

concluded that the rate-determining step involves the displacement or the rupture of the Ge-X bond since the observed rates of hydrolysis vary indirectly with the strength of the Ge-X bond.

It was also found that  $(C_6H_5)_3GeF$  reacted faster than  $(p-CH_3C_6H_4)_3GeF$ . Since the addition of a methyl group in the *para* position would not be expected to exert any steric influence it is concluded that the rate retardation is due to the effect of the more electron-releasing *p*-tolyl group on the transition state in the rate-determining step.

**D. Solvent Effect.**—Two variables were especially considered so far as the solvent was concerned: (a) water was diluted with two organic solvents of widely differing dielectric constants, acetone and *p*-dioxane, and (b) the organic solvent was mixed with varying percentages of water.

The ionizing power of the reaction media used in this investigation has been evaluated<sup>21</sup> for the hydrolysis of *t*-butyl chloride. The ionizing power of a solvent is defined as the log of the rate of solvolysis in that particular solvent relative to the rate of solvolysis in 80% aqueous ethanol. The ionizing power of aqueous acetone is only slightly greater than that for aqueous dioxane at the same concentration even though the dielectric properties of the comparable mixtures differ widely. For example, at 20 volume % water the dielectric constant for the acetone solution is 32 while that of the dioxane solution is only 11. The ionizing power of the reaction medium obviously depends more on the water content than on the dielectric constant.

TABLE III

EFFECT OF EXTRANEIOUS SALTS ON RATE OF HYDROLYSIS

Salt added	Halide			
	$(C_6H_5)_3GeBr$	$(C_6H_5)_3GeCl$	$(C_6H_5)_3GeF$	$(p-CH_3C_6H_4)_3GeF$
Br <sup>-</sup>	Decrease (A)	Increase (B)	Increase (B)	Increase (B)
Cl <sup>-</sup>	Decrease (C)	Decrease (A)	Increase (B)	Increase (B)
F <sup>-</sup>	.....	.....	Decrease (A)	Increase (A)
ClO <sub>4</sub> <sup>-</sup>	Decrease (C)	Decrease (C)	.....	.....

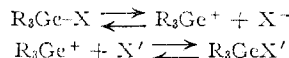
That the experimental rates of hydrolysis vary with the reaction medium leads to the following conclusions; (a) the transition state of the rate-determining step involves an increase in the magnitude of charges relative to the reactant and (b) the transition state does not involve the distribution of a given charge, or a decrease in charge relative to the reactant. Either S<sub>N</sub>1 or S<sub>N</sub>2 is consistent with the observed solvent effect.

(21) E. Grunwald and S. Winstein, *THIS JOURNAL*, **70**, 846 (1948).

**E. Effect of Foreign Salts.**—The effect of the presence of extraneous salts on the rate of hydrolysis is summarized qualitatively in Table III.

In Table III the letter (A) denotes the fact that the salt effects are attributed to the common-ion effect, (B) the ionic strength effect, and (C) to "compound-formation."

Compound-formation is equivalent to the reverse of ionization. Rate retardation would be observed if the ionization of the Ge-X bond led to the formation of the Ge-X' bond, where the rate of substitution of Ge-X is faster than that of Ge-X', thus



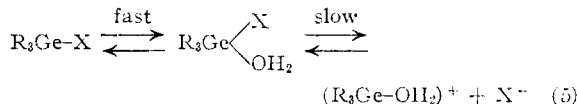
The fact that the observed salt effects do occur is sufficient to establish a unimolecular mechanism, S<sub>N</sub>1.

**F. Probable Mechanism.**—From an interpretation of the experimental results it is possible to eliminate all but one of the five reasonable mechanisms of substitution previously suggested. In each of the other four mechanisms there is some aspect which is not consistent with the conclusions cited.

It has been established that substitution occurs by a unimolecular S<sub>N</sub>1 type of mechanism. The data effectively eliminate mechanisms 2, 3 and 4. It is necessary then to decide between mechanisms 1 and 5.

Mechanism 1 does not explain the effect of changing the nature of the organic group attached to the germanium atom. As previously described, the ionization of the Ge-X bond is favored by electron-release by the organic group to the germanium atom. If mechanism 1 were valid,  $(p-CH_3C_6H_4)_3GeF$  should hydrolyze faster than  $(C_6H_5)_3GeF$  since the *p*-tolyl group is more electron-releasing than the phenyl group. This prediction is contrary to observation.

Mechanism 5 can account for the polar effect of the organic group. In the transition state in the reaction



the germanium atom is less positive, possibly even negative, relative to the germanium atom in the reactant. The reaction would therefore be inhibited by electron-release to the germanium atom of the reactant. Therefore only mechanism 5 is consistent with all of the experimental observations.

