neutral salts or of salts which behave as acids in liquid ammonia.

2. Values for the reaction velocity constant, temperature coefficient, and energy of activation have been calculated.

3. The most probable reaction mechanism is concluded to be that involving a bimolecular reaction between molecules of the thiazole and molecules of ammonia.

AUSTIN, TEXAS RECEIVED MARCH 22, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Photolysis of Ketene and the Structure of Methylene

BY MILTON BURTON, THOMAS W. DAVIS, ALVIN GORDON AND H. AUSTIN TAYLOR

According to Pearson, Purcell and Saigh,[1] methylene produced either thermally or photochemically by the decomposition of ketene at low pressures behaves more like a very reactive molecule than like a free radical. Its half-life before reaction, measured by the Paneth streaming method,[2] runs up to 5×10^{-2} sec. or greater in ketene at ~1.5 mm. pressure and up to 2.3×10^{-1} sec. in nitrogen, but is much less in a stream of diazomethane. On the other hand, the work of Ross and Kistiakowsky[3] on the photolysis of ketene clearly shows that free methylene, presumably formed in the reaction, reacts rather readily with ethylene when it is present in large excess and that under such conditions no additional ethylene is formed.

As will be shown below, knowledge of the precise structure of methylene is of value both for its own sake and because of its implications in connection with other problems. Fortunately, a simple device for distinguishing between free radicals and reactive molecules presents itself in the previously studied reaction[4]

$$R + NO \longrightarrow RNO \qquad (1)$$

where R is a free radical. In the investigation herein reported we have studied the photolysis of ketene over a restricted range of temperature in the presence of varying concentrations of nitric oxide and ethylene.

Experimental

Chemicals.—Nitric oxide was prepared, as previously described[5] and tapped off at will. We found that the most convenient source of ketene was from the pyrolysis of diketene somewhat as described by Boese,[6] although we were not able to obtain a product of as high purity as is recorded in the literature. Fortunately, repeated freezing, distillation and evacuation of our ketene rid it of acetone and other high-boiling impurities, leaving behind only such ethylene, nitrogen and traces of hydrocarbon gas as could not be conveniently removed. Since the reactions were followed analytically, the presence of non-interfering impurities was not particularly troublesome. Tank ethylene was withdrawn as required and purified by repeated freezing in liquid nitrogen, evacuation, and melting before use.

Apparatus.—The apparatus was substantially as already described in the study of the photolysis of azomethane.[7] A General Electric H-4 high pressure mercury vapor lamp without the glass envelope was used as a light source. It was situated about 5 cm. from the 1-liter Pyrex bulb (of accurately known volume) which was used as the reaction vessel. The temperature of the latter was controlled by immersion in a beaker filled with water and maintained manually at constant temperature within about 0.2°. Pyrex cuts off light at slightly less than 3000 Å. so that the full strength of the arc at longer wave lengths was available for photolysis. Since the ketene absorbs and is decomposed by light of λ 3130 Å.,[3] this arrangement proved adequate.

Technique.—Samples of ketene to be photolyzed were introduced into the reaction vessel at known temperature and pressure. Changes in pressure were followed on a mercury manometer. Samples were withdrawn from the vessel for macro-gas analysis both prior and subsequent to reaction. From the percentage composition so determined, the volumes at S. T. P. of gases produced and consumed in the reaction could be determined.

In the early work only the ketene was analyzed initially. In later work (*i. e.*, beginning with Experiment 20) the entire reactant gas was analyzed. (It is known now that there is little advantage in that practice.) The procedure for analyzing the reactant gas was simply to pass it through a small "B-D" auto-bubbler pipet[8] containing standard sodium hydroxide of known volume and then into a Fisher Gas-Analyzer. Nitric oxide was determined by volume decrease in potassium hydroxide after mixing with oxygen

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[1] Pearson, Purcell and Saigh, *J. Chem. Soc.*, 409 (1938).

