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The Photochemistry of Ketene and of Ketene–Benzene Mixtures. Reactions of Methylene Radicals[1]

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Abstract: The photochemistry of ketene both alone and in the presence of added gases has been studied as a function of wavlength but principally in two wavelength regions: 2700–2900 and 3550–4000 A. Previous work by several authors has shown that the apparent ratio of triplet to singlet methylene radicals tends to increase with increase in wavelength. The multiplicities of the methylene radicals were determined mainly by reaction with the 2-butenes. This method is now used and compared with other methods, chiefly reaction with propane. The ratio of *n*-butane to isobutane produced by exposure of a mixture of ketene and propane to radiation is a function of wavelength and decreases markedly as the wavelength increases. It is possible that no chemical method will give the correct ratio of singlet to triplet methylenes since the method itself will affect the ratio. The relative yields of singlet and triplet methylenes from the photolysis of ketene are subject to uncertainty, but some conclusions may be drawn. The photochemistry of benzene–ketene mixtures has also been studied. Toluene and cycloheptatriene are the main products. The effect of ketene in quenching the fluorescence of benzene enables the formation of singlet methylenes to be estimated. The dissociation of ketene may be sensitized either by singlet or by triplet benzene. The fraction of triplet benzene formed at 2520 A following absorption by benzene is 0.71 as estimated from reaction of the resultant methylenes produced by the benzene-sensitized dissociation of ketene. This figure is in reasonably good agreement with that obtained by other methods.

Since the first investigation of the photochemistry of ketene by Norrish, Crone, and Saltmarsh,[2] many articles on the photochemistry of this substance have appeared.[3] Ketene is a frequently used source of methylene radicals, and its photochemistry is often mentioned in summaries of the reactions of these radicals.[4] The identification of the spectra of methylene radicals[5] has led to an enhanced interest in the reactions of these radicals, particularly as regards differences in behavior of singlet as distinguished from triplet methylenes.

It was suggested[6] that the ratio of singlet to triplet methylenes formed during photolysis of ketene might be wavelength dependent with the probability that relatively more triplet would be formed at long wavelengths than at short. Simons and Rabinovitch[7] were the first to demonstrate that both singlet and triplet methylenes are indeed present in ketene vapor exposed to radiation at about 3200 A. The method used was that suggested by Skell and Woodworth[8] and discussed in detail more recently by several authors.[3] The method is based on the expectation that singlet methylenes would react with *cis*- and *trans*-2-butene to give stereospecific products while triplet methylenes would give nonstereospecific products. The differentiation of singlet from triplet

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(1) This work was supported in part by a grant from the Robert A. Welch Foundation.

(2) R. G. W. Norrish, H. G. Crone, and O. D. Saltmarsh, *J. Chem. Soc.*, 1533 (1933).

(3) For recent summaries, see J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, pp 391, 554, 622; H. M. Frey, *J. Chem. Soc.*, 266 (1965).

(4) See W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 15, 219 (1964).

(5) See G. Herzberg, *Proc. Roy. Soc.* (London), **A262**, 291 (1961).

(6) *Cf.* W. A. Noyes, Jr., and I. Unger, *Bol. Acad. Cienc Lisboa*, **36**, 3 (1964); *Pure Appl. Chem.*, **9**, 462 (1964).

(7) J. W. Simons and B. S. Rabinovitch, *J. Phys. Chem.*, **68**, 1322 (1964).

(8) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956); **81**, 3383 (1959).

methylenes by this method has now been questioned,[9] and it appears probable that methylene radicals both in the triplet and in the singlet states insert into C–H bonds. This raises the serious question as to whether present methods based on chemical reactions can ever determine unambiguously the relative amounts of singlet and of triplet methylenes.

A new method proposed by De Graff and Kistiakowsky[10] is based on reactions of methylenes with carbon monoxide. Triplet methylenes react much more rapidly with carbon monoxide than do singlet methylenes. The conclusions so far reported do not disagree markedly with those reached herein.

The present study provides data on a few systems, particularly ketene–butene, ketene–propane, ketene–benzene, and pure ketene, and the results are discussed in the light of the photochemical primary process in ketene.