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[CONTRIBUTION FROM THE GIBBS CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## Reactions of Methylene. III. Addition to Carbon Monoxide

BY THÉRÈSE BREMER WILSON AND G. B. KISTIAKOWSKY

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Methylene generated photochemically from ketene reacts with carbon monoxide to re-form ketene. This reaction was studied by determining yields of  $CH_2C^{13}O$  when labeled  $C^{13}O$  was added, and, independently, by observing the effect of carbon monoxide on the rate of pressure change in irradiated ketene. It is shown to be an association reaction. The ratio of the rates of decomposition and of deactivation of the initially formed energy-rich ketene molecules is 10.5 mm., when the third body is ketene. With the third body efficiency of ketene taken as unity, the deactivation efficiencies of sulfur hexafluoride and nitrogen are found to be 0.8 and of the order of 0.1, respectively. The ratio of rate constants of the reactions of methylene with carbon monoxide and with ketene is found equal to 2.7 by the isotopic measurements and 1.25 by the pressure measurements. The discrepancy between these two values is attributed to the different methods of calculation used and to the assumed mechanism of the reaction of methylene with ketene. Sulfur hexafluoride is found to decrease the rate of pressure change in irradiated ketene.

### Introduction

Previous experiments<sup>1</sup> have shown that when ketene is photolyzed in the presence of carbon monoxide ( $C^{13}O$ ), some labeled ketene  $CH_2C^{13}O$  is formed; this re-formation of ketene was inter-

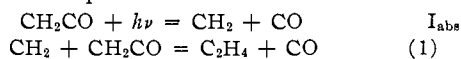
preted as an association reaction of methylene radicals with  $CO$ , corresponding to the over-all equation  $CH_2 + CO = CH_2CO$ . According to Staudinger and Kupfer,<sup>2</sup> ketene is similarly formed when diazomethane is decomposed in the presence of  $CO$ .

(1) G. B. Kistiakowsky and W. L. Marshall, *THIS JOURNAL*, **74**, 88 (1952).

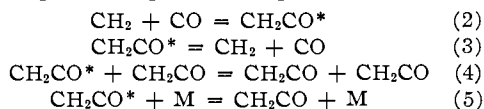
(2) H. Staudinger and O. Kupfer, *Ber.*, **45**, 508 (1912).

The present study was undertaken primarily to confirm the association character of this reaction with CO, as opposed to a possible metathetical process involving some activated ketene molecule or some intermediary radical larger than CH<sub>2</sub>. The pressure dependence of the re-formation of ketene does indeed permit a decision between these two alternatives.

While quite complex in detail,<sup>3</sup> the photolysis of ketene may be represented, in the first approximation,<sup>4</sup> by the steps



If the reaction with CO is an association process involving CH<sub>2</sub>, reactions 2 to 5, where M is an inert gas, would predict a pressure dependence.



Since the activated ketene CH<sub>2</sub>CO\* very likely has a short dissociative lifetime, much shorter than the intermediates<sup>3</sup> possibly formed in reaction 1, inert gases will alter the ratio of the two competing reactions of methylene (1) and (2). But if no methylene were involved, an inert gas would not be expected to have such an effect.

Two different methods were used to verify the essential correctness of the mechanism 1 to 5 and to estimate the ratio of rate constants  $k_1/k_2$ ,  $k_4/k_5$  with SF<sub>6</sub> and N<sub>2</sub> as inert gases, and especially  $k_3/k_4$  which controls the competition between the monomolecular decomposition of the activated CH<sub>2</sub>CO\* and its bimolecular stabilization. In the first method labeled C<sup>13</sup>O was used and the yields of CH<sub>2</sub>C<sup>13</sup>O determined. In the second method, measurements were made of the effect of CO on reducing the rate of pressure increase which accompanies the decomposition of ketene. A comparison of the results obtained by these two techniques provides additional information on the details of these reactions of methylene.

### Experimental

Experiments were made in an all-glass system with good pumping. The cylindrical quartz reaction cell, 130 × 28 mm., was surrounded with a quartz jacket for water circulation, the temperature of which was read but not regulated. Gaseous mixtures were prepared by measuring partial pressures in a separate bulb; they were carefully mixed and then introduced into the reaction cell. To avoid complications caused by mercury vapor, a quartz spiral manometer with photoelectric amplification<sup>5</sup> was used throughout for pressure measurements; its readings were accurate to 0.01 mm.

For irradiation the unfiltered light from a General Electric Uviarc "UA-3" quartz mercury arc was used. The lamp and the reaction cell were enclosed in a cylindrical reflector, a movable shutter being provided to shield the cell. The lamp was allowed to come to a steady state and the cell was then irradiated for 60 seconds. The lamp was switched off and the pressure in the cell, as well as the water jacket temperature, were read again, adequate time being allowed for thermal equilibration.

The intensity of the lamp was controlled by a RCA-935 photocell and kept to a constant value. After several experi-

ments a thin coating opaque to radiation absorbed by ketene, developed on the walls of the reaction cell. Filling the cell to 600 mm. with oxygen, irradiation for one hour and evacuation removed it effectively.