[2] *Cf.* F. Paneth and W. Hofeditz, *Ber.*, **62**, 1335 (1929).

[3] W. F. Ross and G. B. Kistiakowsky, THIS JOURNAL, **56**, 1112 (1934).

[4] *Cf.* G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, Inc., New York, N. Y., 1939, p. 118.

[5] Davis, Jahn and Burton, THIS JOURNAL, **60**, 10 (1938).

[6] A. B. Boese, Jr., *Ind. Eng. Chem.*, **32**, 16 (1940). We are indebted to the Carbide and Carbon Chemical Corp. for the gift of the diketene used.

[7] Burton, Davis and Taylor, THIS JOURNAL, **59**, 1038 (1937).

[8] M. Burton and T. W. Davis, *Ind. Eng. Chem.*, *Anal. Ed.*, **9**, 139 (1937).

and removal of oxygen in chromous chloride, pyrogallol, or both. Ethylene was determined by absorption in bromine (followed by potassium hydroxide to remove bromine). Carbon monoxide was absorbed in acid cuprous chloride and the alkane gases present were determined by combustion. Nitrogen, which was frequently present as an impurity, was determined by difference.

The analysis of the products was made somewhat more elaborate in an effort to establish more exactly their nature. The sample was fractionated by slow passage through a trap (containing silver fragments poisoned with mercury) immersed in liquid nitrogen. Samples were subsequently withdrawn from *s*-butyl chloride mush (temperature ~ −135°), from dry-ice–toluene mush (~ −80°), and at room temperature. Each sample was analyzed separately as already described except that a single portion of standard alkali was used in the B-D pipet for the several fractions. In this way it was possible to distinguish ethylene from other unsaturated products and to establish the production of an alkali-soluble polymer (*S. P.* in Table II) which distilled only at room temperature.

Unfortunately, the B-D pipet did not prove to be useful in the way anticipated. It was hoped to remove the sodium hydroxide solution, to titrate it and thus to establish exactly the amount of ketene absorbed, assuming, of course, the straightforward reaction

$$CH_2CO + OH^- \longrightarrow CH_3COO^-$$

during the absorption process. Using phenolphthalein indicator and the "hot end-point" technique which is known to be satisfactory with sodium hydroxide and weak acids (and which we had used satisfactorily with acetic acid in preliminary work), we were unable to obtain a satisfactory end-point after ketene absorption. The end-point persistently "faded" to pink in acid solution and the titration uniformly indicated ketene volumes 5 to 15% less than corresponded to the amount of gas absorbed whether or not other reactant gases were included in the absorption in the B-D pipet. We established separately that physical absorption of ethylene (*e. g.*, that contained in the initial sample of ketene) could not of itself account for the disparity.

Furthermore, it should be pointed out that all the analytical data cited below have qualitative rather than exact quantitative significance, because of physical absorption of both nitric oxide and ethylene in the B-D pipet. Although means might be devised to determine the amounts of nitric oxide and ethylene so absorbed, it was not considered necessary in this case because the analytical techniques employed, while admittedly rough, were of sufficient accuracy to establish our important conclusions.

Results.—The results of all experiments in which the runs and analyses were satisfactorily completed are summarized in Tables I and II. In these tables the experiments are numbered in actual chronological order. The volume of the reaction system was ~1030 cc. for experiments up to 5 inclusive and ~1040 cc. for the experiments 6 *et seq.* P_0 represents the total initial pressure in each case. V_0 is the volume reduced to S. T. P. for each of the gases indicated and V_f is the final volume for each gas, also at S. T. P. The ratio CO/C_2H_4 is the ratio of volumes of these gases actually produced and is, of course, infinite when C_2H_4 is either *not* produced or actually consumed during the course of the reaction.

