometric Kinetic Studies. The Dissociation of *t*-Butyl Benzoate

BY ROLF ALTSCHUL AND JOANNE HERBERT

This paper has as its primary objective the presentation of an improved method for kinetic measurements of liquid-phase reactions involving isobutene. Such an investigation was relevant to our present effort to expand a previous preliminary study of acid-catalyzed dissociations of tertiary esters.[1] In order to expedite this general project we tested a different analytical procedure, which, with equal accuracy, was to afford identical results with greater facility.

Vapor pressure measurements by a static method served as a basis for this alternate analysis. Two separate problems were involved to adapt this generally useful method to our particular needs: (a) A calibration to establish the vapor pressure of dioxane solutions as a function of their isobutene content. A constant and small amount of sulfuric acid (0.835 mole/liter), necessary to catalyze the subsequent kinetic runs, was included with these standardizations. (b) Application of these data to the reversible dissociation of *t*-butyl benzoate into benzoic acid and isobutene.[1] These manometric rate constants were then matched against parallel experiments resorting to acidimetric analysis by the orthodox procedure.

Since strong mechanical agitation was a prerequisite, a thermostated Van Slyke instrument appeared most opportune for this study.

Experimental

Materials.—Benzoic acid, *t*-butyl benzoate, isobutene, dioxane,[2] and 100% sulfuric acid were prepared, purified, and stored as before.[1] All gave the previous physical constants.

Manometric Determinations.—A Van Slyke instrument was equipped with a thermostated chamber which was maintained at 25 ± 0.05° by means of rapid circulation of water from a constant temperature bath. The detailed directions for this instrument were adapted from manometric analysis of insoluble gases[3] to our problem of measuring saturation pressures of soluble vapor. The optimum procedure described below was checked against pure dioxane, for which the vapor pressure at 25° has been accurately determined.[4] For our description we have adopted the terminology used by Peters and Van Slyke in their detailed outline.[5]

(a) **Calibration.**—Five cc. of 1.670 molar anhydrous sulfuric acid in dioxane is placed in the cup above the chamber, and, with the 3-way cock open and the mercury in the leveling bulb at slight negative pressure, the solution is drawn slowly into the chamber by careful opening and closing of the 4-mm. connecting stopcock. This is followed by the introduction of 5 cc. of an isobutene solu-

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[1] Altschul, THIS JOURNAL, **68**, 2605 (1946).

[2] The solvent was purified by Mr. Jon J. Sugrue.

[3] Peters and Van Slyke. "Quantitative Clinical Chemistry," Volume II, The Williams and Wilkins Company. Baltimore, Md.. 1932, Chapters 1, 3, 7.

[4] p_d = 3.55 cm.: Teague and Felsing. THIS JOURNAL, **65**, 485 (1943).

[5] See ref. 3, pp. 267–280. Figure 37 on p. 272 will be especially relevant to the following discussion. Descriptions of the manometric Van Slyke instrument have also been published in the literature: Van Slyke and co-workers, *J. Biol. Chem.*, **61**, 523 (1924); **73**. 121 (1927).