Making allowance for the spectral energy distribution of the lamp, as given by the manufacturer, the absorption spectrum of ketene<sup>6</sup> and the quantum yield of its decomposition,<sup>4</sup> it can be estimated that the reaction was mainly caused by the 2700–3100 Å. spectral region.

In experiments with concentrated C<sup>13</sup>O, the ratios  $\alpha_f = \text{CH}_2\text{C}^{13}\text{O}/\text{CH}_2\text{C}^{12}\text{O}$  and  $\beta_f = \text{C}^{13}\text{O}/\text{C}^{12}\text{O}$ , in the ketene and the carbon monoxide present at the end of the reaction, were measured with a Consolidated-Nier "Isotope Ratio" 21-101 mass spectrometer. In order to avoid dealing with ketene itself in the mass spectrometer, the determination of  $\alpha_f$  was done on the isolated CO group of the ketene molecule, in the following way. At the end of a photolysis run, the products of the reaction were pumped through a liquid nitrogen cooled trap and the non-condensable fraction, composed mainly of the initial unreacted carbon monoxide and of the carbon monoxide produced by the decomposition of ketene, was collected in a bulb for determination of the ratio  $\beta_f$ . The condensable fraction, containing mainly ketene, ethylene, sulfur hexafluoride, etc., was exposed to radiation of an auxiliary mercury arc until there was no further pressure increase; the products of this decomposition of the residual ketene were then separated as before and the non-condensable fraction, *i.e.*, carbon monoxide, collected for measurement of the ratio  $\alpha_f$ . For each sample, not only the ratio of the mass peaks 28 and 29 but the entire spectrum was observed, to guard against impurities. The technique used resulted in very clean mass spectra, requiring only small corrections on the desired ratios.

Ketene was prepared by the hot wire pyrolysis of acetic anhydride and purified by bulb-to-bulb fractional distillation; it was stored at liquid nitrogen temperature.

Sulfur hexafluoride (Matheson c.p. grade) was dried and the middle fraction isolated by bulb-to-bulb distillation. The mass spectrum<sup>7</sup> showed it to be pure.

Concentrated C<sup>13</sup>O was prepared from barium carbonate (Eastman Kodak, 53.7 atom % C<sup>13</sup>), by reducing CO<sub>2</sub> over zinc at 385°<sup>8</sup> and purifying by passage through a liquid nitrogen cooled trap.

Cylinder dry nitrogen was used after passage over hot copper.

### Results

(a) **Isotopic Measurements.**—In a few preliminary experiments with labeled carbon monoxide, only the isotopic composition of the residual ketene,  $\alpha_f$ , was determined. These experiments demonstrated that when the CO/CH<sub>2</sub>CO ratio was held constant but the total pressure was increased, there was a distinct increase in the C<sup>13</sup>/C<sup>12</sup> ratio of the final ketene. A similar increase in the amount of ketene reformed was obtained by addition of sulfur hexafluoride to mixtures of constant partial pressures of ketene and carbon monoxide; this is shown in Table I which presents the data on the final experiments in which both the carbon monoxide and the ketene were analyzed at the end of each run. The quantities  $\alpha_0$ ,  $\alpha_f$ , and  $\beta_0$ ,  $\beta_f$  are the initial and the final C<sup>13</sup>/C<sup>12</sup> ratios in ketene and in carbon monoxide, respectively. In all these runs, the ratios of the partial pressures of carbon monoxide and ketene were initially equal to about two.

By applying stoichiometry, assuming that there is no isotopic fractionation and assuming that carbonyl groups are conserved, *i.e.*, that no by-products containing carbonyl groups are formed, the partial pressures of ketene and carbon monoxide

(3) G. B. Kistiakowsky and K. Sauer, *THIS JOURNAL*, **80**, 1066 (1958).

(4) A. N. Strachan and W. A. Noyes, Jr., *ibid.*, **76**, 3258 (1954).

(5) G. B. Kistiakowsky and J. C. Sternberg, *J. Chem. Phys.*, **21**, 2218 (1953).

(6) K. Knox, R. G. W. Norrish and G. Porter, *J. Chem. Soc.*, 1447 (1952).

(7) V. H. Dibeler and F. L. Mohler, *J. Research Natl. Bur. Standards*, **40**, 25 (1948).

(8) J. L. Huston and T. H. Norris, *THIS JOURNAL*, **70**, 1968 (1948).