It is evident that, unlike Ross and Kistiakowsky, we have limited the photolyses to a small fractional decomposition. Consequently, errors involved in the absorption of ketene in alkali and other errors introduced (by physical absorption of ethylene, for example) are magnified. Nevertheless, Table I clearly indicates, in agreement with them, that in the presence of a substantial excess of ethylene (*cf.* expt. 35, temp. 0°, and expt. 33, temp. 50°), methylene formed in the primary process

$$CH_2CO \xrightarrow{h\nu} CH_2 + CO \qquad (2)$$

disappears exclusively by a combination with ethylene molecules. On the other hand, mere variation of the total initial pressure (expts. 26, 24 and 25) is without effect on the CO/C_2H_4 ratio. Incidentally, expts. 26 and 24 clearly indicate the magnitude of the possible errors involved in the absorption of ketene for in these cases it would appear that less ketene disappears than corresponds to the amount of carbon monoxide produced. As a matter of fact, we are quite certain that the V_f values for ketene must all be too high for in each case they include ~0.3 − 0.5 cc. of gas which distils from liquid nitrogen and which is counted as ketene. We have been unable to establish the nature of this gas. Furthermore, the general course of the work seems to indicate that unsaturated products other than ethylene have a higher solubility in alkaline solution than does that gas, so that the apparent decrease of ketene in the reaction is, consequently, still further reduced. Nevertheless, the average ratio of ketene decomposed to carbon monoxide produced for all the experiments listed in Table I is greater than one (1.2) and suggests that ketene itself may react with methylene radicals. The presence of traces of hydrogen and larger quantities of alkane also indicates complicating reactions. The nature of these alkanes could not be established since they appeared to be incompletely combustible, a behavior frequently found with cyclo-alkanes.[9] However, the possibility of the production of cyclopropane from ethylene and methylene radicals should not be overlooked.

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(9) R. A. Day, Jr., and R. N. Pease, THIS JOURNAL, **63**, 912 (1941).

TABLE I

EFFECT OF PRESSURE, TEMPERATURE AND INITIAL ETHYLENE CONCENTRATION IN THE PHOTOLYSIS OF KETENE

Expt.	Time, min.	P_0, mm.	V_0, cc. S. T. P.			V_f, cc. S. T. P.							CO/C_2H_4
			CH_2CO	C_2H_4	Total	CH_2CO	C_2H_4	H_2	CO	Alk.	Total Measd.	Total Calcd.	
						Temp., 0°C.							
28	105	94.0	121.7	5.8	127.8	110.8	10.7	0.1	10.2	0.7	132.5	132.5	2.1
35		138.9	124.5	64.3	189.0	119.6	63.7	...	4.2	.7	188.1	188.0	∞
						Temp., 20°							
7	60	97.4	121.1	2.2	124.1	107.4	5.8	0.6	10.5	1.5	125.8	128.0	≯2.9
14		98.5	122.3	2.4	124.7	109.5	5.2	...	7.5	0.3	122.5	128.3	2.7
11		98.3	119.0	4.9	124.5	103.6	9.1	.2	13.8	.8	127.4	130.6	3.1
8		97.2	117.6	5.4	123.8	107.4	6.8	.1	6.6	2.1	122.5	126.3	≯4.6
10		100.0	118.7	6.3	126.5	107.1	9.0	.1	9.8	1.5	127.5	130.8	3.6
9		98.9	109.4	9.7	126.0	97.5	15.2	.1	8.4	4.4	125.6	128.1	2.7
5	90	97.5	121.3	2.0	124.2	97.9	8.5	...	17.7	6.7	130.7	129.7	2.7
26	105	49.7	58.8	4.1	62.9	54.4	7.0	...	5.6	0.3	67.1	65.7	1.9
24		100.0	120.4	5.7	126.6	112.0	10.1	.1	9.5	.4	132.1	130.7	2.2
25		201.9	241.5	13.6	255.8	229.7	19.6	...	11.1	.5	260.8	259.6	2.0
17		97.8	119.2	4.3	123.8	106.5	8.0	...	13.1	.9	128.5	129.9	3.5
6	150	98.4	122.9	2.0	125.3	96.3	8.7	.4	19.6	3.7	127.0	132.9	2.9
						Temp., 50°							
34	105	110.6	119.9	7.0	127.1	111.9	10.0	...	8.5	0.4	130.9	130.5	2.8
33		162.5	120.4	66.1	186.7	112.7	63.5	...	7.6	.7	184.5	186.8	∞