Experimental Section

1. **Materials.** Ketene was prepared by pyrolysis at 500° in Vycor of Baker Analyzed reagent grade acetic anhydride. The effluent was passed through two traps at −78° to remove acetic acid and acetic anhydride. Ketene was collected in a third trap at −196°. The crude ketene was distilled two times from −78 to −196° and two times from −120 to −196°. The first and last fractions were discarded in each case. Gas chromatography showed less than 0.05% C_2H_6 and C_2H_4.

trans-2-Butene and propane were Phillips Research Grade used after degassing. Gas chromatography showed about 0.1% *cis*-2-butene in the *trans*-2-butene and about 0.05% ethane in the propane.

Oxygen was prepared by heating potassium permanganate, and nitrogen, helium, and tetrafluoromethane (Matheson) were used as inert gases.

Diazomethane was prepared by decomposition of N,N-dinitroso-N,N-dimethyl terephthalate (Dupont EXR 101) by 40% aqueous sodium hydroxide in the presence of cyclohexane as solvent. The diazomethane–cyclohexane solution was distilled two times and the diazomethane stored at −196°. Analysis by gas chromatography showed the impurities (C_2H_4, C_2H_6, and cyclohexane) to be less than 2%.

Phillips Research Grade benzene, 99.91% pure with toluene as an impurity, was purified by an Auto-Prep Aerograph Model 700 gas chromatograph with a 4-m silicone gum rubber column. Analysis of the purified benzene by gas chromatography indicated the impurity (toluene) to be less than 0.005%.

2. **Apparatus.** A conventional grease-free vacuum line was employed. The quartz reaction vessel was 100 mm in length and had a volume of 78 cm^3. The effect of ketene on the fluorescent emission of benzene was measured in a 60-mm T-shaped quartz cell.

3. **Light Sources.** A dc-operated 500-w Osram lamp was used with the following color filters: (1) 100-mm thickness of a solution made of 24 g of $NiSO_4 \cdot 6H_2O$ and 4.5 g of $CoSO_4 \cdot 7H_2O$, 50-mm thickness of Cl_2 at 1 atm, 8-mm thickness of liquid CCl_4.[11] transmission 2700–2900 A; (2) Corning glass CS-7-83, transmission 3550–4000 A.

For the ketene–benzene and ketene–benzene–propane systems a Bausch and Lomb grating monochromator, Model 33-86-45, was employed. The reciprocal linear dispersion of this monochromator is 16 A/mm. Entrance and exit slit widths were 2 mm. Several runs at 2535.5 A were performed and a Hanovia S-100 medium-pressure mercury lamp was used instead of the Osram lamp.

Light transmitted through the cell was monitored with a RCA 935 phototube, and emission of benzene was measured by a RCA 1P28 photomultiplier.

4. **Gas Mixtures.** Gas mixtures of ketene and *trans*-2-butene, or propane, were prepared and stored in a blackened 2-l. flask.

5. **Analytical Methods.** Samples for analysis were condensed in the capillary tube with supercooled nitrogen (−215°). The sample was injected into the gas chromatograph by a solid sample injector (F and M Corp.).

Carbon monoxide was measured in the fraction not condensed at −215°. Since methane yields were small the error in the determination of carbon monoxide is small.

Analysis of the Products

1. **Ketene.** In the photolysis of ketene, ethylene and CO were the major products, and ethane, acetylene, and methane were detected in very small amounts. These products were measured by a column packed with diisodecyl phthalate on Chromosorb P.

2. **Ketene–*trans*-2-Butene System.** For the ketene–*trans*-2-butene system the reaction products consisted of *trans*-1,2-dimethylcyclopropane (TD), *cis*-1,2-dimethylcyclopropane (CD), *trans*-2-pentene (T_2Pe), *cis*-2-pentene (C_2Pe), 2-methylbutene-2 (2MB2), 3-methylbutene-1 (3MB1), ethylene, ethane, methane, and carbon monoxide. The products were determined by vapor phase chromatography. A Wilkens HyFi Aerograph equipped with a flame detector was employed.

Quantitative analysis of reaction products was performed with 6.1 m of benzyl ether on firebrick, 6.1 m of dimethylsulfonane on firebrick, and 3.1 m of diisodecyl phthalate on Chromosorb P columns in series. The ratio of ethane to ethylene was determined separately by a 1.5-m silica gel column. 1-Pentene (Phillips Research Grade) was used as an internal standard in most of the runs.