TABLE I  
ISOTOPIC STUDY OF THE REACTION OF METHYLENE WITH CARBON MONOXIDE  
 $\alpha_0 = 0.0115$ ;  $\beta_0 = 1.135$ ; pressures in mm.;  $t = 6.4$  to  $9.0^\circ$

CH <sub>2</sub> CO		CO		SF <sub>6</sub>	$\alpha_f$	$\beta_f$	$\Delta P$	Ketene reformed $\Delta K$	Ketene dec. $\Delta CO$	$\frac{\Delta CH_2CO}{\Delta P}$
$P_0$	$P$	$P_0$	$P_f$	$P$						
7.46	5.35	15.13	17.24		0.0527	0.838	0.863	0.432	2.542	2.48
7.29	5.65	14.53	16.17	17.0	.0603	.863	.682	.530	2.170	2.41
7.68	5.94	15.23	16.97	37.0	.0651	.861	.592	.612	2.352	2.94
7.42	5.82	14.62	16.22	70.0	.0672	.858	.570	.621	2.221	2.81
4.98	3.28	10.13	11.83		.0512	.806	.653	.258	1.958	2.60
5.10	3.90	10.12	11.32	25.3	.0648	.850	.435	.401	1.601	2.76
Av.										2.66

after irradiation ( $P_f$ ) were calculated from two equations: the first expressing the conservation through the reaction of the total number of CO groups present in the ketene and in the carbon monoxide, the second the conservation of the C<sup>13</sup>O groups.

By considering the final ketene ( $P_f$ ) to be made up of the ketene re-formed ( $\Delta K$ ) and the unreacted ketene, similar stoichiometric arguments, applied to the partial pressures of labeled carbonyl groups in the final ketene, gave the quantity  $\Delta K$ ; the additional assumption was made that the isotopic composition of the carbon monoxide recombining with CH<sub>2</sub> was the average of  $\beta_0$  and  $\beta_f$ .

Finally, the quantity ( $\Delta CO$ ) of ketene decomposed photochemically into carbon monoxide and other products was calculated from the equation  $\Delta CO = (P_0 - P_f)_{CH_2CO} + \Delta K$ . Only the assumption of the conservation of the carbonyl groups for isotopic measurements, as made here, may introduce significant errors in these calculations (see below); but no alternative hypothesis appeared better.

The increase of pressure  $\Delta P$  during the reaction was also measured, for each of these runs; the last column of Table I gives the ratio of the net decomposition of ketene ( $\Delta CH_2CO = P_0 - P_f$ ) to the observed  $\Delta P$ , with an average value of 2.6. Were the reaction quantitatively  $2CH_2CO = C_2H_4 + 2CO$  this ratio would be 2.

If the complexities of the reaction of methylene with ketene are neglected, a kinetic expression can be obtained for the ratio  $\Delta CO/\Delta K$  on the basis of reactions (1) to (5), by applying the steady-state assumption to CH<sub>2</sub> and the energy-rich complex CH<sub>2</sub>CO\* and treating the data of Table I as differential rates.

$$\frac{\Delta CO}{\Delta K} = \frac{2k_1k_3(CH_2CO)}{k_2k_4(CO) [(CH_2CO) + (k_5/k_4)(M)]} + \frac{2k_1(CH_2CO)}{k_2(CO)} + 1 \quad (6)$$

The ratio  $(CH_2CO)/(CO)$  being essentially the same in all experiments of Table I, a plot of  $\Delta CO/\Delta K$  against

$$\frac{(CH_2CO)}{(CO) [(CH_2CO) + (k_5/k_4)(M)]}$$

should give a straight line.

By trial and error the best value of  $k_5/k_4$ , the ratio of efficiencies of SF<sub>6</sub> and ketene in deactivating the "hot" ketene molecule, was found to be 0.8. This ratio can be varied over a 20% range without materially affecting the fit of the experimental

points to the straight line. The resulting plot using the average pressures of ketene and CO in each run is shown in Figure 1. The intercept and the slope of the line give  $k_1/k_2 = 2.7$  and  $k_3/k_4 = 9$  mm.

(b) **Pressure Measurements.**—Numerous experiments were made in which the rate of total pressure change under illumination of a mixture of ketene and carbon monoxide, with or without an inert gas, was compared with the rate of pressure change of pure ketene at the same partial pressure.

From the same reaction mechanism (1) to (5) and the same steady-state assumption as before, a kinetic expression can be derived for the ratio  $r$  of the initial rates of pressure change in mixtures of ketene and carbon monoxide and in pure ketene.

$$\frac{(CO)r}{(CH_2CO)(1-r)} = \frac{k_1k_3}{k_2k_4[(CH_2CO) + (k_5/k_4)(M)]} + \frac{k_1}{k_2} \quad (7)$$

Table II presents the results of runs with mixtures of ketene and carbon monoxide,  $\Delta P$  being the pressure change after 60 seconds of irradiation. For each experiment is given also the value of  $\Delta P_a$ , the pressure change in absence of carbon monoxide but otherwise under identical conditions. The values of  $\Delta P_a$  were interpolated from plots of  $\Delta P_a$  against the initial pressure of ketene<sup>9</sup>; experiments with and without carbon monoxide were intermingled to avoid systematic errors.