TABLE II

EFFECT OF NITRIC OXIDE IN THE PHOTOLYSIS OF KETENE

Expt.	Time, min.	P_0, mm.	V_0, cc. S. T. P.			
			CH_2CO	C_2H_4	NO	Total
			Temp., 20°			
19	105	109.2	117.0	3.0	13.5	133.9
16	150	149.4	122.4	2.6	63.6	189.2
12	60	151.7	118.8	8.7	64.3	192.9
18	105	155.7	124.0	2.7	70.3	197.2
15	60	153.0	119.2	4.8	69.4	193.7
23	105	153.0	130.2	48.3	13.8	193.7
			Temp., 0°			
31	105	108.9	121.2	3.8	22.1	148.0
			Temp., 50°			
30	105	120.6	119.2	4.4	13.7	138.5

Expt.	V_f, cc. S. T. P.											CO/C_2H_4
	CH_2CO	C_2H_4	H_2	CO	Alk.	NO	N_2	Unsatd.	*S. P.*	Total Meas.	Total Calcd.	
						Temp., 20°						
19	103.1	5.1	...	13.1	0.3	2.5	1.4	0.2	0.2	125.5	130.4	<6.2
16	91.3	8.5	...	16.9	.9	38.1	4.2	.2	.7	160.8	168.2	2.9
12	100.0	12.2	...	9.2	.8	44.2	3.9	.3	.2	170.8	185.3	2.5
18	111.1	5.3	...	9.9	.9	45.4	9.1	.5	.2	182.1	185.6	3.8
15	114.2	6.4	.3	4.6	1.4	53.2	1.6	...	...	181.7	190.5	2.9
23	111.4	50.8	...	9.0	.8	5.7–10.3	1.4	.2	.2	184.1	184.1	3.0
						Temp., 0°						
31	102.0	7.6	0.1	10.0	0.8	14.3	1.5	0.1	0.4	136.8	140.0	2.6
						Temp., 50°						
30	102.5	8.0	...	9.5	1.1	7.5	0.7	0.1	0.7	129.8	133.9	2.6

In general, it may be seen from Table I that if the ethylene concentration is reasonably low the CO/C_2H_4 ratio does not depart markedly from a value of the order of 2 over a range of temperature of 0–50° and of initial pressure of 50–200 mm.

It may be seen from Table II that nitric oxide, unlike ethylene, does not appreciably affect the CO/C_2H_4 ratio at any temperature from 0 to 50° even when its partial pressure is more than one-third of the whole. The conclusion seems to be either that the energy of activation of the reaction

$$CH_2 + C_2H_4 \longrightarrow C_3H_6 \qquad (3)$$

is much less than that of reaction (1) or, more reasonably, that the reverse reaction

$$CH_2NO \longrightarrow CH_2 + NO \qquad (4)$$

occurs with high probability. This instability of CH_2NO may be related to the fact that, unlike such compounds as CH_3NO, it is a free radical. The possibility also presents itself that the instability of CH_2NO may be due to the reaction

$$CH_2 + CH_2NO \longrightarrow C_2H_4 + NO \qquad (5)$$

which might be expected to go relatively easily. At any rate, these results show quite clearly that methylene does not behave like a free radical in its reaction with nitric oxide.

