Discussion of Relaxation Times

None of the compounds showed any considerable distribution of relaxation times, the values of α, the distribution parameter, never exceeding 0.05. The much larger relaxation time of phenyl isocyanate as compared to those of chlorobenzene, bromobenzene and the more polar nitrobenzene[15] gives evidence of the greater protrusion of the linear NCO group from the ring in a direction close to that of the bond from the ring to the group, as indicated by the previously discussed dipole moment values. The large increase in relaxation time from the isocyanate to the isothiocyanate (Table II) presumably results from the greater length of the protruding group and from the stronger intermolecular forces arising from the great polarizability of the sulfur atom and, to some extent, from the larger molecular dipole moment. The greater resistance to molecular motion is shown by the much higher values of $\Delta\eta/c$. The surprisingly large decrease in the values of $\Delta\eta/c$ for *p*-tolyl isocyanate as compared to phenyl isocyanate is qualitatively analogous to the decrease in viscosity from benzene to toluene,[15] but much greater than would be anticipated. Its explanation must await further measurements of this character. The considerable increase in the relaxation time of *p*-tolyl isocyanate over that of the phenyl compound parallels those observed for the corresponding chloro and nitro compounds, 19.5 for *p*-chlorotoluene[16] and 19 for *p*-nitrotoluene,[17] and results from a similar lengthening of the molecular axis in which the dipole lies. The small decrease in relaxation time resulting from the attachment of a second isocyanate to the ring, in spite of an increase in molecular volume, dipole moment and $\Delta\eta/c$, may result from the fact that the molecular dipole is now at a considerable angle to the longest axis of the molecule, instead of being in it or nearly in it.

Although 1-naphthyl isocyanate has a larger molecular volume and much larger values of $\Delta\eta/c$ than *p*-tolyl isocyanate, its relaxation time is slightly shorter, as are those of 1-chloro- and 1-nitronaphthalene as compared to the corresponding toluenes. In all three cases, this presumably arises from the fact that the molecular axis in which the dipole lies is considerably longer in the substituted toluenes than in the 1-substituted naphthalenes. The longest relaxation times and the largest values of $\Delta\eta/c$ in Table II are found for the long molecule of 2-biphenylyl isocyanate, which has a moment component in the long axis of the molecule as well as perpendicular to it. The large value is consistent with the large size of the molecule and is slightly smaller than the value 42.5×10^{-12} reported[18] for 2-biphenylyl chloride at 23°, which it should exceed slightly because of the larger size of the isocyanate group. Since, however, the value for 2-biphenylyl chloride is obtained from a single measurement at a wave length far removed from the region of maximum absorption, one should merely expect it to be of the same order of magnitude as that of 2-biphenylyl isocyanate, as observed.

PRINCETON, NEW JERSEY

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[16] A. J. Petro and C. P. Smyth, THIS JOURNAL, **79**, 6142 (1957).

[17] R. J. W. LeFèvre and E. P. A. Sullivan, *J. Chem. Soc.*, 3287 (1954).

[18] E. Fischer, *Physik. Z.*, **40**, 645 (1939).

[CONTRIBUTION FROM THE GIBBS CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Reactions of Methylene. 2. Ketene and Carbon Dioxide

BY G. B. KISTIAKOWSKY AND KENNETH SAUER

RECEIVED SEPTEMBER 17, 1957

Flash irradiation of twin reaction vessels, one of which was filled with mixtures of ketene and ethylene and the other with mixtures of ketene and xenon or carbon dioxide or sulfur hexafluoride, showed only minor changes in the ratio of carbon monoxide yields from the two cells with flash intensity. No effect of radiation frequency on the relative yields was observed. It is concluded that the association reaction of methylene is unimportant, even under conditions of high radiation intensity and that the reaction of methylene with ketene is very fast. Methylene reacts with carbon dioxide about 2×10^{-2} as fast as with ketene, giving carbon monoxide and probably formaldehyde. It reacts to a slight extent also with sulfur hexafluoride. A large number of by-products of ketene decomposition have been identified. Formation of H_2 and C_2H_2 in the presence of CO_2 is strongly enhanced by increasing radiation intensity; that of CH_4, C_2H_6 and C_3H_8 is not. Formation of H_2 and C_2H_2 (and especially of H_2 in the presence of C_2H_4) is increased by radiation below 2300 Å., while that of the other by-products is not. Under steady irradiation the yields of by-products increase with decreasing pressure of ketene but are eliminated by the addition of oxygen. The significance of these findings is discussed.