3. **Ketene–Propane System.** In the ketene–propane system *n*-butane, isobutane, ethane, ethylene, methane, propene, 2,3-dimethylbutane, 2-methylpentane, and *n*-hexane were found and identified. Analyses were performed as for the ketene–2-butene system. 2,3-Dimethylbutane, 2-methylpentane, and *n*-hexane were measured separately by the 6.1-m benzyl ether column at 40°.

4. **Diazomethane–*trans*-2-Butene System.** For the diazomethane–*trans*-2-butene system only C_5 products were quantitatively measured.

5. **Ketene–Benzene System.** In the ketene–benzene system cycloheptatriene (CHT), toluene (T), ethylene, ethane, and a very small amount of methane and acetylene were identified. Quantitative measurements of cycloheptatriene and of toluene were made by a dioctyl phthalate on Chromosorb P column.

Ethylene, ethane, methane, and acetylene were determined separately by the silica gel column.

6. **Ketene–Benzene–Propane System.** In the ketene–benzene–propane system *n*-butane, isobutane, ethylene, ethane, and methane were measured as in the ketene–propane system. Cycloheptatriene and toluene were measured separately as in the ketene–benzene system.

Results

Carbon monoxide and ethylene are the main gaseous products from the photolysis of ketene at temperatures up to 100°.[3] Below 3000 A the ratio of carbon monoxide to ethylene is 2.20 ± 0.05 as found in several laboratories.[12] At longer wavelengths the ratio tends to increase. Values of 2.17 at ~2800 A and 2.25 at ~3800 A were found, in satisfactory agreement with earlier work. If ethylene and carbon monoxide were

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[9] D. F. Ring and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **88**, 4285 (1966).

[10] B. A. De Graff and G. B. Kistiakowsky, *J. Phys. Chem.*, **71**, 1553 (1967).

[11] M. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948).

[12] For a review see W. A. Noyes, Jr., G. B. Porter, and J. E. Jolley, *Chem. Rev.*, **56**, 49 (1956).

the only products, the ratio would be exactly 2.00 and this value has never been found.

Details of the data for pure ketene will not be given since they are generally in agreement with data already in the literature.

Ketene–*trans*-2-Butene Mixtures. The products from photolysis of mixtures of ketene and *trans*-2-butene were as follows: C_5 hydrocarbons, propene (in low yield), ethane, ethylene, methane, and carbon monoxide.

Since detailed data on product distribution in mixtures of ketene and the 2-butenes are available, we do not reproduce the data here.[13]

One run was performed with 18 torr of added oxygen at 2800 A in a mixture of ketene and *trans*-2-butene. *cis*-1,2-Dimethylcyclopropane, 3-methylbutene-1, *cis*-2-pentene, ethane, and methane were suppressed by oxygen.

Several experiments with varying *trans*-2-butene pressure at constant ketene pressure and with varying CF_4 pressure at constant pressures of ketene and *trans*-2-butene were performed. The yields of C_5 products relative to their sum were measured. Since yields of *cis*-1,2-dimethylcyclopropane, 3-methylbutene-1, and *cis*-2-pentene are suppressed and depend on wavelength, these products are assumed to be formed by triplet methylenes. The apparent fraction of triplet methylene was calculated by

$$\alpha_T = 2.6[CD] + [3MB1] + [C2Pe] \qquad (1)$$

The factor 2.6 for [CD] arises because *trans*-1,2-dimethylcyclopropane is favored by a factor of 1.6 over the *cis* isomer.[7,14] The values of $\alpha_S = 1 - \alpha_T$ are given in Table I.