Like Ross and Kistiakowsky we also observed the deposition of a condensate during the photolysis of ketene, liquid, however, rather than solid. This material appeared, very early (in the first five to twenty-five minutes) in the photolysis, in the illuminated zone as a fog settling out completely in some cases before the end of the experiment. The pressure change when nitric oxide is present is always slow during the first twenty minutes, which is presumably the time of greatest fog development, and after that time the pressure decreases at a steady rate. Nitric oxide generally brought about pressure decreases rather than increases, the decrease ranging from 3 to 16% depending on the time of illumination and the proportion of nitric oxide. The addition of ethylene to the original reaction complex buffered the total pressure change, as illustrated, for example, by expt. 23.

Since the CO/C_2H_4 ratios are not much affected by nitric oxide, it would seem that reaction (1), in which R is methylene, is less likely than reaction (3). However, it should be remembered that the free radical CH_2NO must be very reactive, reacting readily with ketene, perhaps, to give a condensed product. This would appear to be a more probable explanation of the pressure decrease observed than the alternative over-all reaction

$$CH_2 + 2NO \longrightarrow CH_2(NO)_2 \qquad (6)$$

since in presence of nitric oxide distinctly more ketene is used up than corresponds to the carbon monoxide produced. The average ratio of ketene consumed to carbon monoxide produced is 1.6 as against 1.2 when nitric oxide is absent. The occurrence of nitrogen in the product gases substantiates just such a complexity.

In order to avoid some slight tendency toward a continued dark reaction the gases were generally removed from the reaction vessel within about five minutes after the completion of the run. However, it is interesting to note from Table II that there must have been a continued polymerization or condensation of the components in the presence of nitric oxide when the gases were stored over liquid nitrogen, for in those cases the total product measured over mercury (reduced to S. T. P.) was less than that corresponding to the final observed pressure (*i. e.*, total V_f, calcd.).

Discussion

Methylene may be considered as a stable molecule or as a free radical, depending on whether it is assumed that the non-bonding electrons (on the carbon atom) are both *s* or that one is *s* and that the other is in a promoted or *p* state. Whether the two configurations imply any substantial difference in the properties to be expected for methylene depends then on the promotion energy for the change $s \rightarrow p$.

The results of these experiments might at first sight suggest a molecular structure for CH_2 since the reaction with NO occurs less readily than might be expected for a free radical. However, if this structure is accepted, and it is consequently concluded that there is a real and substantial difference between the promoted and non-promoted structures, then it is difficult to understand the high reactivity of CH_2 with C_2H_4. The more readily acceptable view that the radical CH_2NO is either unstable or very reactive leads to the conclusion that there is no evidence in these results against the promoted structure for methylene.

Summary

The photochemical decomposition of ketene at $\lambda > 3000$ Å. has been studied over the range of temperature 0–50° and of pressure 50–200 mm. in presence of varying concentrations of ethylene and of nitric oxide. Although the ethylene yield is decreased to zero when the initial partial pressure of ethylene is about one-third of the total, it is substantially unaffected by equal concentrations of nitric oxide. All the results obtained

may be explained on the basis of one of two structures for normal methylene: (a) a free radical structure, (b) a molecular (unpromoted electron) structure with heat of formation but slightly above that of the free radical.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Physical-chemical Investigation of Certain Nucleoproteins. III. Molecular Kinetic Studies with Calf Thymus Nucleohistone

BY R. OWEN CARTER[1,2]

In an earlier report certain striking physical and chemical properties of the nucleohistone of the calf thymus gland have been presented.[3] The electrophoretic behavior of this nucleohistone also has been considered.[4] Further characterization of the material has been carried out by making observations of its sedimentation and diffusion behavior in solutions containing relatively large amounts of sodium chloride or calcium chloride.