The results of the first study[1] of the flash photochemical decomposition of ketene were interpreted as evidence for the occurrence of the association reaction of methylene. The original objective of the present experiments was a determination of the rate of this reaction by an adaptation of the rotating sector method[2] to the technique of flash photolysis.[3] While the work was in progress, evidence was accumulating for an extremely fast reaction of methylene with ketene,[4-6] implying the virtual absence of the association reaction. The present experiments support this conclusion and re-

[1] K. Knox, R. G. W. Norrish and G. Porter, *J. Chem. Soc.*, 1477 (1952).

[2] F. Briers, D. L. Chapman and E. Walters, *ibid.*, 563 (1929).

[3] G. Porter, *Proc. Roy. Soc.* (*London*), **A200**, 284 (1950).

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

[5] G. B. Kistiakowsky and P. Kydd, *ibid.*, **79**, 4825 (1957).

[6] H. M. Frey and G. B. Kistiakowsky, *ibid.*, **79**, 6373 (1957).

veal other new aspects of the photochemical decomposition of ketene.

Experimental

The special feature of these experiments was the simultaneous irradiation of twin reaction vessels, one of which contained ketene and an excess of ethylene, the other an equal amount of ketene with an added "inert" gas.

An all-glass system with good pumping was employed. The desired gases were introduced one by one into a flask, pressures measured, the mixtures homogenized by stirring and transferred to one of the reaction vessels. The latter were constructed by sealing a fused plate into a 180 × 30 mm. quartz tube so as to divide it into two closed half-cylinders, each provided with a separate connection to the filling and analytical systems. The latter was of the usual micro-gas type.[7] A trap for freezing out condensable gases and means for transferring samples to a gas chromatograph or a Consolidated-Nier Model 21-201 ("Isotope Ratio") mass spectrometer were provided. The latter was not very satisfactory for the analysis of complex mixtures, and extensive use was made of gas chromatography in later stages of the work. Thermostated columns 6 ft. long and 6 mm. i.d. were used in conjunction with a thermal conductivity detector whose amplified signal was displayed by a Brown recorder. The sensitivity was such that 10^{-9} mole of a hydrocarbon produced a peak significantly above the thermal noise level. Activated alumina packing, operated at 90–125° with helium as eluent, gave the best results. Relative retention times[8] were normally used to characterize the components of a mixture, and provision was made for withdrawing separated fractions for mass spectrometric identification. For quantitative analysis the product of the peak height and half width $\Delta t_{1/2}$ was measured,[9] but it was found that more precise results were obtained by substituting for the half-width an empirical relation: $\Delta t_{1/2} = 0.080 t_r$, where t_r is the absolute retention time. This was found to be valid within 2% under all conditions investigated. The columns were equivalent to 1000 theoretical plates, according to the convention of Desty.[8]

A Porter-type[3] quartz flashlamp, 120 × 0.6 cm. wound into a helix was placed coaxially with the twin reaction cell, the whole being enclosed in a magnesium oxide-coated reflector. Probably because of considerable inductance in the circuit, the radiation intensity had a considerable rise-time. On reducing the capacitance from 68 to 1 μf. at 10 Kv., the half-width of the flash decreased only from 300 to 70 μsec. Most of the experiments were made with multiple flashes of small energy, spaced seconds apart. The lamp was triggered externally by a sawtooth oscillator whose output was passed through the primary of an automobile spark coil. A photoelectrically-actuated counter recorded the number of flashes. A Vycor or a Pyrex cylinder could be slipped over the reaction cells, cutting off the radiation below *ca.* 2300 and 2900 Å., respectively. For low intensity the steady irradiation by a Cooper–Hewitt 110-7U4 A1 mercury arc, run at 2.8 amp., was used.

Ketene was prepared from acetic anhydride by a method similar to that of Jenkins[10] for methyl ketene. It was fractionally distilled in a Podbielniak-type column, 99.9% of the purified material being absorbed by Ascarite. Other gases were also suitably purified. At −196°, 99.995% of carbon dioxide was condensable; at −78°, only 0.006%. A gas chromatogram of sulfur hexafluoride showed 0.01% of air and 0.05% of an unknown impurity. Xenon was mass spectrometrically pure (99.995%). Gas chromatographic analysis of ethylene showed 0.006% CH_4, 0.02% C_2H_6 and less than 0.02% of propane, propylene, etc. C^{13}-enriched (53.7 atom % of C^{13}) carbon dioxide was found mass spectrometrically to contain 0.02% of NO and N_2.

