power dependency of r_s appearing in equation 8. The value $\nu = 10^{16}$ molecules cm.$^{-2}$ is undoubtedly high. From a consideration of the geometry of the closest packing of molecules on a surface Brunauer[14] gives for the area covered by one molecule

$$\text{Area} = (4)(0.866)\left(\frac{M}{4\sqrt{2}N_A\delta_1}\right) \qquad (10)$$

where M is the molecular weight of the gas adsorbed, δ_1 is the density of the liquefied gas, and N_A is Avogadro's number. Taking the density of liquid hydrogen as 0.070 g. cm.$^{-3}$, the value $\nu = 7 \times 10^{14}$ molecules cm.$^{-2}$ can be calculated.

The significance of the calculations concerning the absolute rate is that the same choice of values for these variables gave agreement with experiment for both the low surface coverage case and the high surface coverage case, using different catalyst systems.

The agreement of the theoretical and experimental temperature dependencies both for the low surface coverage cases such as that investigated by Harrison and McDowell and for the higher surface coverage case investigated here, together with the pressure dependencies investigated for these two cases strengthens the model assumed in the theory for the conversion. This agreement is all the more striking in view of the fact that the theory predicts a negative temperature dependency for the low surface coverage case and a positive temperature dependency for the high surface coverage case.

It is a pleasure to acknowledge the assistance of Dr. Clarence M. Cunningham in the preparation of the catalysts and of Mr. L. E. Cox, foreman of the Cryogenic Laboratory Shop, in the construction of the catalyst chamber.

COLUMBUS, OHIO

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[14] S. Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., 1945, p. 287.

[CONTRIBUTION FROM THE GIBBS CHEMICAL LABORATORY, HARVARD UNIVERSITY]

The Photolysis of Methyl Ketene

BY G. B. KISTIAKOWSKY AND BRUCE H. MAHAN[1]

RECEIVED DECEMBER 19, 1956

The gas phase photolysis of methyl ketene was investigated using light of 3650, 3130 and 2400 Å. wave length. The principal photolytic products were found to be CO, C_2H_4 and C_4H_8. The experimentally determined effects of temperature, wave length of light, methyl ketene and inert gas concentrations are explained by a mechansim involving vibrationally excited ethylidene radicals rearranging at measurable rates into ethylene. The alternative mechanism involving only photoexcited methyl ketene molecules is shown to be inconsistent with observations.

Introduction

Extensive investigations of the photolysis of ketene[2-7] have demonstrated the formation of the methylene radical and have provided some information on its kinetic behavior. The photolysis of the next homolog, methyl ketene, has not been described in the literature. By analogy, it should result in the formation of the ethylidene radical, CH_3CH. Previous attempts to study the chemistry of this radical have involved the pyrolysis and photolysis of diazoethane, CH_3CHN_2, and acetaldazine, $CH_3CHNNCHCH_3$. The decomposition of the latter was found to be quite complicated[8] and apparently does not involve the ethylidene radical to any important extent. Investigations of the properties of the ethylidene radical produced from diazoethane have been hampered by the hazards involved in handling this material.

Rice and Glasebrook[9] observed no reaction of the ethylidene radical with antimony mirrors when pyrolyzing diazoethane at 650° and higher. The only decomposition products detected were ethylene and nitrogen. The authors concluded that if ethylidene was formed at all under their conditions, it isomerized to ethylene so fast as to exclude all other reactions.

Barrow, Pearson and Purcell[10] observed the removal of selenium and tellurium mirrors when pyrolyzing diazoethane at 400°. As the furnace temperature approached 600° the rate of mirror removal progressively decreased, thus confirming the speculation of Rice and Glasebrook on the thermal instability of the ethylidene radical. The products resulting from the reaction with selenium mirrors were shown by Barrow, *et al.*, to have the properties of selenoacetaldehyde. The same product was obtained when the authors decomposed diazoethane photochemically in the presence of selenium mirrors.

The ultraviolet photolysis of diazoethane was also studied by Brinton and Volman[11] who detected small amounts of butene-2, hydrogen and acetylene among the products, in addition to ethylene and nitrogen. The authors suggested that butene-2 originated from the reaction

$$CH_3CH + CH_3CH \longrightarrow CH_3CHCHCH_3$$

Repeated explosions of diazoethane led to the discontinuation of this work. As the following will

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[1] General Electric Fellow, 1955–1956.

[2] (a) R. G. W. Norrish and G. Porter, *Disc. Faraday Soc.*, **2**, 97 (1947); (b) G. B. Kistiakowsky and N. W. Rosenberg, THIS JOURNAL, **72**, 321 (1950).

[3] M. Vanpee and F. Grard, *Bull. soc. chim. belg.*, **60**, 208 (1951).

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

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

[6] H. Gesser and E. W. R. Steacie, *Can. J. Chem.*, **34**, 113 (1956).

[7] J. Chanmugam and M. Burton, THIS JOURNAL, **78**, 509 (1956).

[8] R. K. Brinton, *ibid.*, **77**, 842 (1955).

[9] F. O. Rice and A. L. Glasebrook, *ibid.*, **56**, 741 (1934).

[10] R. F. Barrow, T. G. Pearson and R. H. Purcell, *Trans. Faraday Soc.*, **31**, 880 (1935).

[11] R. K. Brinton and D. H. Volman, *J. Chem. Phys.*, **19**, 1394 (1951).

show, the photolysis of methyl ketene provides a more satisfactory source of ethylidene radicals.