Table I. Summary of Fraction of Singlet Methylenes under Various Experimental Conditions[a]

	1. 2800 A, 27°					
2BT, torr	50	100	216	303	400	500
α_S (ketene, 20 torr)	0.78	0.82	0.87	0.88	0.86	0.87
	2BT, 50 torr					
CF_4, torr	0	111	218	316	400	0
N_2, torr	0	0	0	0	0	425
α_S (ketene, 10 torr)	0.78	0.76	0.77	0.77	0.79	0.85
	2. 3800 A, 27°					
2BT, torr	50	100	200	300	400	
α_S (ketene, 20 torr)	0.34	0.33	0.43	0.40	0.42	
(ketene, 40 torr)	0.33	0.33	0.36	0.39	0.42	
(ketene, 60 torr)	0.34	0.35	0.36	0.40	0.41	
(ketene, 80 torr)	0.34	0.35	0.39	0.41	0.41	
(ketene, 100 torr)	0.33	0.34	0.37	0.42	0.46	
α_S (av) (3800 A)	0.33	0.34	0.38	0.40	0.42	
	3. Diazomethane, 25 torr; Ketene, None; 3800 A; 27°					
2BT, torr	42	90	207	492		
α_S	0.73	0.74	0.81	0.88		

[a] Symbols: 2BT, *trans*-2-butene; CD, *cis*-1,2-dimethylcyclopropane; 3MB1, 3-methylbutene-1; C2Pe, *cis*-2-pentene; α_S and α_T, fractions of singlet and of triplet methylenes. For details the thesis of S.-Y. Ho, University of Texas, 1967, should be consulted. The fractions of singlet methylenes are calculated by $\alpha_S = 1 - \alpha_T$ and $\alpha_T = 2.6[CD] + [3MB1] + [C2Pe]$.

Diazomethane–*trans*-2-Butene Mixtures. The C_5 products were found to be about the same as in the ketene–*trans*-2-butene system except for 2-methylbutene-1 (2MB1) which was found as a product in the diazomethane–*trans*-2-butene system. The relative yields of the insertion products *trans*-2-pentene and 2-methylbutene-2 are higher in the diazomethane–*trans*-2-butene mixture at 3800 A than those in the ketene–*trans*-2-butene system at 2800 A. The data of C_5 products are in good agreement with the results of Frey.[15] The fraction of singlet methylene has been calculated by eq 1, and the values of α_S are listed in Table I.

At higher pressures of 2-butene, $\alpha_S = 0.87$ at 2700–2900 A, and $\alpha_S = 0.42$ at 3550–4000 A for ketene–*trans*-2-butene mixtures. For the diazomethane–*trans*-2-butene system α_S approaches 0.88 at 3550–4000 A. The agreement is excellent. The lower values of α_S at lower pressures may be due to the isomerization of the "hot" molecules initially formed by reaction of methylene with *trans*-2-butene.

Ketene–Propane System. Table II gives yields of butanes, ethane, ethylene, and methane relative to CO and the ratio of *n*-butane to isobutane. The relative yields of 2,3-dimethylbutane, 2-methylpentane, and *n*-hexane were measured and the results are listed in Table III. Propene was detected but was not measured quantitatively because the amount was small.

Table II. Products of Ketene–Propane Photochemical Reaction Relative to CO

Total pressure, torr	Ketene/ propane	Total butanes	*n*-butane/ isobutane	C_2H_4	C_2H_6	CH_4
		1. At 2800 A and 27 ± 1°				
6	0.10	0.623	2.02	0.098	0.073	0.002
50	0.10	0.651	1.98	0.090	0.060	0.017
72	0.20	0.561	0.89	0.127	0.061	0.009
104	0.10	0.691	1.93	0.080	0.055	0.007
104[a]	0.10	0.750	1.99	0.079	0.034	0.004
196	0.20	0.576	1.83	0.131	0.059	0.008
200	0.10	0.728	1.98	0.064	0.049	0.006
55 (94°)	0.20	0.463	2.74	0.194	0.048	0.033
412[b]	0.10	0.732	1.67	0.090	0.168	0.010
590[c]	0.20	0.574	1.46	0.169	0.195	...
		2. At 3800 A and 27 ± 1°				
10	0.10	0.357	0.330	0.077	0.198	0.048
59	0.10	0.466	0.383	0.050	0.170	0.057
101	0.10	0.397	0.374	0.056	0.190	0.064
204	0.10	0.390	0.383	0.067	0.171	0.095

[a] Light intensity decreased to one-fifth that of the other run at 104 mm pressure. [b] With 361 mm of helium, products in mole fractions. [c] With 540 mm of CH_4 added, products in mole fractions.