Results

The absorption spectrum of ketene was measured with a Cary recording spectrophotometer. The absorption coefficients in the low frequency absorption band agree well with those previously reported,[1] but in the second band they are about ten times higher. This region consists of three maxima[11] at 2128, 2086 and 2038 Å., with decadic extinction coefficients of 3700, 2100 and 1700, respectively, in liters/mole-cm. Using pressures of *ca.* 1 mm., to ensure that the flash radiation was distributed uniformly throughout the reaction cell, Vycor filter was found to reduce the decomposition of ketene by a factor of 13; Pyrex filter by a factor of 50. Thus, in absence of filters most of the flash photolysis is caused by radiation below 2300 Å., while in the presence of Vycor the effective range is 2300–2900 Å. With a given filter the extent of ketene decomposition was roughly proportional to the electrical energy of the flash.

The Effects of Radiation Intensity.—In the presence of excess ethylene the preponderant secondary reaction[12] is $CH_2 + C_2H_4 = C_3H_6$, and the quantum yield of carbon monoxide is essentially equal to the primary quantum yield. In ketene alone, or in presence of inert gases, the secondary reaction[13] is $CH_2 + CH_2CO = C_2H_4 + CO$ and the quantum yield of the carbon monoxide is doubled. However, were methylenes to react with each other, the quantum yield of carbon monoxide would be lowered to the value observed in the presence of ethylene. Having first established, therefore, that the ratio of yields of carbon monoxide was unity within experimental error (10%) when the twin reaction vessels were filled with the same gas mixture, they were then filled, one with ketene–ethylene, the other with a ketene–inert gas mixture and irradiated. In experiments without filters the partial pressure of ketene was usually *ca.* 1 mm., that of the other gas 100 mm.; in experiments with filters ketene was at 5 to 10 mm., the other gas at 100 to 150 mm. pressure. Total decomposition of ketene in the cell containing ethylene varied from 2 to 40%. Figure 1

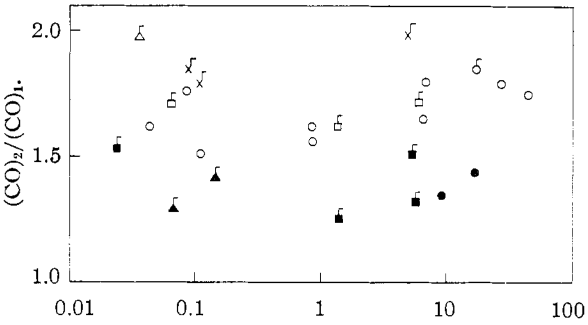

Fig. 1.—The effect of flash energy on the ratio of CO yields from the cell containing an added gas and that containing ethylene. Crosses, xenon and no filter; open symbols, carbon dioxide; solid symbols, sulfur hexafluoride; circles, no filter; squares, Vycor filter; triangles, Pyrex filter. Flags denote those runs in which the total decomposition was below 20%, making the correction for depletion of ketene insignificant.

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

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TABLE I

PHOTOLYSIS AND FLASH PHOTOLYSIS OF KETENE–CARBON DIOXIDE MIXTURES

(P_i, initial pressure in mm. of mercury; R, ratio of the yield of a product to that of ethylene)

Flash photolysis

$P_i(CH_2CO)$	$P_i(CO_2)$	No. of flashes	Total decomp., %	Filter	R_{CO}	$R_{C_2H_6}$	$R_{C_2H_2}$	$R_{C_3H_6}$	$R_{C_3H_8}$
1.67	32.4	40	20.5	None	7.4	0.23	0.67	0.12	0.019
5.23	101.4	20	9.3	Vycor	7.0	.22	.43	.13	.022
5.88	114.0	20	10.3	Pyrex	6.8	.20	.33	.14	.018
0.99	99.1	3500	12.6	None	8.1^a	.47^a	.47^a	.08^a	.10^a
1.00	20.8	30	38	None	9.6^a	.24^a	1.82^a	.10^a	.07^a

Mercury arc photolysis

$P_i(CH_2CO)$	$P_i(CO_2)$	Duration, sec.	Total decomp., %	Filter	R_{CO}	$R_{C_2H_6}$	$R_{C_2H_2}$	$R_{C_3H_6}$	$R_{C_3H_8}$
5.62	104.02	300	7.1	Pyrex	4.1	0.21	0.085	0.036	0.030
6.21	115.1	1200	19.3	Pyrex	5.1	.19	.048	.048	.041
5.24	103.7	1200	22.2	Pyrex	5.4	.22	.060	.046	.047

^{a} Determined mass spectrometrically. Absolute values of the ratios are in doubt.

shows the observed CO yield ratios, plotted against % decomposition of ketene per flash in the cell (no. 1) containing ethylene. Since the decomposition in the other cell was larger, a correction for the depletion of ketene should be applied to the observed ratios, which would increase them. The exact magnitude of this correction depends on assumptions made and hence is uncertain. It can be estimated to amount to at most 20% in experiments shown in Fig. 1.