Experimental Details

Methyl ketene was prepared by the method of Jenkins.[12] The vapor of propionic anhydride was pyrolyzed at low pressure in a quartz tube heated externally to 600°. The products passed through a trap cooled to −78° where unreacted anhydride and propionic acid were condensed. Methyl ketene was collected in a subsequent trap which was cooled to −161°. more volatile gases being removed continuously by a diffusion pump. The contents of the second trap were analyzed as 99% methyl ketene and were further purified by two slow bulb-to-bulb distillations. The delivery bulb was kept at −78° and the receiver bulb at −111°, continuous pumping by a diffusion pump assisting in the removal of non-condensables. The first and last quarters of each distillation were discarded. The freshly distilled product was 99.9% absorbed by Ascarite and no ethylene or other lower boiling gases were ever detected as impurities. Although the purified methyl ketene was stored in a trap cooled with liquid nitrogen, the amount of impurity non-absorbable in Ascarite slowly increased with the age of the preparation and could not be removed by a repetition of the purification procedure described above. The impurity was not identified chemically but the mass spectrum of older preparations suggested the presence of some C_3 and C_5 hydrocarbons. An attempt to remove these impurities by a low pressure column fractionation failed, since methyl ketene rapidly polymerized in the still pot and on the column packing. The presence of the impurities in methyl ketene, which may have amounted to 0.5% in some kinetic experiments, made it advisable to express the results of photochemical experiments mainly in terms of carbon monoxide and ethylene yields, since analyses for these products were not complicated by the above-mentioned impurities.

The ketene which was used as an internal actinometer for the quantum yield measurements was prepared by the pyrolysis of acetic anhydride and was purified and stored in an identical manner to methyl ketene.

Hydrogen used in the analytical procedure was Matheson Extra Dry grade (99.8%), which was passed over heated platinized silica gel and $Mg(ClO_4)_2$ to remove oxygen and water vapor.

Oxygen from an Airco tank was treated similarly before use in the combustion analyses.

The *n*-butane was Phillips Petroleum Company Research Grade material (99.9%) and was used after removing non-condensables at −161°.

Sulfur hexafluoride, Matheson C.P. Reagent grade, was distilled twice from −111 to −161°, the first and last quarters of each distillation being discarded.

Carbon dioxide, Matheson Bone Dry grade (99.8%), was used after the removal of non-condensables at −161°.

Diethyl ketone, used for actinic measurements, was Eastman White Label grade, subjected to two bulb-to-bulb vacuum distillations before use.

The photochemical experiments were carried out in a static system. This consisted of the usual pumping arrangement, cold traps and bulbs for the storage of the required chemicals, a gas mixing manifold, a reaction cell, a quartz spiral manometer and a semi-micro gas analytical system.

The light source for almost all the experiments was a low pressure mercury arc of the type described by Bates and Taylor.[13] Its high intensity made it especially suited for this research, since enough products could be obtained for analysis after only five minutes irradiation time. Methyl ketene dimerizes at a measurable rate in the vapor phase. By keeping the pressure of methyl ketene at 30 mm. and below and limiting the runs to five minutes, dimerization was kept to negligible proportions (considerably less than 0.5% in the reaction cell).

The lamp consisted essentially of three concentric quartz tubes. The discharge was maintained in the outermost annular space by a 20 Å. direct current, at a 47-volt potential drop. The light intensity was kept reasonably constant by a servo-mechanism controlled by an RCA 935 photoelectric cell.

A Pyrex reaction cell was axially located in the innermost space of the lamp. To maintain a constant temperature, either water or a filter solution was circulated through the annular space immediately surrounding the reaction cell. The other annular space of the lamp could be filled with a second filter solution, the thickness of each layer being 7 mm. To isolate the 3130 Å. group of the mercury spectrum the outer filter space was filled with an aqueous solution containing 300 g. of $NiSO_4 \cdot 6H_2O$ and 75 g. of $CoSO_4 \cdot 7H_2O$ per liter. A solution containing 0.5 g. of K_2CrO_4 per liter of water was circulated through the inner compartment. To isolate the 3650 Å. spectral region the circulated medium was an aqueous solution containing 0.02 g. of 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene hydrochloride per liter while the second solution contained 500 g. of $CuSO_4 \cdot 5H_2O$ and 75 g. of $CoSO_4 \cdot 7H_2O$ per liter.

A few experiments were made using the strongly reversed resonance line of a British Thomson-Houston high pressure mercury lamp. The radiation from this almost point source was collimated by a quartz lens, passed through a 3 cm. filter of chlorine gas (1 atm. pressure) and through another filter cell containing nitrogen saturated with mercury vapor at room temperature. Following the filters were a cylindrical quartz reaction cell of 12 cm. length and a front surface aluminized mirror to reflect the radiation back into the reaction cell. The asymmetrically broadened resonance line of this lamp extended from approximately 2550 to 2300 Å., the average wave length being about 2400 Å.

The reaction mixtures were prepared by admitting the components successively into a one-liter flask and measuring their pressures with the quartz spiral manometer. A glass stirrer, driven magnetically, ensured rapid mixing of the components prior to admission to the reaction cell. Since the rate of thermal dimerization of methyl ketene was affected by inert gases and was subject to wall effects, it was impossible to prepare and keep inert gas–methyl ketene mixtures of accurately predetermined composition. This mixture was therefore made up to the approximate composition desired and a sample of it was analyzed while the irradiation was taking place.

The progress of the (dark) dimerization of methyl ketene and of the photochemical reaction were followed manometrically, using the quartz spiral manometer, but reliance was placed on the chemical analysis of the reaction mixtures. This was carried out in a system similar to that described by Nash.[14] The product gases were passed through a trap cooled by liquid nitrogen and the non-condensables separated, measured and analyzed by combustion over CuO. Methyl ketene was separated from the condensables by passing them through either Ascarite or anhydrous magnesium perchlorate. The latter agent proved to be an excellent absorber of methyl ketene and thus provided means for analyzing mixtures of methyl ketene and carbon dioxide. The condensable reaction products were then separated into two fractions, one volatile at −161°, and both fractions were analyzed by combustion with added oxygen on platinized silica gel, or catalytic hydrogenation. Samples could be withdrawn for infrared or mass spectrometric analysis. The performance of the entire analytical system was checked repeatedly with known gas mixtures.

Experimental Results

1. The Absorption Spectrum and the Nature of the Products.—The absorption spectrum of methyl ketene was compared with that of ketene using a Cary recording spectrophotometer. As Fig. 1 shows, the two spectra are very similar, except that the absorption of methyl ketene is slightly shifted to lower frequencies. The low resolution tracings showed no evidence of vibrational structure in either spectrum.

Figure 1 shows that with the radiation of a mercury arc filtered only by the Pyrex walls of the reaction cell, the effective radiation must consist of the 3130, 3440 and 3650 Å. line groups. Experiments designed to determine the nature of the reaction products were carried out with this polychromatic

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[12] A. D. Jenkins, *J. Chem. Soc.*, 2563 (1952).