In the ketene–propane system the interesting feature is the wavelength dependence of the ratio of *n*-butane to isobutane. At short wavelengths the ratio was found to be 1.93, while at long wavelengths the ratio was about 0.37. Increase in temperature and addition of foreign gas both cause a decrease in the ratio.

Among the three C_6 hydrocarbon products the relative yield of 2,3-dimethylbutane was much higher than the yield of 2-methylpentane which was much higher

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[13] Detailed data are given in the Ph.D. thesis of S.-Y. Ho, University of Texas, 1967.

[14] R. W. Carr, Jr., and G. B. Kistiakowsky, *J. Phys. Chem.*, **70**, 118 (1966).

[15] H. M. Frey, *Proc. Roy. Soc.* (London), **A251**, 575 (1959).

Table III. Products of Ketene–Propane Photochemical Reaction[a]

Total pressure, torr	Ketene/ propane	C_4H_{10}	n-C_4H_{10}/ i-C_4H_{10}	C_2H_4	C_2H_6	2,3-Dimethyl-butane	2-Methyl-pentane	n-Hexane
			1. At 2800 A and 27 ± 1°					
54[b]	0.10	10.970	1.89	1.239	1.000	0.298	0.130	Trace
			2. At 3800 A and 27 ± 1°					
54	0.10	2.210	0.375	0.317	1.000	0.575	0.245	Trace
100	0.10	2.005	0.367	0.246	1.00	0.435	0.179	Trace

[a] Relative to ethane. [b] Average of two runs.

Table IV. Benzene and Ketene (27°)[a]

Benzene, torr	Ketene, torr	$\frac{[CHT]}{[CHT] + [T]}$	Wave-length, A
6	1	0.94	3650
24	11	0.94	3650
26 (76°)	10	0.83	3650
20 (+4 torr O_2)	10	0.93	3650
20	10	0.73	3030
87	19	0.75	3030
10	0.2	0.20	2520
10	1	0.14	2520
10	5.5	0.23	2520
10	10	0.27	2520
24	5	0.48	2520
42	5	0.63	2520
62	5	0.61	2520
80	5	0.66	2520
64 (+160 torr N_2)	21	0.75	2520
16	6	0.83	>2900
16	6	0.74	>2900
33	12	0.75	>2900
85	35	0.77	>2900
85	35	0.72	>2900
85	35	0.37	>2900

[a] CHT = cycloheptatriene, T = toluene. [CHT]/([CHT] + [T]) tends to decrease at a given time of exposure with increase in intensity and at a given intensity with increase in time of exposure.

than the yield of n-hexane. C_5 compounds were formed only in traces.

Photolysis of Ketene at 2520 A. No measurable absorption by ketene at 2520 A was observed. Photolysis of 10 torr of ketene at 2520 A for 5 hr gave very small amounts of ethylene which can be neglected compared with the result in the benzene-sensitized decomposition of ketene at 2520 A.

Effect of Ketene on Benzene Emission. The effect on benzene emission at an incident wavelength of 2520 A was measured. Q_K and Q_0 denote the fluorescent emission efficiences of benzene at 11.5 torr pressure with and without ketene, respectively

$$Q_0/Q_K = 1 + 0.236P_K$$

where P_K is the ketene pressure in torr. If one takes the mean lifetime of benzene in the $^1B_{2u}$ state to be 5.9 × 10^{-7} sec,[16] one calculates about 1 A^2 as the effective cross section for quenching by ketene. No effect of propane on benzene emission at 2520 A was observed.

Ketene–Benzene System. In the ketene–benzene system the major products of the reaction of methylene radicals with benzene were cycloheptatriene and toluene. Table IV gives the yields of cycloheptatriene and toluene relative to their sum.

Ethylene, ethane, methane, and acetylene were also found in the ketene–benzene system, and relative yields were similar to those in pure ketene. At 2520 A the yield of ethane relative to ethylene increased with decrease in ketene pressure at constant pressure of benzene. The total amount of cycloheptatriene and toluene was generally larger than the total amount of ethylene, ethane, and methane when the ratio of ketene to benzene was smaller than unity.