The reaction products not condensable in liquid nitrogen and subjected to micro-gas analysis were found to contain also hydrogen and methane. Figure 2 shows the yield of hydrogen under a variety of conditions. Data shown are mostly averages of several determinations, the scatter of individual points being about 50%. Methane analyses were interfered with by incomplete separation from the C_2 hydrocarbons. Roughly, the amounts were independent of flash intensity but were reduced from about 10% of carbon monoxide in absence of filters to *ca.* 1% with Vycor and Pyrex filters.

Acetylene was determined mass spectrometrically and gas chromatographically. Some representative relative yields are shown in Table I. The absolute values of $R_{C_2H_2}$ determined mass spectrometrically are not reliable, but the trends are.

Reaction with Carbon Dioxide.—Carbon dioxide was chosen in belief[12] that it was an inert gas, but the determinations of the C_2H_4/CO ratios from experiments using it showed consistent deficiencies of ethylene. Mass 29 peak in the mass spectra was considerably stronger than expected from the hydrocarbon mixtures analyzed, and this mass peak is characteristic of formaldehyde and other aldehydes.[14] Ketene, with a 20-fold excess of C^{13}-enriched carbon dioxide, was irradiated by flashes decomposing 0.4% of ketene per flash, and by the mercury arc, in both cases using the Pyrex filter. Total carbon monoxide yields were 13 and 19% of initial ketene, the content of $C^{13}O$ being 9.7 and 15%, respectively. Taking the total quantum yield of CO on steady irradiation as 2.0 and on flash irradiation as 1.8, the relative reaction probabilities of methylene with CO_2 and with CH_2CO are 1:75 and 1:51, for an average of 1:63.

Much other work was done with chromatographic analyses of ketene–carbon dioxide mixtures. The results reveal nothing definite about the mechanism of secondary reactions, and therefore only a few sample data are shown in Table I.[15] Notwithstanding the non-uniform degree of decomposition of ketene, the results are given as ratios of the yields observed to those of ethylene because the elution time of carbon monoxide had to be short if other components were to be observed; consequently its determination was quite inaccurate. Not much weight should be given, therefore, to absolute R_{CO} values in this and subsequent tables, although trends are significant.

By-products of the decomposition of ketene were investigated chromatographically after irradiating ketene alone with the mercury arc, using the Pyrex filter. Oxygen-containing compounds, other than carbon monoxide, were irreversibly absorbed in the columns; however, yields of a number of hydrocarbons were determined. Table II shows the effect of the initial pressure of ketene on the yields of several by-products. The degree of decomposition of ketene was varied in other experiments from 3 to 60%, and it was established that: (a) the relative propylene yield is proportional to the degree of decomposition and is zero at the start; (b) the relative propane yield follows the same pattern: (c) on the other hand, the relative yield of ethane is completely constant and (d) that of acetylene is of comparable magnitude and decreases slightly with increasing degree of decomposition; and (e) the methane yield is only about 0.001 and is independent of the degree of decomposition. Some of these results are illustrated in Fig. 3.

The effect of oxygen on the by-products was studied under steady irradiation after adding 9 to 22% oxygen to ketene.[13] $R_{C_3H_6}$ was approximately the same as shown in Table II; but ethane, acetylene and propane were totally absent, *i.e.*, their R values were less than 0.0005. In two runs the oxygen present was exhausted before the end

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(14) Catalogue of Mass Spectral Data of the Am. Petr. Inst. Research Project 44.

(15) Complete information will be found in the Ph.D. thesis of Kenneth Sauer, Harvard University, 1957.