Experimental Procedures

Sedimentation Velocity Measurements.—Measurements of sedimentation velocity were made, using the refractive index method,[5] in a standard Svedberg oil-turbine ultracentrifuge at a speed of 50,000 r. p. m., corresponding to a centrifugal force of about 200,000 times gravity at the center of the sector-shaped solution cell. A 6-mm. cell was used, with a scale distance which varied between 5 and 10 cm., depending upon the concentration of the solution in the cell. The temperature in the cell varied somewhat from experiment to experiment, sometimes reaching a low value near 22°, and at other times rising as high as 27°. During any individual experiment the variation in temperature from the time of attainment of full speed did not exceed 2°. Solvent experiments were made under identical centrifuging conditions and the scale photographs obtained in this way were used as standard reference scales from which the deviations, caused by the sedimentation of the nucleohistone, were measured.

The line positions in the scale photographs were measured to the nearest micron with a Gaertner micro-comparator. The sedimentation curves, obtained by plotting the line displacements as a function of distance from the center of rotation, were for the most part regular and normal in character.

The sedimentation constants were calculated from the equation

$$s = \frac{\Delta x}{\Delta t} \times \frac{1}{\omega^2 x_{\mathrm{m}}}$$

and, for purposes of comparison, reduced to the basis of sedimentation in water at 20° by the expression

$$s_{20} = s\left(\frac{\eta_{\mathrm{t}}}{\eta_{20}}\right)_{\mathrm{H_2O}}\left(\frac{(1 - V\rho_{20})}{(1 - V\rho_{\mathrm{t}})}\right)_{\mathrm{H_2O}} \cdot \frac{\eta}{\eta_0}\,\frac{(1 - V\rho_0)}{(1 - V\rho)}$$

The symbols used have now been standardized. The partial specific volume, V, of sodium nucleohistone is 0.658.

Sedimentation Equilibrium Measurements.—The low-speed ultracentrifuge with direct motor drive developed by Svedberg was used in the sedimentation equilibrium studies. In this form of instrument the rotor rests upon the conical top of the vertical shaft of the motor and is surrounded by a brass rotor casing so that it can be thermostated.

In this case the shape of the cell was of no concern, but a centrifugal force giving optimal concentration distribution had to be found in order to have a reasonably accurate result. The cell and counter cell were fitted into the rotor and the rotation was continued at constant temperature until test measurements showed that equilibrium between sedimentation and diffusion was attained.

Provisions are made in the instrument for passing light through a uniform linear scale and the cell contained in the rotor, in order, during the operation. The method of observation of the concentration gradient in the cell was again that of Lamm.

The molecular weights of the nucleohistone were computed from the equation

$$M = \frac{2RT \ln z_2x_1/z_1x_2}{(1 - V\rho)\omega^2\,(x_2^2 - x_1^2)} = 4.02 \times 10^6\,\frac{\log z_2x_1/z_1x_2}{(x_2^2 - x_1^2)}$$

where z_2 and z_1 are the refractive-index gradients at the distances x_2 and x_1 from the center of rotation. The calculations followed closely the procedures recently described in detail by Svedberg and Pedersen.[5c]

Diffusion Measurements.—The method used for measuring the diffusion constants was that of Lamm and Polson.[6] In this method a uniform transparent scale is photographed through the glass diffusion cell. The gradient in refractive index at the diffusion boundary produces a distorted image of the scale, with scale line displacement being proportional to the concentration gradient when the refractive index is a linear function of the concentration.

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[1] More complete details of this work may be found in a thesis by R. Owen Carter presented in June, 1939, to the Faculty of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Present address: Research Laboratory, The Procter and Gamble Co., Cincinnati, Ohio.

(3) Carter and Hall, THIS JOURNAL, **62**, 1194 (1940).

(4) Hall, *ibid.*, **63**, 794 (1941).

(5) (a) Lamm, *Z. physik. Chem.*, **A138**, 313 (1928); **A143**, 177 (1929); Dissertation, Upsala (1937); (b) McFarlane, *Biochem. J.*, **29**, 407 (1935); (c) Svedberg and Pedersen, "The Ultracentrifuge," Clarendon Press, Oxford, 1940.

(6) Lamm and Polson, *Biochem. J.*, **30**, 528 (1936); **31**, 1903 (1937).