At wavelengths longer than 2900 A and for longer times of exposure, an unidentified compound was observed and it is probably bicyclo[3.2.0]hepta-2,5-diene.[17,18] This compound decreased with decrease in time of exposure. Biphenyl was not found.

Ketene–Benzene–Propane System. Table V gives mole fractions of n-butane, isobutane, ethylene, ethane, and methane in the products. The ratio [CHT]/([CHT] + [T]) has the same trend as in the ketene–benzene system. The ratio is higher at 2537 A than that at 2520 A at about the same pressure.

For those runs with varying ketene pressure at constant pressure of propane and of benzene at 2520 and 2537 A, the ratio of n-butane to isobutane was plotted *vs.* the pressure of ketene as shown in Figure 1. The intercept at zero pressure of ketene is 0.30, and above 5 torr it is about 1.35.

Discussion

The possible steps of photochemical reaction in the ketene–*trans*-2-butene system may be

$$K + h\nu = {}^1CH_2 + CO \quad \beta I_a \qquad (2)$$

$$= {}^1K_v \quad (1 - \beta)I_a \qquad (3)$$

$${}^1K_v + M = {}^1CH_2 + CO + M \qquad (4)$$

$$= {}^3K + M \qquad (5)$$

$$= {}^1K_0 + M \qquad (6)$$

$${}^1K_0 + M = {}^3K + M \qquad (7)$$

$$= {}^1CH_2 + CO + M \qquad (8)$$

$${}^3K + M = {}^3CH_2 + CO + M \qquad (9)$$

$$= K + M \qquad (10)$$

$${}^1CH_2 + M = {}^3CH_2 + M \qquad (11)$$

$${}^1K_v + K = C_2H_4 = 2CO \qquad (12)$$

$${}^1CH_2 + B = P_1 \qquad (13)$$

$${}^1CH_2 + K = C_2H_4 + CO \qquad (14)$$

$${}^3CH_2 + B = P_3 \qquad (15)$$

$${}^3CH_2 + K = C_2H_6 + CH_4 + C_2H_4 + C_2H_2 + \text{polymer} + CO \qquad (16)$$

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(16) J. W. Donovan and A. B. F. Duncan, *J. Chem. Phys.*, 35, 1389 (1961).

(17) K. R. Kopeck, G. S. Hammond, and P. A. Leermakers, *J. Am. Chem. Soc.*, 83, 2397 (1961).

(18) T. Terao and S. Shida, *Bull. Chem. Soc. Japan*, 37, 687 (1964).

Table V. Benzene–Ketene–Propane (27 ± 1°)

Benzene, torr	Ketene, torr	Propane, torr	n-C_4H_{10}/ i-C_4H_{10}	Total C_4H_{10}	C_2H_4	C_2H_6	CH_4	$\frac{[CHT]}{[CHT] + [T]}$
				1. At 2520 A				
10	0.2	10	0.40	0.526	0.107	0.341	0.026	...
10	0.5	10	0.51	0.550	0.101	0.339	0.020	...
10	1.2	10	0.81	0.615	0.115	0.261	0.000	...
10	3	10	1.15	0.502	0.267	0.216	0.011	...
10	5.5	10	1.44	0.464	0.393	0.136	0.008	...
10	10	10	1.29	0.433	0.439	0.109	0.109	...
10	10	41	1.35	0.623	0.234	0.116	0.023	...
5	0.2	5	0.36	0.478	0.138	0.372	0.018	0.19
5	1	5.5	0.74	0.536	0.249	0.203	0.012	0.26
5	3	5.5	1.11	0.450	0.361	0.171	0.018	0.30
5	5	5.5	1.38	0.410	0.502	0.083	0.005	0.28
16	5	15	1.18	0.654	0.199	0.141	0.006	0.46
				2. At 2537 A				
12	0.2	7	0.40	0.515	0.157	0.315	0.016	0.71
11	1	6	0.74	0.497	0.219	0.272	0.012	0.66
12	3	6.0	1.10	0.425	0.404	0.165	0.006	0.67

where K, ${}^1K_v$, ${}^1K_0$, and ${}^3K$ denote ground state, excited singlet (in high vibrational levels), excited singlet (in lower vibrational levels), and triplet ketene molecules, respectively. β is the fraction of the absorbing ketene molecules which undergo reaction 2. The M's are collision partners. In reactions 5–11, M is necessa at long wavelengths to have eq 17–19 fit the data. At short wavelengths M may be needed for eq 7–11. M may or may not be necessary in step 4.