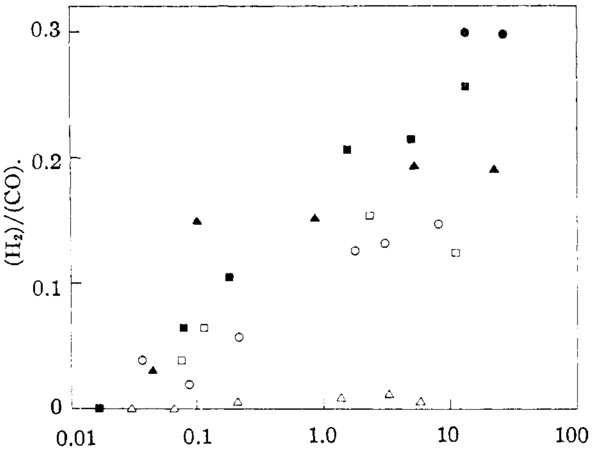

Fig. 2.—The effect of flash energy on the relative yield of hydrogen. Squares, in presence of carbon dioxide; circles, in presence of sulfur hexafluoride; triangles, in presence of ethylene. Solid symbols signify runs without filters; open symbols runs with Pyrex or Vycor filter.

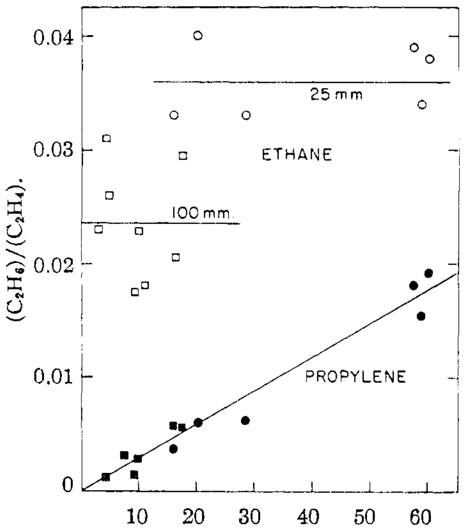

Fig. 3.—The effect of the extent of decomposition on the relative yields of ethane and of propylene from steady irradiation of ketene. Open symbols signify ethane yields; solid symbols propylene yields. Circles, 25 mm. initial pressure of ketene; squares, 100 mm. initial pressure.

of the run, and the above three hydrocarbons were observed to be formed.

The reaction with ethylene was also studied under steady irradiation. The results are expressed as ratios of products observed to propylene and are presented in Table III. It will be noted that *n*-butane and propane are the main by-products of the reaction with ethylene.

TABLE II

PHOTOLYSIS OF KETENE

(Mercury arc photolysis using Pyrex filter; P_i, initial pressure in mm. of mercury; R, ratio of the yield of a product to that of ethylene)

P_i-(CH_2CO)	Total decomp., %	R_{CO}	$R_{C_2H_6}$	$R_{C_2H_2}$	$R_{C_3H_6}$	$R_{C_3H_8}$
0.48	16.5	2.78	0.106	0.087	0.008	0.010
1.69	19.2	2.61	.098	.073	.027	.020
5.1	34.4	2.98	.077	.038	.047	.035
26.4	20.1	2.17	.040	.0231	.060	.0168
99	16.2	2.72	.0206	.0114	.057	.0080
295	7.5	2.18	.0143		.031	.0027

Discussion

Extending earlier findings,[16] the present experiments demonstrate the great complexity of the reactions investigated. Altogether at least twenty hydrocarbons have been identified[15] by the analytical techniques used after moderate (30–40%) degree of decomposition of ketene. Disappointingly, neither carbon dioxide nor sulfur hexafluoride turned out to be wholly inert, and their presence added to the complications.

The effects of radiation intensity were studied over an intensity range of about 10^6, if the mercury arc results are included. It should particularly be noted that, owing to the design of the flashlamp, principally the intensity rather than the duration of the flashes was altered by changing the capacitance and voltage used. Moreover, due to the low partial pressures of ketene and large excesses of non-absorbing gases, adiabatic heating by flash irradiation was kept below 30°, except in those experiments in which more than 5% of ketene (Fig. 1) was decomposed per flash (including one run with xenon). The other two experiments with xenon, after allowing for the depletion of ketene, provide the most clear-cut evidence that the quantum yield of carbon monoxide is not changed by a high intensity of radiation.