In the runs with pure ketene, which were carried out to an appreciable amount of decomposition, the formation of propylene by reaction of methylene with ethylene formed in reaction (1) cannot be neglected. The occurrence of this reaction was not considered in establishing equation 7. Therefore, in order to calculate the value of  $r$ , a small correction was applied to the observed  $\Delta P_a$  to compensate for the reaction of ethylene. This correction, which increased the  $\Delta P_a$  by 10% in the worst case, was calculated by using 2.5 as the ratio of the rates of reaction of methylene with ethylene and with ketene.<sup>10</sup> It was assumed on the other hand that the formation of propylene can be disregarded in the runs with carbon monoxide at a pressure at least equal to the pressure of ketene.

The quantity of ketene decomposed in each run was assumed equal to  $2.6\Delta P$  or  $2.6(\text{cor. } \Delta P_a)$ , in accordance with the last column of Table I. The

(9) These plots indicate that  $\Delta P_a/P$  decreases with rising pressure of ketene.

(10) G. B. Kistiakowsky and N. W. Rosenberg, *THIS JOURNAL*, **72**, 321 (1950).

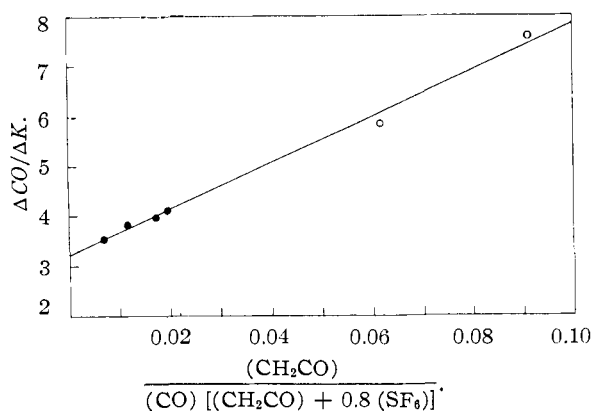


Fig. 1.—A plot of the results of experiments with isotopically enriched carbon monoxide: open circles, carbon monoxide and ketene alone; solid circles, with added sulfur hexafluoride.

initial values of  $r$  were then calculated from these depletions of ketene, by using a first-order rate equation. The data of Table II are plotted in Fig. 2 in terms of equation 7.

TABLE II

RATES OF PRESSURE CHANGE IN IRRADIATED MIXTURES OF KETENE AND CARBON MONOXIDE AND MIXTURES OF KETENE, CARBON MONOXIDE AND SULFUR HEXAFLUORIDE  
Pressures in mm.

Temp., °C.	CH <sub>2</sub> CO P <sub>0</sub>	CO P <sub>0</sub>	SF <sub>6</sub> P	ΔP	ΔP <sub>a</sub>	r
3.9	31.2	35.7		2.55	3.95	0.59
15.9	25.1	33.4		1.89	2.79	.63
17.8	23.1	24.8		1.99	2.63	.70
4.4	20.9	23.9		2.01	2.89	.63
4.0	18.05	45.3		1.20	2.52	.40
15.9	16.57	22.1		1.35	2.01	.61
4.0	14.03	16.1		1.50	2.10	.62
4.2	11.95	30.0		0.88	1.83	.39
16.0	11.09	14.8		1.09	1.49	.66
4.5	9.30	10.6		1.15	1.42	.71
8.5	7.46	15.1		0.86	1.21	.60
4.0	6.07	6.9		.96	1.07	.78
9.0	4.98	10.1		.65	0.88	.62
4.5	4.03	4.6		.71	0.75	.82
6.4	7.68	15.3	37.0	.59	1.08	.45
6.7	7.42	14.6	70.0	.57	1.01	.47
6.5	7.29	14.6	17.0	.68	1.14	.49
6.9	5.10	10.1	25.3	.43	0.84	.48

TABLE III

EFFECT OF SULFUR HEXAFLUORIDE ON THE RATE OF PRESSURE CHANGE IN IRRADIATED KETENE  
Pressures in mm.;  $t = 10.1$  to  $11.0^\circ$

CH <sub>2</sub> CO P <sub>0</sub>	SF <sub>6</sub> P	ΔP	ΔP <sub>a</sub>	R
23.40	193	2.27	2.95	0.77
15.55	128	1.59	2.15	.74
13.27	129	1.45	1.91	.76
8.83	85	1.08	1.38	.78
5.85	57	0.84	1.01	.83

Table II shows also the effect of sulfur hexafluoride on mixtures of ketene and carbon monoxide. The values of  $r$  were calculated as before and the data corresponding to these experiments are also plotted in Fig. 2, with  $k_5/k_4 = 0.8$  as obtained from