[13] J. R. Bates and H. S. Taylor, THIS JOURNAL, **49**, 2438 (1927).

[14] L. K. Nash, *Ind. Eng. Chem.*, **18**, 505 (1946).

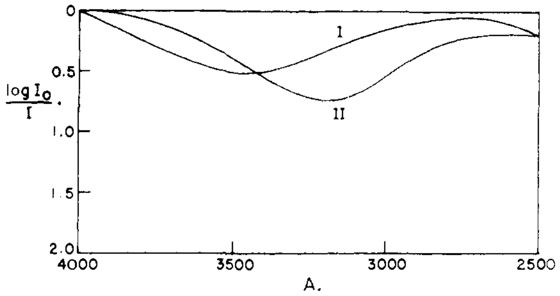

Fig. 1.—Absorption spectra of methyl ketene (I) and of ketene (II), both in a 10 cm. layer at 86 mm. pressure.

radiation. Followed manometrically, the reaction was observed to be accompanied by a pressure increase, the rate decreasing with irradiation time in a manner quite similar to that observed with ketene. This fact suggests that the intermediates formed in the photochemical decomposition of methyl ketene react with the stable products of the reaction just as methylene reacts with the ethylene formed in the decomposition of ketene. Subsequent experiments on the methyl ketene system showed that ethylene was one of the reaction products, and that the rate of pressure increase was lowered by adding ethylene to the reaction mixture.

Gaseous products which were not condensed in a trap at −196° were found analytically to be pure carbon monoxide. A mass spectrometric examination of this fraction indicated the presence of traces of methane.

The fraction non-condensable at −161° was shown by catalytic hydrogenation to be a pure mono-olefin or an equimolar mixture of acetylene and ethane. A mass spectrometric analysis showed it to be ethylene with at most 0.5% ethane and no higher hydrocarbons. The infrared spectrum of the sample showed the 10.52 μ band of ethylene and no other bands, because of the small size of the sample available.

The hydrogenation of the fraction non-volatile at −161° showed it to contain on the average one double bond per mole. Combustion with oxygen, the results of which are shown in Table I, identified the material as a C_4 hydrocarbon. A mass spectrometric analysis was consistent with the identification as a C_4 mono-olefin, but the size of the sample precluded the identification of the butene isomer present.

TABLE I

TWO COMBUSTION ANALYSES OF THE PRODUCT FRACTION CONDENSABLE AT −161°

All quantities are in micromoles

	I	II
Condensable at −161°	0.636	0.586
Mole no. change on combustion	−1.82	−1.70
Calcd. for C_4H_8	−1.91	−1.75
CO_2 in products	2.41	2.64
Calcd. for C_4H_8	2.54	2.34

The results of these analyses were taken to mean that, within the accuracy of the measurements, methyl ketene is decomposed by ultraviolet light into a mixture of carbon monoxide, ethylene and butene

$$2CH_3CHCO + nh\nu \longrightarrow 2CO + (2 - x)C_2H_4 + \frac{x}{2}C_4H_8 \quad (1)$$

Table II shows that this is quantitatively correct and also demonstrates that the composition of the hydrocarbon fraction depends on the pressure of methyl ketene in the reaction cell. The higher the pressure the less ethylene and the more butene is obtained, but the sum of ethylene plus twice the amount of butene remains equal to carbon monoxide, as indicated by eq. 1.

TABLE II

THE COMPOSITION OF PRODUCTS FORMED BY POLYCHROMATIC RADIATION AT 24° IN 300 SECONDS

—CH_3CHCO— Initial pressure mm.	μmoles	CO produced, μmoles	$(CO)/(C_2H_4)$	$(C_4H_8)/(C_2H_4)$	Total hydrocarbons as C_2, μmoles
2.6	5.8	1.01	1.22	0.13	1.04
4.6	10.2	1.12	1.39	.19	1.10
4.8	10.7	1.37	1.14	.10	1.42
6.9	15.3	1.34	1.61	.32	1.39
8.5	18.9	1.45	1.61	.37	1.55
9.0	20.0	1.63	1.60	.43	1.78
10.7	23.8	2.43	2.10	.53	2.38
11.6	25.9	2.51	2.32	.63	2.45
17.7	39.4	3.98	2.25	.68	4.17
19.3	42.9	3.97	2.41	.67	3.85
19.7	43.8	5.92	2.74	.60	4.76
25.6	56.9	3.46	1.98	.55	3.66

2. Quantum Yields.—Primary quantum yields of ketene and methyl ketene decompositions under exposure to 3130 Å. radiation at 24° were determined using diethyl ketone as the internal actinometer. The absorption coefficients of all three were determined with the Cary spectrophotometer. Only the ratios, of course, were required for the calculations. The quantum yield of diethyl ketone was found to be approximately unity[15] at room temperature and low radiation intensities. At higher intensities, comparable to those used here, the yield may be as low as 0.6.[16] The latter experiments were made with diethyl ketone concentrations one-half to one-third as great as those of Table III, thus favoring radical recombination processes. The value to be used in the calculations thus lies between 1.0 and 0.6 and Table III shows therefore that the primary quantum yield of ketene decomposition is between 1.12 and 0.67. Experiments were made with different pressures of ketene at this wave length and the ratio of carbon monoxide production to the pressure of ketene was found to be independent of pressure. Since the fraction of absorbed radiation was small, this shows the independence of the quantum yield of pressure and so suggests, but does not prove, that the quantum yield is unity. In any case, the uncertainty does not affect the validity of the conclusions to be made below.

To determine the primary quantum yield of methyl ketene decomposition some assumption

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[15] W. Davis, THIS JOURNAL, **70**, 1868 (1948).

[16] K. O. Kutschke, M. H. J. Wijnen and E. W. R. Steacie, *ibid.*, **74**, 714 (1952).