Economic reasons, clearly unfortunate in the present case, made us use two other "inert" gases that could be condensed in liquid nitrogen, essential for the chemical analysis of carbon monoxide. As Fig. 1 and the other data presented show, neither is inert. Nonetheless, the results are not wholly invalidated. With carbon dioxide the quantum yield relative to the ethylene-containing cell changes from 1.95 under steady irradiation[15] to 1.80 (after an estimated correction for ketene depletion) with weak flashes. Experiments with xenon demonstrate that methylene association is unimportant under these conditions. The CO quantum yields, in the presence of CO_2, remain then essentially constant to the highest flash energies. In the presence of carbon dioxide some reactions between long-lived intermediates must be involved, since our measurements of the C_2H_4/CO ratio indicated greater depletion of ethylene after flash than after steady irradiation (Table I), even though the rate of labeled carbon monoxide formation was found to be slightly lower, if anything, with flash irradiation. Interposition of filters with the flash lamp had negligible effect on the C_2H_4/CO ratios.

Experiments with sulfur hexafluoride also show no trend of carbon monoxide ratios (Fig. 1) with radiation intensity, but the ratios are only 1.4, instead of 2. However, experiments of Bremer-Wilson[17] established that, under steady irradiation

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

(17) T. Bremer-Wilson and G. B. Kistiakowsky, *ibid.*, **80**, in press (1958).

TABLE III

PHOTOLYSIS OF KETENE–ETHYLENE MIXTURES[a]

(Mercury arc photolysis using Pyrex filter; P_i, initial pressure in mm. of mercury; R, ratio of that yield of a product to that of propylene)

$P_i(CH_2CO)$	$P_i(C_2H_4)$	Total decomp., %	R_{CO}	$R_{C_2H_6}$	$R_{C_3H_8}$	$R_{C_4H_8}$	$R_{n\text{-}C_4H_{10}}$	$R_{iso\text{-}C_4H_{10}}$
22.1	87.7	3.2	1.77	0.036	0.015	0.030	0.110	0.005
24.8	98.6	8.0	1.73	.024	.013		.074	.003
21.1	83.0	8.3	1.58	.034	.016	.020	.110	.003
23.8	93.6	18.9	1.62	.011	.009	.023	.081	.004

[a] The production of acetylene and cyclopropane are not reported, as the chromatographic column used did not resolve them. In the last run the yield of methylcyclopropane was observed to be 0.005 of that of propylene. The absolute value of R_{CO} is in doubt.

with a mercury arc, sulfur hexafluoride in 10:1 mixtures with ketene reduces the ratio to *ca.* 1.5, in satisfactory agreement with the present data. Hence, with appropriate reservations because of the nature of all these data, we conclude that the association of methylene is unimportant, at least up to 5% decomposition per flash. With this radiation intensity, then, the rate of the reaction of methylene with ketene is substantially faster than the rate of association of methylene. The recombination probability on collision of methyl radicals is greater than 10^{-1}, unless the total pressure is below *ca.* 10 mm.[18] If ethylene is formed on the recombination of methylene, it might be expected to have a shorter lifetime than ethane because of fewer vibrational degrees of freedom. However, in a study[17] of the reaction $CH_2 + CO$ the lifetime of "hot" ketene, which has even fewer degrees of freedom, has been found to be shorter than that of ethane by less than a factor of ten. Hence, it is reasonable to set the lower limit for the recombination probability of methylene and therefore for its reaction probability with ketene, as 10^{-2}, at the pressures used in these experiments (100 mm.).

An independent argument in favor of an extremely rapid reaction of methylene with ketene is that the former reacts with a variety of compounds at about the same rate.[6,12,16,19–21] If the collision yields of the observed reactions were low, it would indeed be a miracle of chemical kinetics that they are all so close together. Moreover, the effects of temperature[13,20–22] on relative reaction probabilities are so small that they could easily be due not to activation energies but to thermal effects on steric factors and on quenching of "hot" methylene.[6]

Reaction with ketene was proposed[4] to proceed *via* "hot" cyclopropanone, which isomerizes randomly (and therefore in the ratio of 2:1) into the very unstable compound CH_2CH_2CO, decomposing rapidly into ethylene and carbon monoxide, and into CH_2COCH_2, which lives long enough to react with oxygen or give rise to various by-products. This is clearly an oversimplified picture, since it has now been established definitely that methylene not only adds to the double bond but also substitutes into the C–H bonds and abstracts hydrogen.[6,19] Applied to the ketene reaction these findings alter the simple statistics previously proposed and suggest that the complete mechanism of the reaction with ketene is more complicated, as is also suggested by the complex mixtures of by-products identified in this research.[15] The proposal that cyclopropanone is the main primary product in this reaction, however, is only strengthened by the recent study of the reaction of methylene with ethylene.[6]