B is *trans*-2-butene and ${}^1CH_2$ and ${}^3CH_2$ are singlet and triplet methylenes, respectively. P_1 denotes the stereospecific products of ${}^1CH_2$, and P_3 the nonstereospecific products of triplet methylenes. I_a is the number of einsteins absorbed per second per liter by ketene if the concentrations in the rate expressions are in moles per liter.

Reaction 2 implies dissociation prior to vibrational relaxation. Such a step appears to be necessary at short wavelengths.[19] Reaction 3 shows formation of excited molecules. Reaction 5 is included both because the data seem to require it and by analogy with other carbonyl compounds which show high crossover yields to the triplet state.[6,20]

The fraction of singlet methylenes is still appreciable[14,21] at 3800 A. Thus (3) and (4) seem to be necessary. Either ${}^1K_0$ or ${}^3K$ or both dissociate with an activation energy.[12,20] Step 6 indicates merely loss of vibrational energy. After loss of vibrational energy, ${}^1K_0$ may undergo either reaction 7 or reaction 8.

Reaction 9 with an activation energy is demanded by the data which show the quantum yield of CO to increase with increase in temperature at 3700 A.[16] It is analogous to reactions for many other carbonyl compounds.[12,20]

Reaction 10 is necessary at long wavelengths where the primary dissociation yields are below unity and decrease with increase in pressure.[19] Reaction 11 may occur since the reaction ${}^1CH_2 = {}^3CH_2$ is exothermic and competes with other reactions of ${}^1CH_2$ such as reaction either with *trans*-2-butene or with ketene.

Reaction 12 is included because even with a large excess of *trans*-2-butene ethylene is formed. It is not proven but it is a possible minor reaction.

When the ketene pressure is low and the *trans*-2-butene pressure is high, [M] should be approximately equal to [B] and we have approximately

$$1/\alpha_S = 1 + k_{11}/k_{13} = \text{constant} \tag{17}$$

At 3800 A reaction 2 is very slow and β may be very small or zero. The mechanism requires that the value of $1/\alpha_S$ approach constancy at high 2-butene pressures if the mechanism is correct. The data indicate that $1/\alpha_S$ is constant at high 2-butene pressures both at 2800 and 3800 A. The present results are in good agreement with the triplet methylene fractions determined by Carr and Kistiakowsky[14] which are independent of 2-butene pressure.

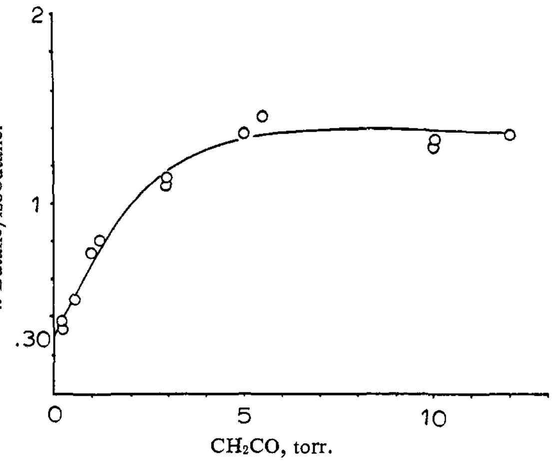

Figure 1. Effect of ketene pressure on the ratio of n-butane to isobutane in the ketene–benzene–propane system at 2520 A.

At pressures below 200 torr the higher values of $1/\alpha_S$ may be due to the isomerization of "hot" molecules initially formed in the reactions of methylenes with *trans*-2-butene.

At 3700 A, β = and if M is not necessary in reaction 4 we have approximately the relationship shown (18)

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[19] A. N. Strachan and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **76**, 3258 (1954).

[20] J. G. Calvert and J. N. Pitts, Jr., ref 3, Chapter 4.