TABLE III

THE PRIMARY QUANTUM YIELD OF KETENE DECOMPOSITION AT 3130 Å.[a]

p, mm.	Compound	CO, moles/sec. × 10^{-15}	I_{abs}, quanta/sec. × 10^{-15}	I_0, quanta/sec. × 10^{-16}
37	$(C_2H_5)_2CO$	1.43	1.43	3.3
32	$(C_2H_5)_2CO$	1.28	1.28	3.4
			Av.	3.35 × 10^{16}
17	CH_2CO	3.6	1.6	

Ratio of primary quantum yield of ketene to quantum yield of diethyl ketone: 1.12.

[a] For these experiments the lamp was run at reduced intensity.

must be made regarding secondary reactions. Consideration of the data presented in Table II and analogy with the ketene mechanism suggest the set of reactions

$$\begin{aligned} &CH_3CHCO + h\nu \longrightarrow CO + CH_3CH \\ &CH_3CH \longrightarrow CH_2CH_2 \qquad (2) \\ &CH_3CH + CH_3CHCO \longrightarrow C_4H_8 + CO \end{aligned}$$

The amount of carbon monoxide directly resulting from the primary process is therefore

$$CO_{primary} = C_2H_4 + 1/2(CO_{obsd} - C_2H_4) \quad (3)$$

Use of this equation in the quantum yield calculations avoids the least accurately determined quantity, the yield of butene. On this basis, the primary quantum yield of carbon monoxide, using 3130 Å. wave length radiation, is found to depend slightly on the pressure of methyl ketene and to tend to the same value as that of ketene (unity?) at low pressures, as shown in Fig. 2.

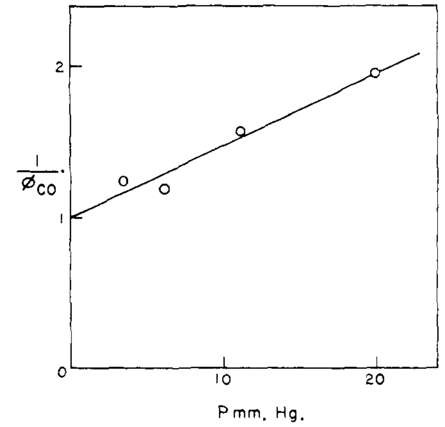

Fig. 2.—Primary quantum yields of methyl ketene decomposition by radiation of 3130 Å. wave length, calculated assuming that of ketene is unity.

The primary quantum yield of methyl ketene decomposition in the 3650 Å. wave length region was determined at 24° using ketene as the internal actinometer. The quantum yields for ketene at this wave length were interpolated from the graph given by Strachan and Noyes.[5] The results are shown in Fig. 3. The total light intensity entering the reaction cell at this wave length was 2 × 10^{18} quanta/second. The decrease of the quantum yield with increasing pressure of methyl ketene is seen to be more exaggerated than the corresponding behavior of ketene reported by Strachan and Noyes.

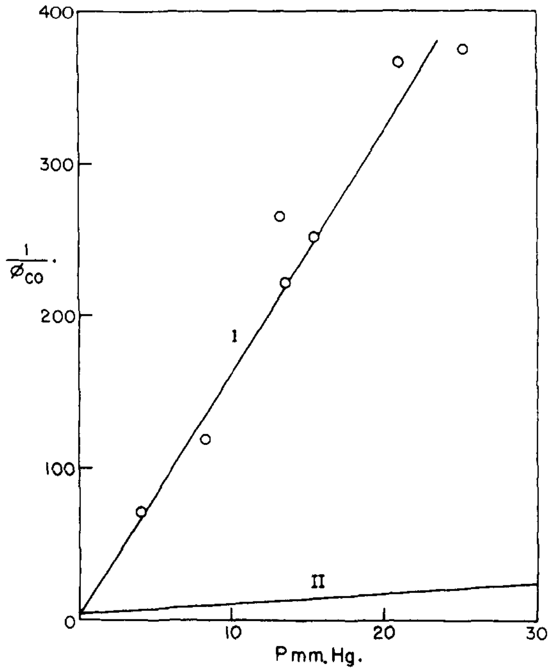

Fig. 3.—Primary quantum yields (I) of methyl ketene decomposition in radiation of 3650 Å. wave length. Line II shows data of Strachan and Noyes (ref. 5) obtained with ketene at this wave length.

3. **Effects of Temperature.**—The provisional reaction mechanism specified above suggests that if the unimolecular rearrangement of the ethylidene radical into ethylene and the competing step (attack on a methyl ketene molecule) have different activation energies, the carbon monoxide–ethylene ratio should change with temperature at constant methyl ketene concentration. Experiments were therefore carried out at 5 and 49° using polychromatic radiation. The results, together with those of Table II obtained at 24°, are plotted in Fig. 4. The carbon monoxide–ethylene ratio is seen to be a linear function of the concentration of methyl ketene. Temperature has no observable effects.

For purposes of comparison the butene–ethylene ratio is also plotted in this figure. The data are consistent with a straight line having zero intercept. As already noted in a preliminary publication,[17] the forms of the relations between the methyl ketene concentration and the carbon monoxide–ethylene and butene–ethylene ratios are consistent with the provisional mechanism proposed above.

4. **The Effects of Radiation Frequency.**—Separate measurements of the carbon monoxide–ethylene ratio in the initial stage of the reaction were made using spectrally isolated radiation of 3650, 3130 and 2400 Å. wave length. The results are presented graphically in Fig. 5. It is seen that while the behavior remains qualitatively the same over this entire spectral region, the probability of forming ethylene, rather than butene, at a

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(17) G. B. Kistiakowsky and B. H. Mahan, *J. Chem. Phys.*, **24**, 922 (1956).

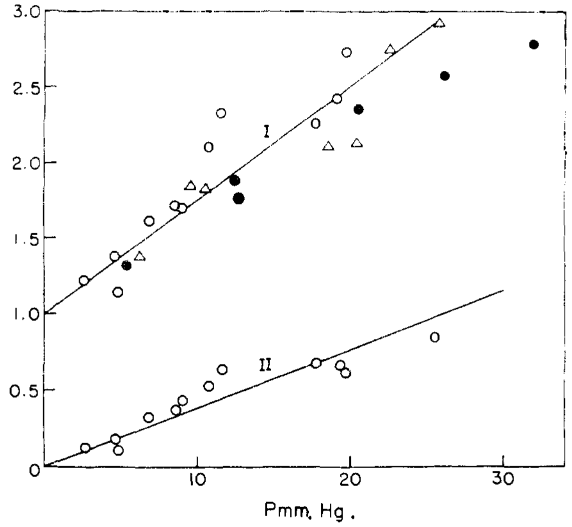

Fig. 4.—Line I shows the carbon monoxide:ethylene ratios obtained at different pressures of methyl ketene and different temperatures in polychromatic radiation: dots, at 5°; circles, at 24°; triangles, at 49°. Line II shows the butene:ethylene ratios at 24°.