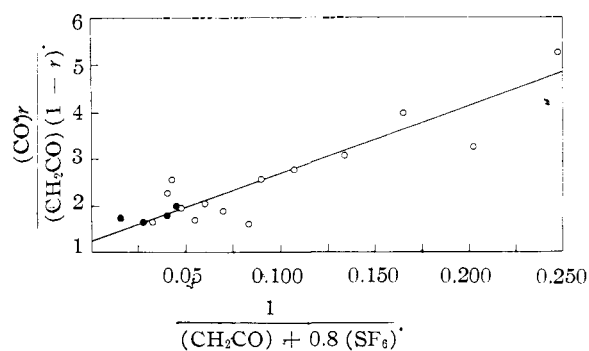


Fig. 2.—A plot of the results of experiments on the rates of pressure changes: open circles, carbon monoxide and ketene alone; solid circles, with added sulfur hexafluoride.

the isotopic measurements. However, a series of runs with mixtures of ketene and sulfur hexafluoride, without carbon monoxide, indicates that sulfur hexafluoride alone has an effect on the rate of pressure change in ketene. The data on these experiments are given in Table III;  $R$  is the ratio of the observed pressure increase in a mixture of ketene and sulfur hexafluoride to the pressure increase in pure ketene at the same partial pressure, without correcting for the formation of propylene. This ratio  $R$ , which averages to 0.77, should be unity, were sulfur hexafluoride truly "inert." Therefore the  $\Delta P_a$  entering in the calculation of  $r$  in Table II were the  $\Delta P_a$  observed in mixtures of sulfur hexafluoride and ketene at the same partial pressures as in the runs with carbon monoxide.

Figure 2 shows that all the results of experiments with mixtures of ketene and carbon monoxide, with or without sulfur hexafluoride, gave a satisfactory straight line when plotted according to equation 7. The following values of the ratios of rate constants were obtained:  $k_1/k_2 = 1.25$  and  $k_3/k_4 = 12$  mm.

Experiments were also made to find out whether nitrogen alone modifies the rate of pressure change of ketene. No effect was observed, the average ratio  $R$  being  $1.03 \pm 0.06$  in ten experiments in which the nitrogen pressure varied from 120 to 250 mm. and that of ketene from 4.3 to 13.8 mm.

Table IV gives the data on experiments performed to determine the effect of nitrogen on mixtures of ketene and carbon monoxide. The values of  $r$  were calculated as for the runs of Table II. The small pressure changes in these experiments were subject to large random scatter due to the high total pressures employed. Therefore, in order to obtain a rough estimate of the ratio  $k_5/k_4$  of the third body efficiencies of nitrogen and ketene, the values of  $(CO)r / [(CH_2CO)(1-r)]$  were calculated from the data of Table IV and equation 7 solved for  $k_5/k_4$ , with  $k_1/k_2 = 1.25$  and  $k_3/k_4 = 12$  mm. as obtained from Fig. 2. The resultant values of  $k_5/k_4$  for nitrogen are shown in the last column of Table IV, their average being 0.1.

### Discussion

The effect of total pressure observed in the present experiments definitively proves that the reaction of carbon monoxide to re-form ketene is an association reaction, therefore involving methylene.

TABLE IV  
RATES OF PRESSURE CHANGE IN IRRADIATED MIXTURES OF  
KETENE, CARBON MONOXIDE AND NITROGEN  
 $t = 7.0$  to  $11.1^\circ$

$\text{CH}_2\text{CO}$ $P_0$	$\text{CO}$ $P_0$	$\text{N}_2$ $P$	$\Delta P$	$\Delta P_a$	$r$	$k_3/k_4$
7.75	19.9	112	0.65	1.16	0.445	0.09
6.65	17.2	262	.64	1.20	.41	.07
5.57	14.85	81	.47	0.87	.425	.21
4.25	10.7	237	.37	.90	.75	.15
3.98	10.25	58	.46	.64	.596	.03
3.79	9.13	302	.40	.63	.47	.04
3.02	7.57	169	.39	.56	.57	.02
2.71	6.54	209	.26	.52	.37	.37
2.69	6.50	214	.26	.50	.39	.22

Av. 0.13

Moreover, the satisfactory straight line fit of the results obtained by two independent methods, according to kinetic equations derived from reactions 1 and 5, shows the essential validity of the simplified mechanism adopted.

Although of little significance for the main purpose of this work, the discrepancy between the results given by the isotopic and by the pressure measurements cannot be disregarded. The ratio  $k_1/k_2$  derived from experiments on the isotopic enrichment of ketene is 2.7, compared with 1.25 from the pressure runs. A large part of this discrepancy is probably due to the difference in the procedures used for converting the results of Table I and II to graphical representation. The data of Table I were treated as differential rates and the average pressures of ketene and carbon monoxide were used, whereas from the data of Table II initial rates were calculated with corrections for the depletion of ketene and for the reaction of methylene with ethylene. It can be estimated that if the data of Table I could be treated by the procedure applied to Table II, the value of  $k_1/k_2$  would decrease to the neighborhood of 2.3. This in turn would raise  $k_3/k_4$  to about 11 mm., in excellent agreement with the results of the pressure change measurements. There still would remain, however, a substantial disagreement between the two values of  $k_1/k_2$ , larger than could be explained by the uncertainty in evaluating the intercept of the line in Fig. 2.