Several of the by-products observed in the reaction with ketene are definitely not formed from stable products of the photolysis. They are divided into those (H_2 and C_2H_2) whose yield is strongly dependent on radiation intensity and those (CH_4 and C_2H_6) whose yield is not. That the by-products are the result of reactions of some comparatively long-lived free radicals, such as methyl, is clearly indicated by their absence in presence of oxygen. A competition between first- and second-order reactions in intermediates is probably involved in the formation of the first group of by-products but not of the second. The absorption of radiation, whether in the first or in the second absorption band of ketene, by and large, gives similar product ratios, the exceptions being an increase in the yields of hydrogen and acetylene, and a large increase of hydrogen when excess ethylene is present.

The yields of acetylene and ethane relative to ethylene increase on steady irradiation (Table II) with decreasing pressure of ketene. The same trend is observed for propane (Table II) which is a by-product of the reaction with ethylene (Table III). Plots show that the yields of these by-products are linear in the inverse square root of ketene pressure. The reasons for this relationship are not clear. The rapid increase in the formation of by-products at low pressures of ketene may explain the findings of Porter,[23] which are not likely to be due to a diffusion of methylene to the walls, since large yields of by-products are observed even in the presence of comparatively high pressures of carbon dioxide or ethylene.

Reactions with Sulfur Hexafluoride and with Carbon Dioxide.—Mass spectrometric analysis of sulfur hexafluoride after irradiation with ketene and passage over Ascarite showed only the mass peaks present in the fresh compound plus those of the normal products of ketene photolysis; so the nature of the reactions taking place is uncertain.

The qualitative evidence for the presence of

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(18) R. E. Dodd and E. W. R. Steacie, *Proc. Roy. Soc.* (*London*), **A223**, 283 (1954).

(19) W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, THIS JOURNAL, **78**, 3224 (1956).

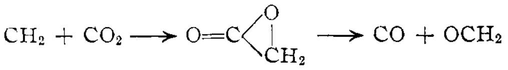
(20) H. Gesser and E. W. R. Steacie, *Can. J. Chem.*, **34**, 113 (1956).

(21) M. Vanpee and F. Grard, *Bull. soc. chim. Belg.*, **60**, 208 (1951).

(22) J. H. Knox and A. F. Trotman-Dickenson, *Chem. and Ind.*, 731 1957).

(23) G. B. Porter, THIS JOURNAL, **79**, 827 (1957).

formaldehyde and the formation of an equivalent amount of carbon monoxide suggest that the mechanism of the reaction with carbon dioxide is



$$CH_2 + CO_2 \longrightarrow O{=}C\overset{O}{\underset{CH_2}{<|}} \longrightarrow CO + OCH_2$$

by analogy with the attack on ethylene[6] and on carbonyl compounds.[24] Under high radiation intensity some other reactions must also occur because of the excessive reduction of ethylene yields.

Summing up the results of this investigation, it must be regretfully admitted that few problems have been solved; however the extreme complexity of the reactions involved has been brought out more forcefully than hitherto.

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[24] C. D. Gutsche in R. Adams, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 364.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF ROCHESTER]

The Thermal Decomposition of Methyl *n*-Propyl Ketone[1]

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The liquid products of the gas-phase thermal decomposition of methyl *n*-propyl ketone in the range 500–530° have been examined. Large quantities of methyl vinyl ketone and some acetone were found. Analysis shows that at least 37% of the methyl *n*-propyl ketone decomposing forms methyl vinyl ketone at the start of decomposition. Previously proposed mechanisms are revised to contain these results.

Knowledge of the thermal decomposition of aliphatic ketones in the gas phase has been advanced in recent papers on methyl *n*-butyl ketone[3] and methyl *n*-propyl ketone.[4] Since only the gaseous products were determined for the methyl *n*-propyl ketone decomposition,[4a] it seemed of interest to examine the liquid products. Because of the similar free radical nature of the decompositions of these two ketones, one would look for the products methyl vinyl ketone and acetone which had been found in the methyl *n*-butyl ketone decomposition.