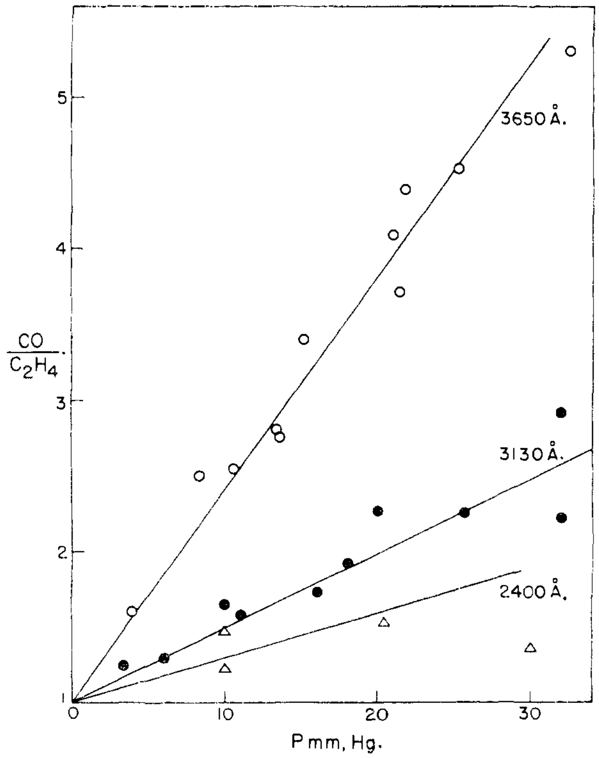

Fig. 5.—The carbon monoxide:ethylene ratios in monochromatic radiation of three wave lengths as functions of methyl ketene pressure.

given pressure of methyl ketene, increases rapidly with increasing energy of the light quanta used in the photolysis.

5. The Effects of Inert Gases.—The effects of some inert gases were studied using 3130 Å. radiation at 24°. The results in Table IV are shown graphically in Fig. 6, where the quantity $((CO)/(C_2H_4) - 1)/P_{CH_3CHCO}$ is plotted against the ratio

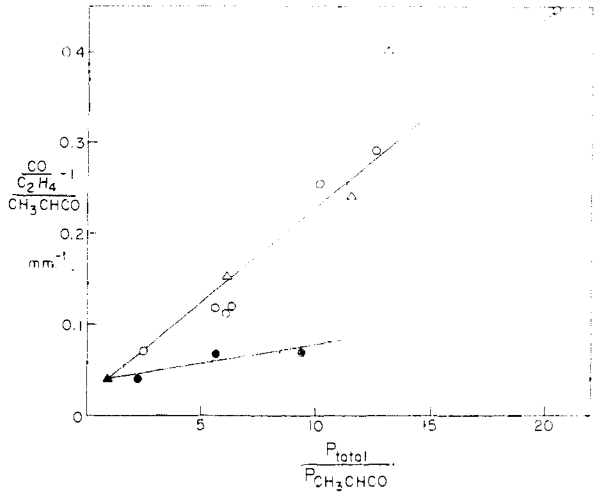

Fig. 6.—Effect of inert gases on a function of the carbon monoxide:ethylene ratio:solid triangle, no inert gas; dots, carbon dioxide; circles, *n*-butane; open triangles, sulfur hexafluoride; 3130 Å. radiation.

of the total pressure to the pressure of methyl ketene. While it seemed highly probable that sulfur hexafluoride and carbon dioxide would not participate chemically in the reaction, butane might be suspected of reacting with ethylidene radicals. A sample of the products non-condensable at −161° was therefore subjected to a mass spectrometric examination, which showed only a negligible amount of ethane to be present. This does not prove the absence of an addition reaction[18] but it does make more legitimate the inclusion of butane in Fig. 6.

TABLE IV

EFFECTS OF INERT GASES WITH 3130 Å. RADIATION

Column 3 gives the rate of primary CO production in molecules per second

CH_3-CHCO, mm.	CO_2, mm.	(CO)/sec.	$\frac{(CO)/(C_2H_4) - 1}{(CH_3CHCO)}$
23.5	31.9	0.590×10^{15}	0.0396
5.4	24.4	.296	.068
18.9	149.4	.368	.68
	SF_6, mm.		
24.6	125.4	0.40	0.153
10.3	117.1	.20	.242
6.0	78.0	.19	.405
	n-C_4H_{10}, mm.		
18.5	98.5	0.544	0.120
24.2	125.1	.740	.110
4.2	81.6	.204	.443
30.2	40.2	.565	.070
22.3	102.2	.456	.119
7.3	66.7	.266	.245
5.8	67.4	.193	.292

An attempt was made to determine the effect of inert gas when the mixture was irradiated with 3650 Å. light. Preliminary runs indicated that the total yield of CO was decreased and the ratio of carbon monoxide to ethylene was increased by the addition of an inert gas (carbon dioxide and *n*-

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(18) W. E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, This Journal, **78**, 3224 (1956).

butane just as with 3130 Å. radiation). The amounts of products obtained under these conditions were so small that quantitative separation from the large excess of inert gas was extremely difficult. These experiments were not pursued further.

Discussion

The experimental data show that the products of the photochemical decomposition of methyl ketene are carbon monoxide and a mixture of ethylene and butene in varying proportions. An increase of collisional frequency, either through addition of an inert gas or through an increase of the methyl ketene concentration lowers the primary quantum yields, far more so with 3650 Å. radiation than at 3130 Å. The limiting (zero pressure) quantum yield is approximately unity for 3130 Å. radiation but may be less than unity with 3650 Å. radiation. The carbon monoxide–ethylene ratio is increased by increasing the wave length of absorbed radiation and by increasing the concentration of methyl ketene and inert gases, but is independent of temperature.