The source of this discrepancy is more fundamental and probably resides in the present insufficient knowledge of the mechanism of photolysis of pure ketene itself; more specifically, in the acceptance of reaction (1) as representing the interaction of methylene with ketene. One aspect of this question is indicated by the results of the last column of Table I, which demonstrates that more ketene is decomposed than would be expected from the pressure changes, if they were interpreted by the stoichiometric equation:  $2\text{CH}_2\text{CO} = \text{C}_2\text{H}_4 + 2\text{CO}$ . This in turn accounts for the consistent observation that even at initial times of reactions, when less than 1% of ketene is decomposed, the ratio of carbon monoxide to ethylene formed is not 2 but 2.2, at pressures of ketene below 100 mm.<sup>4,10,11</sup> The small yields of by-product hydrocarbons<sup>3</sup> which are observed under these conditions are by them-

(11) H. Gesser and E. W. R. Steacie, *Canadian J. Chem.*, **34**, 113 (1956).

selves insufficient to explain the present observation, although they may contribute to the reduced pressure rise by formation of longer hydrocarbon chains than that of ethylene. Contributing also to a small  $\Delta P$  is the formation of the non-volatile deposit on the walls of the reaction cell. If the formal reaction is written  $\text{CH}_2 + 2\text{CH}_2\text{CO} = (\text{CH}_2)_3\text{CO} + \text{CO}$ , the first product being regarded as non-volatile due to subsequent polymerization, it is found that if 10% of all methylene produced photochemically undergoes this reaction instead of giving ethylene, both the 2.2 ratio of carbon monoxide to ethylene and the 2.6 ratio of ketene disappearing to pressure rise are accounted for. Such a reaction could be visualized as involving, for instance, the symmetrical diradical  $\text{CH}_2\text{-CO-CH}_2$  previously suggested.<sup>12</sup> However, while the deposit formed has been shown to contain carbonyl groups,<sup>1</sup> its quantity is decidedly too small to explain these observations quantitatively.

It should be pointed out that the difficulty encountered here in the comparison of the results given by the two methods used is not specifically related to the reaction of methylene with carbon monoxide. A similar discrepancy exists between two sets of measurements of the rate of reaction of methylene with ethylene. Kistiakowsky and Rosenberg<sup>10</sup> found a value of 2.5 for the ratio of the rate constant of this reaction to the reaction of  $\text{CH}_2$  with ketene, by measurement of pressure changes; on the other hand, Holroyd and Noyes<sup>13</sup> found the same ratio to be unity, by studying yields of carbon monoxide, as done here to get the results of Table I. The discrepancy between these two values is quantitatively the same as between the two present measurements of the carbon monoxide reaction. More needs to be known about the reaction of methylene with ketene to be able to explain mechanistically the reasons for this disagreement. But in any case, this does not discredit the interpretation of the reaction with carbon monoxide.

Table III shows that sulfur hexafluoride has a very definite, although small effect on the rate of pressure rise in irradiated ketene. In a previous paper<sup>3</sup> it was shown that the rate of carbon monoxide production is reduced in very nearly the same ratio as the pressure rise (to 0.72 instead of 0.77 presently) and that this reduction seems unaffected by radiation intensity and by the spectral distribution of the absorbed energy. Table III shows, moreover, that the reduction of pressure rise is unaffected by total pressure. These latter findings are arguments against the simplest explanation of the effect of sulfur hexafluoride, the quenching of electronically excited ketene molecules before they decompose into methylene and carbon monoxide. However, the nature of the effect of sulfur hexafluoride remains unknown: a mass spectrometric analysis<sup>3</sup> of a mixture of sulfur hexafluoride and ketene, after irradiation, does not show any peaks which would indicate that a chemical reaction between sulfur hexafluoride and ketene has taken place. Therefore, the experiments with sulfur

(12) G. B. Kistiakowsky and K. Sauer, *THIS JOURNAL*, **78**, 5699 (1956).

(13) R. A. Holroyd and W. A. Noyes, Jr., *ibid.*, **78**, 4831 (1956).

hexafluoride as an added "inert" gas are subject to some question. But however disturbing, the observed effect of this gas on the photolysis of pure ketene itself, being in the opposite direction to the effect it has on the reformation of ketene, does not weaken the interpretation of its acting as a third body by reaction (5).

The ratio  $k_5/k_4 = 0.8$  for the relative efficiencies of sulfur hexafluoride and ketene shows that sulfur hexafluoride is almost as good as a third body as ketene itself.