Experimental

Materials and Apparatus.—Two samples of methyl *n*-propyl ketone were obtained, one from Matheson, Coleman and Bell Division and one from Eastman Kodak, practical grade. The latter was used by Waring and Garik.[4a] It was purified as in the previous work[4a] through the bisulfite product and redistillation. Two separate purification batches of the Matheson material had b.p. 102.2 ± 0.2° and 102.0 ± 0.2° at 760 mm. pressure. The purified Eastman Kodak batch boiled at 101.9 ± 0.2°. This compares with recorded values, 102.35 to 102.4°[5] and 102.4°.[6] Waring and Garik[4a] found 101.7°. The bisulfite treatment did remove from the distilled Eastman Kodak ketone a substance which absorbed at 9.15 and 9.62 μ, probably an ester. The index of refraction of the Matheson ketone after purification was 1.3905 corrected[5] to 20°. This compares with 1.3901[5] and 1.3903[6] previously reported. Waring and Garik[4a] found 1.3898 for theirs.

The purification and properties are of special interest because the rates of pressure increase in Garik's thesis[7] are 1.8 times those observed in this work at 500, 510 and 520°. Therefore, the rate of pressure increase of C.P. acetone at 526° was used to check the apparatus. It was found to be about 20% faster in the present apparatus than reported before.[8] As no special purification of the acetone was attempted, this is satisfactory agreement. Thus, it does not seem that an error in the temperature measurement is responsible for our slower rate with methyl *n*-propyl ketone.

The apparatus was similar to that previously used in this Laboratory.[9] The volume of the reaction bulb was 309 ± 2 ml. A platinum *versus* platinum–13% rhodium thermocouple measured the temperature at the center of the reaction bulb. It was checked at the freezing point of zinc.

Analysis of the Products.—Methyl vinyl ketone was identified in four ways. (1) Boiling point—the liquid products of a large number of static experiments at 510–530° and 150–300 mm. initial pressure were trapped at −78° after a pressure increase of about 80%. This product was distilled in a semi-micro column as done by Barry and Walters.[3] There was a good plateau at 81° in the distillation curve. (2) Infrared—the material boiling in the neighborhood of 81° had the characteristic sharp odor of methyl vinyl ketone and gave all the infrared absorptions of methyl vinyl ketone in the region 2.5–15.5 μ. Absorptions of other ketones assumed to be acetone or methyl propyl ketone were also present in this fraction of the products. Using the ultraviolet method described below, this fraction collected near 81° analyzed 53% methyl vinyl ketone. (Attempts to prepare the semicarbazone with this mixture failed. It was found that the semicarbazone would not form properly in the 81° fraction of a known mixture of the three ketones in the proportions expected.) (3) The very intense ultraviolet absorption of methyl vinyl ketone, $\epsilon = 1.07 \times 10^4$ l./mole cm. at 210 mμ was found in the product. The absorption was parallel to the pure methyl vinyl ketone band from 210 to 240 mμ. (4) The polarographic half-wave potential of a solution of the product in 0.1 *N* KCl in 10% methanol was 1.45 volts *versus* the saturated calomel electrode. 1.41–1.43 volts has been reported for aqueous solutions.[10] The current–voltage curve coincided with that for known solutions of methyl vinyl ketone.

Acetone[4b] was identified as the 57° fraction of the product distillation described above. It gave a fluffy semicarbazone like that with known acetone. This washed, dried derivative melted from 178–187° (not recrystallized). The commonly used value is 187°.

The ketene absorption at 4.6–4.7 μ occurred in the gaseous infrared spectrum of the total products but not in the

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[3] W. T. Barry and W. D. Walters, THIS JOURNAL, **79**, 2102 (1957).

[4] (a) C. E. Waring and V. L. Garik, *ibid.*, **78**, 5198 (1956). (b) Recent work (J. R. McNesby and A. S. Gordon, *ibid.*, **80**, 261 (1958)) on the photolysis of methyl *n*-propyl ketone at higher temperatures and the pyrolysis has shown the presence of acetone.

[5] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publ. Co., New York, N. Y., 1950, p. 362.

[6] P. Pomerantz, *et al.*, *J. Research Natl. Bur. Standards*, **52**, 59 (1954).

[7] V. L. Garik, Ph.D. thesis, Univ. of Connecticut, 1953, Univ. Microfilms Pub. No. 6328, Ann Arbor, Mich.

[8] F. O. Rice and W. D. Walters, THIS JOURNAL, **63**, 1701 (1941); C. H. Klute and W. D. Walters, *ibid.*, **67**, 550 (1945).

[9] D. W. Vanas and W. D. Walters, *ibid.*, **70**, 4035 (1948).

[10] E. I. Fulmer, J. J. Kolfenbach and L. A. Underkofler, *Ind. Eng. Chem., Anal. Ed.*, **16**, 469 (1944).