These observations are readily explained by a reaction mechanism which involves ethylidene radicals. It must be postulated that the ethylidene radicals are produced with excess vibrational and translational energies and have reactivities which depend on the wave length of radiation used to produce them. Denoting by K a molecule of methyl ketene, by M any molecule, including methyl ketene, by * the electronic excitation of methyl ketene, and by ′, ″, increasing amounts of vibrational energy, the mechanism applicable to 3130 Å., and undoubtedly to 2400 Å. radiation, is

$$\begin{array}{lll} \mathrm{K} + h\nu & = K^{*\prime\prime} & I_{\mathrm{abs}} \\ \mathrm{K}^{*\prime\prime} + \mathrm{M} & = \mathrm{K}^{*} + \mathrm{M} & k_2 \\ \mathrm{K}^{*\prime\prime} & = \mathrm{CH_3CH}^{\prime\prime} + \mathrm{CO} & k_3 \\ \mathrm{CH_3CH}^{\prime\prime} & = \mathrm{CH_2CH_2} & k_4 \\ \mathrm{CH_3CH}^{\prime\prime} + \mathrm{K} & = \mathrm{C_4H_8} + \mathrm{CO} & k_5 \\ \mathrm{CH_3CH}^{\prime\prime} + \mathrm{M} & = \mathrm{CH_3CH} + \mathrm{M} & k_6 \\ \mathrm{CH_3CH} + \mathrm{K} & = \mathrm{C_4H_8} + \mathrm{CO} & k_7 \\ \mathrm{K}^{*} + \mathrm{M} & = \mathrm{K} + \mathrm{M} & k_8 \end{array} \qquad (4)$$

The essential feature of this mechanism is the assumption that ethylidene rearranges into ethylene with measurable velocity only when it has excess vibrational energy but that it reacts with methyl ketene to form butene even after vibrational deactivation. It is also to be noted that electronically excited methyl ketene molecules which have lost most of their vibrational energy through collisions are assumed to have only one possible fate: loss of electronic energy by some further collision process. This assumption recognizes the experimental fact that the quantum yields obtained with 3650 Å. radiation were two orders of magnitude lower than those obtained at 3130 Å., indicating that photo-excited molecules with small amounts of vibrational energy dissociate only rarely compared with molecules which have a large amount of excess vibrational energy.

If the uncertain limiting quantum yield with 3650 Å. radiation is actually unity, mechanism 4 applies here also, but with altered rate constants because of the lower excitation energy of the ethylidene radicals. If the limiting quantum yield at this wave length is below unity, it may be supposed that additional thermal activation[5] is required for decomposition. This energy may be acquired either before or after the absorption of radiation. In the latter case mechanism 4 is modified by the reactions

$$\begin{array}{lll} \mathrm{K} + h\nu_{3650} \longrightarrow \mathrm{K}^{*\prime} & I_{\mathrm{abs}} & \\ \mathrm{K}^{*\prime} + \mathrm{M} \longrightarrow \mathrm{K}^{\prime\prime *} + \mathrm{M} & K_1 & (5) \\ \mathrm{K}^{*\prime} + \mathrm{M} \longrightarrow \mathrm{K}^{*} + \mathrm{M} & k_{-1} & \end{array}$$

These reactions are then followed by reactions 2–8 of mechanism 4, with, as noted above, altered values of the individual constants.

The expression for the primary quantum yield according to (4) is

$$1/\phi_{\mathrm{CO}} = 1 + \frac{k_1}{k_3}(\mathrm{M}) \qquad (6)$$

whereas according to (5) it is

$$\frac{1}{\phi_{\mathrm{CO}}} = \frac{k_1 + k_{-1}}{k_1} + \frac{k_2(k_1 + k_{-1})}{k_1 k_3}(\mathrm{M}) \qquad (7)$$

Figure 2 shows that the quantum yield measurements done with 3130 Å. radiation are consistent with eq. 6. Either eq. 6 or 7 represents the quantum yield measurements made at 3650 Å. depending on whether an intercept of unity or greater than unity is inferred from Fig. 3.

The expressions for the ratios $(\mathrm{CO})/(\mathrm{C_2H_4})$ and $(\mathrm{C_4H_8})/(\mathrm{C_2H_4})$ given by mechanism 4 or 5 are

$$\frac{(\mathrm{CO})}{(\mathrm{C_2H_4})} = 1 + \frac{2k_5}{k_4}(\mathrm{K}) + \frac{2k_6}{k_4}(\mathrm{M}) \qquad (8)$$

$$\frac{(\mathrm{C_4H_8})}{(\mathrm{C_2H_4})} = \frac{k_5}{k_4}(\mathrm{K}) + \frac{k_6}{k_4}(\mathrm{M}) \qquad (9)$$

The data of Figs. 4 and 5 show that these ratios are linear functions of the methyl ketene pressure, and that the slopes of the two lines are in the ratio of two to one. Furthermore, the intercepts are one and zero, exactly as predicted by eqs. 8 and 9.

The proposed free radical mechanism is completely consistent with the experimental data but it is not unique in this respect. A mechanism based on photo-excited methyl ketene molecules leads to formally identical rate equations

$$\begin{array}{llll} \mathrm{CH_3CHCO} + h\nu & \longrightarrow \mathrm{CH_3CHCO}^{*\prime\prime} & I_{\mathrm{abs}} & \\ \mathrm{CH_3CHCO}^{*\prime\prime} + \mathrm{M} & \longrightarrow \mathrm{CH_3CHCO} + & \mathrm{M}k_2 & \\ \mathrm{CH_3CHCO}^{*\prime\prime} & \longrightarrow \mathrm{CH_2CH_2} + \mathrm{CO} & k_9 & \\ \mathrm{CH_3CHCO}^{*\prime\prime} + \mathrm{CH_3CHCO} & \longrightarrow \mathrm{C_4H_8} + 2\mathrm{CO} & k_{10} & (10) \\ \mathrm{CH_3CHCO}^{*} + \mathrm{CH_3CHCO} & \longrightarrow \mathrm{C_4H_8} + 2\mathrm{CO} & k_{11} & \\ \mathrm{CH_3CHCO}^{*} + \mathrm{M} & \longrightarrow \mathrm{CH_3CHCO} + & \mathrm{M}k_8 & \end{array}$$