As nitrogen definitely does not react with methylene, it can be safely considered as an inert gas. The scatter of the individual values of the ratio  $k_5/k_4$  listed in Table IV is very large, but they are all positive, and their average  $k_5/k_4 = 0.1$  demonstrates that nitrogen does increase the rate of the reaction of methylene with carbon monoxide. Its efficiency is however low compared to ketene or sulfur hexafluoride. This finding justifies, *a posteriori* and by analogy, the omission of a third body effect of carbon monoxide in equations 6 and 7.

The average value of the ratio of rate constants

$k_3/k_4$ , given by the two methods used, is 10.5 mm. This value is of the order of magnitude of what could be expected for the association reaction of molecules of the size of  $\text{CH}_2$  and  $\text{CO}$ , but is somewhat smaller than might have been predicted, since it is only about four times larger than the ratio of corresponding rate constants determining the formation of ethane from methyl radicals. Ethane has 17 vibrational degrees of freedom whereas ketene has only 9; yet the value of  $k_3/k_4$  suggests that the lifetime of the activated ketene molecule is only about one-fourth that of the activated ethane.

Finally, it is interesting to note that the rate constants of the reactions of methylene with ketene, with carbon monoxide and with ethylene are of the same order of magnitude.

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## The Pyrolysis of Decaborane<sup>1</sup>

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Rate constants for the homogeneous first-order disappearance of decaborane in vapor phase pyrolysis were obtained over the range 170–238°, and an activation energy of 41.4 kcal. was calculated. Inhibition by hydrogen, but not by other gases was shown. Comparison of the rates for decaborane and deuterio-decaborane indicated that the rupture of B–H or B–D bonds was rate determining. Decaborane was also found to disappear by a rapid polymerization reaction without immediate loss of hydrogen to form an intermediate polymer consisting of decaborane-like units. This was followed by further loss of hydrogen and molecular weight increase with cross-linking to yield non-volatile solid hydrides. No products or intermediates more volatile than decaborane were observed. Evidence for the presence of free radical intermediates and absence of hydrogen atoms was interpreted as indicating an initial split of molecular hydrogen with formation of a diradical intermediate. Hydrogen was found to split out preferentially at the external B–H bonds initially, rather than at the bridged hydrogen positions. The pyrolysis of diiodo-decaborane was shown to yield only hydrogen and non-volatile solid products.

### Introduction

The pyrolysis of decaborane was first described qualitatively by Stock and Pohland,<sup>2</sup> but the kinetics and mechanism of this reaction so far have not been reported. The purpose of this work was to determine the kinetics and mechanism of the initial reaction by which decaborane disappears in vapor phase pyrolysis, and to investigate the nature of the reactions forming the solid, non-volatile boron hydrides, which, with hydrogen, are the sole products of decaborane pyrolysis. Similar non-volatile products also occur during pyrolysis of the lower members of the volatile boron hydrides series, in addition to the principal volatile products.<sup>3–5</sup>

### Experimental

**Apparatus.**—Kinetic measurements and vapor pressure determinations were made in an all glass apparatus which

incorporated a glass manometer diaphragm and pointer such as described by Daniels,<sup>6</sup> sealed in a section of 25 mm. Pyrex tubing, 10–11 inches in length, dividing it into two parts. In the sample chamber (approximately 3 inches in length) decaborane or other material could be sealed *in vacuo*, or in the presence of gases. The balancing chamber was connected through a stopcock to an external mercury manometer system with which pressures in the sample chamber could be measured indirectly by matching pressures so that the pointer would be at a reference position previously determined with both ends of the apparatus open to the atmosphere.

Samples for infrared analysis were prepared in ampoules made from 25 mm. Pyrex tubing with smaller ampoules of 8 mm. tubing attached. Intermediate pyrolysis products could be washed into these smaller ampoules and separated from the unreacted decaborane by repeated sublimation and melting of the decaborane.

Heating, in most cases, was done with a molten salt or wax bath. Where temperature control was not critical, a tubular electric furnace was used. For kinetic measurements, bath temperatures were regulated to  $\pm 0.2^\circ$  with standard thermoregulators.

**Materials. Decaborane.**—Pure decaborane (m.p. 99.7°) was obtained by recrystallizing the crude material resulting from diborane pyrolysis. This purified material was stored in a vacuum desiccator.

(1) Taken from the Ph.D. thesis by John F. Haugh, submitted to the faculty of the University of Delaware, June, 1957.

(2) A. Stock and E. Pohland, *Ber.*, **62B**, 90 (1929).

(3) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(4) H. I. Schlesinger and A. B. Burg, *Chem. Revs.*, **31**, 1 (1942).

(5) F. G. A. Stone, *Quart. Revs.*, **9**, 174 (1955).

(6) F. Daniels, *This Journal*, **50**, 1115 (1928). The diaphragm was similar to type No. 4 in the Figure on p. 1116.