Aside from the fact that no free radicals are involved here, this mechanism differs from the mechanism 4 in an extremely important detail. The reactivity of a photo-excited molecule in a bimolecular step such as 10 cannot be expected to be overwhelmingly dependent on the amount of vibrational energy possessed by such a molecule. Therefore step 11, the reaction of a vibrationally deactivated but electronically excited molecule, must be included in the mechanism 10. However, to account for the decreased quantum yields found experimentally at 3650 Å., it must be concluded that k_{11} is much smaller than k_{10} in mechanism 10; that is, the bimolecular reactivity of the excited molecule must be strongly dependent on its vibrational excitation. Despite this inconsistency, let us examine the behavior predicted by the excited molecule mechanism when an inert gas is present in the reaction mixture. Mechanism 10 gives the expression

$$\frac{\frac{(\mathrm{CO})}{(\mathrm{C_2H_4})} - 1}{(\mathrm{K})} = 2\,\frac{k_{10}}{k_9} + 2\left(\frac{k_{11}}{k_9}\right)\left[\frac{k_2(\mathrm{M})}{k_{11}(\mathrm{K}) + k_8(\mathrm{M})}\right] \quad (11)$$

Since the quantum yields obtained at 3650 Å. were generally less than 0.01, k_{11} is necessarily much smaller than k_8. In the presence of a large amount of inert gas, $k_8(\mathrm{M})$ is very much greater than $k_{11}(\mathrm{K})$, and so we may, to a very good approximation, eliminate the latter term from the denominator of the last term in eq. 11. The excited molecule mechanism is then seen to predict that the quantity $(\mathrm{CO})/(\mathrm{C_2H_4}) - 1/(\mathrm{K})$ is independent of the pressure of inert gas. This prediction is to be contrasted to the expression obtained from the free radical mechanism

$$\frac{(\mathrm{CO})/(\mathrm{C_2H_4}) - 1}{(\mathrm{K})} = 2\,\frac{k_5}{k_4} + 2\,\frac{k_6}{k_4}\,\frac{(\mathrm{M})}{(\mathrm{K})} \quad (12)$$

Reference to Fig. 6 shows that the quantity $[(\mathrm{CO})/(\mathrm{C_2H_4}) - 1]/(\mathrm{K})$ is indeed a linear function of the ratio of total pressure to the pressure of methyl ketene, as predicted by the free radical mechanism 4 and eq. 12. The excited molecule mechanism, carried to its logical conclusion, predicts the effect of inert gases incorrectly.

Equations 8 and 12, and Figs. 5 and 6 give the ratio k_5/k_6 as 1.8 when the quenching gas is *n*-butane or sulfur hexafluoride and 7.5 for carbon dioxide. Varied information in the literature referring to rates of intermolecular energy exchange, suggests that a vibrationally excited ethylidene radical probably does not lose most of its excess energy in a single collision, but does so after a small number, when collisions are with a complex molecule. Hence a value of $10^{-1}Z_0$ for k_5 appears to be reasonable and therefore (see eq. 8 and Fig. 5) $k_4 \cong 10^8$ sec.$^{-1}$ when ethylidene radicals are produced by the 3130 Å. radiation.

If the quenching rate constant, k_6, is the same for radicals produced by the 3650, 3130 and 2400 Å. radiation, the isomerization rate constants, k_4, are in the ratio 1:2.9:4.7, as shown by Fig. 5. Qualitatively, this is readily understood because radicals produced by radiation of higher frequency undoubtedly acquire larger vibrational energy and the specific unimolecular rate constant of a molecule having energy E, when E_0 is the minimum energy required for the reaction, has been estimated[19] to be proportional to

$$\left(\frac{E - E_0}{E}\right)^{n-1} \quad (13)$$

Here n denotes the number of internal degrees of freedom among which the energy is randomly distributed. A quantitative application of the expression 13 to the two ratios of k_4 obtained above is questionable because it is not known what fraction of the total energy of the radiation is present as vibrational energy of the ethylidene radical. An extreme assumption can be made that this energy is equal to the energy of the light quanta less the dissociation energy of the C–C double bond in methyl ketene. A consistent answer can then be obtained only if the dissociation energy is taken to be about 68 kcal., which gives $E_0 \cong 3$ kcal. if $n = 6$. This value of the dissociation energy is probably too low because, assuming that the dissociation energies of ketene and methyl ketene are the same, it gives 79 kcal. for the heat of formation of the methylene radical. From this it follows that the energies of successive separation of hydrogen atoms from methane are: 102, 98, 118, 80 kcal., a rather improbable sequence. Undoubtedly some of the radiation energy is converted into translational energy of the two fragments resulting from the decomposition of methyl ketene. Qualitatively, these calculations are important because they show that the formation of vibrationally excited ethylidene radicals from methyl ketene molecules, which have absorbed 3650 Å. radiation, is consistent with the experimental data; this in turn shows that E_0, the minimum activation energy for rearrangement into ethylene, is quite small. The small value of E_0 suggests, according to mechanism 4, which neglects thermal activation, that the reaction of quenched ethylidene radicals with methyl ketene (reaction 7) is very fast. In this respect, ethylidene behaves very much like methylene.[20]

In conclusion a few comments should be made on the primary quantum yields. From the dependence of the quantum yield on pressure with 3130 Å. radiation, the lifetime before decomposition (the reciprocal of the specific dissociation probability) of an excited methyl ketene molecule can be estimated as 3×10^{-9} second if every collision results in deactivation. The specific dissociation probability after absorption of 3650 Å. radiation is 230 times smaller if quenching occurs on every collision. If the quantum yields extrapolated to zero pressure are less than unity, fluorescence or radiationless transitions to a long lived electronic state (which is quenched even at the lowest pressures investigated), as well as the previously mentioned possibility of thermal excitation (mechanism 5) might be responsible. One of the present authors (BHM) and Dr. R. Williams failed to observe any fluorescence from solutions of ketene in a rigid medium at −195° upon irradiation with 3650 Å. light. This suggests that if the limiting quantum yields for these molecules are indeed less than one at 3650 Å., internal conversion to the ground state is responsible.

It is interesting to note that comparison of the pressure dependence of the quantum yield of carbon monoxide from ketene irradiated with 3650 Å. light[6] with our similar data obtained with methyl ketene indicates that the dissociative lifetime of ketene is shorter than that of methyl ketene by a factor of 25. All these dissociative lifetimes are short compared with the radiative lifetimes, which may be estimated from the integrated absorption coefficients as 3×10^{-6} and 7×10^{-6} sec. for ketene and methyl ketene, respectively. The near ultraviolet absorption of ketene probably represents a singlet–singlet transition, and it has been recently demonstrated[20] that methylene radicals resulting from the photochemical decomposition of ketene are in a singlet state. Therefore the

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[19] L. S. Kassel, "The Kinetics of Homogeneous Gas Reactions," (The Chemical Catalog Co.), Reinhold Publ. Co., New York, N. Y., 1932.

[20] G. B. Kistiakowsky and K. H. Sauer, THIS JOURNAL, **78**, 5699 (1956).

relatively long lifetimes to decomposition of ketene and methyl ketene molecules are not due to electronic multiplicity correlation rules. The lifetimes of these molecules can be likened to those of thermally activated molecules, the delay in both cases being due to migration of vibrational amplitude among several bonds of the molecule. On this basis, the lifetime of the photo-excited molecules behave as qualitatively predicted by eq. 13; the lifetimes decrease with total energy and increase with the complexity of the molecule.

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Reactions of Gaseous Ions. I. Methane and Ethylene

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RECEIVED OCTOBER 1, 1956

At elevated pressures in a mass spectrometer ion source reactions occur between certain ions and the neutral species present. We have studied the various secondary ions formed in methane and ethylene at elevated pressures and have determined the reactions by which they are formed and the rates of these reactions. The rates are all extremely fast. The reaction rates have been treated by classical collision theory and it has been shown that to a fair approximation the cross-sections and reaction rate constants can be predicted from a simple balance of rotational and polarization forces.

Introduction

Secondary processes in mass spectrometers were first observed by early workers in the field[1] but were treated, for the most part, as nuisances due to experimental difficulties that had to be overcome in the development of analytical mass spectrometry. In recent years, however, a number of studies of secondary processes have been reported[2] which are of considerable interest because of the information afforded concerning the gaseous reactions of ions with molecules. Tal'roze and Lyubimova[3] reported the formation of CH_5^+ in methane. Stevenson and Schissler[4] published specific reaction rates for the formation of CD_5^+ in deuterated methane, D_3^+ in deuterium, and for the reactions of A^+ with H_2, D_2 and HD. In a recent note Schissler and Stevenson[5] have reported many more ion–molecule reactions included in which are reactions forming $C_2H_5^+$ and $C_2D_5^+$ in methane and deuterated methane, respectively, and $C_2H_5^+$, $C_3H_3^+$ and $C_3H_5^+$ in ethylene. These reactions were reported to exhibit cross-sections that decreased to zero at finite values of ion-energy and small negative temperature coefficients.

This paper comprises a detailed study of the ion–molecule reactions taking place in methane and ethylene when these compounds are subjected to ionization by electron impact in a mass spectrometer.

Theoretical

Consider the reaction of a primary ion with a neutral molecule to consist of the formation of a transition-state ion which then decomposes unimolecularly to various product ions and neutral fragments. That is

$$P^+ + M \xrightarrow{k_1} PM^+ \qquad (R1)$$

$$PM^+ \xrightarrow{k_{S_j^+}} S^+_j + F_j \qquad (R2)$$

where there will be a set of the above reactions for each primary ion that reacts with neutral molecules. If the time of decomposition of the transition-state ion is short compared with ionic residence times in the ionization chamber, the number of secondary ions of the jth type that are formed will be

$$n_{S_j^+} = \frac{k_{S_j^+}}{\sum\limits_j k_{S_j^+}} n_{PM^+} \qquad (1)$$

where the n's are the number of ions of the various kinds formed per unit time. Since the primary ions are formed in the electron beam at a constant rate, in the following for the sake of simplicity we shall in general refer to the n's as the number of ions formed, the rate aspect of the process to be kept in mind at all times. The number of transition-state ions formed is equal to the product of the number of primary ions formed, the number of collisions made by one primary ion with neutral molecules during its ionization chamber residence time, and the collision efficiency or

$$n_{PM^+} = fQ[M]n^0_{P^+} \qquad (2)$$

where

$n^0_{P^+}$ = number of primary ions formed
f = collision efficiency for the formation of PM^+
Q = total no. of collisions made by a single primary ion with neutral molecules at unit concn.
[M] = no. of molecules per unit volume

Combining (1) and (2) and introducing τ, the time in which the primary ion makes collisions with neutrals (the primary ion residence time), gives

$$n_{S_j^+} = \frac{k_{S_j^+}}{\sum\limits_j k_{S_j^+}} n^0_{P^+} f \frac{Q}{\tau_{P^+}} [M]\tau_{P^+} \qquad (3)$$

Q/τ_{P^+} is the time-average collision rate, and the product of this quantity and the collision efficiency is the rate constant for the formation of the transition-state ion. Recognizing this and rearranging (3) gives

$$\frac{n_{S_j^+}}{n^0_{P^+}} = \frac{k_{S_j^+}}{\sum\limits_j k_{S_j^+}} k_1 [M]\tau_{P^+} \qquad (4)$$

The number of primary ions formed will be propor-

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[1] H. D. Smyth, *Rev. Mod. Phys.*, **3**, 347 (1931).

[2] For a complete review see F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, New York, N. Y., in press.

[3] V. L. Tal'roze and A. K. Lyubimova, *Doklady Akad. Nauk. S.S.S.R.*, **86**, 909 (1952).

[4] D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **23**, 1353 (1955).

[5] D. O. Schissler and D. P. Stevenson, *ibid.*, **24**, 926 (1956).