[21] S.-Y. Ho, I. Unger, and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **87**, 2297 (1965).

$$\Phi_{CO} = a_1 + \frac{a_2}{a_3 + a_4[K]} \qquad (18)$$

where the a's are constants. If a_1 is small, eq 18 may be written approximately

$$1/\Phi_{CO} = a + b[K] \qquad (19)$$

where a and b are constant. Equation 19 is in good agreement with the data of Strachen and Noyes.[19]

The fraction α_T of triplet methylenes formed in the primary process in the ketene-*trans*-2-butene system will be given by (20) provided (11) does not occur with M = *trans*-2-butene.

$$\alpha_T - 2.6[CD] + [3MB1] + [C2Pe] + 2[C_2H_6] + [CH_4] \qquad (20)$$

The data of Table I give $\alpha_T = 0.17$ and the fraction of singlet methylenes $\alpha_S = 0.83$ at 2800 A. At 3800 A we have $\alpha_T = 0.60$ and $\alpha_S = 0.40$.

From the data of C_5 products (Table I), we have $\alpha_T = 0.13$, and $\alpha_S = 0.87$ at 2800 A, and $\alpha_T = 0.58$ and $\alpha_S = 0.42$ at 3800 A.

These values are in good agreement with the previous values: $\alpha_S = 0.88 \pm 0.04$ at 2700 A and $\alpha_S = 0.40 \pm 0.10$ at 3700 A.[20] The present values generally agree with the values of fraction of triplet methylene, 0.15 at 2800 A and 0.40 at 3800 A, of Carr and Kistiakowsky,[14] despite the differences in experimental conditions. They agree as well as could be expected with the values of De Graff and Kistiakowsky.[10]

At 2700 A reaction 3 is certainly small and may be negligible so that methylene radicals formed at 2700 A may all be in the singlet state. The apparent fraction 0.87 may be due entirely to competition between (11) and (13).

The diazomethane-*trans*-2-butene mixtures at 3800 A agree with the results of Frey[15] at 4358 and 3660 A. Different methylene sources give almost the same value of α_S. These data provide indirect support for the belief that some singlet methylenes are converted to triplet methylenes by the method.

In the photolysis of ketene in the presence of propane, reactions 2–12 and 14 and 16 should be the same as for the ketene-*trans*-2-butene system. Since propane is a saturated hydrocarbon, the singlet methylene undergoes mainly insertion and the triplet methylene mainly abstraction. Because no pentanes were found, the dissociation of "hot" butane molecules, initially formed by insertion, into ethyl radicals may be neglected. The reactions of methylene with propane may be

$$^1CH_2 + C_3H_8 = n\text{-}C_4H_{10} \qquad (21)$$

$$= i\text{-}C_4H_{10} \qquad (22)$$

$$^3CH + C_3H_8 = CH_3 + n\text{-}C_3H_7 \qquad (23)$$

$$= CH_3 + i\text{-}C_3H_7 \qquad (24)$$

Radical–radical reactions will be the customary ones of addition and disproportionation.

The detailed mechanism would suggest that the total amount of singlet and triplet methylene radicals should be equal to $[C_4H_{10}] + 2[C_2H_6] + [C_2H_4] + [CH_4]$, which should be approximately equal to $[CO] - [C_2H_4]$. The data are consistent within experimental error with this statement. It is assumed that only singlet methylenes insert into C–H bonds and only triplet methylenes abstract hydrogen atoms to give methyl radicals. Probably neither of these assumptions is rigorously true.

Since C_6 products have been found, some butane must be formed by the recombination of methyl and propyl radicals. For evaluation of the fraction of triplet methylene in the ketene–propane system we must determine the amount of butane formed from triplet methylene in the total butane which we have measured experimentally.

The concentrations of propane are much higher than those of ketene, and we assume that methane and ethane are formed from the reaction of triplet methylene with propane. The yield of methane is very small and may be neglected for calculation of the fraction of triplet methylene.

The yield of n-hexane is very small compared to that of 2,3-dimethylbutane, and the yield of n-butane from triplet methylene should be small and neglected. By use of relative rate constants[22] one may state

$$N' \sim N_{i\text{-}C_4H_{10}} = 1.96/([C_2H_6][2,3\text{-dimethylbutane}])^{1/2}$$

where N' = total number of moles of butane. The values of N' relative to ethane are shown in Table VI. These data show that for each mole of ethane formed there is about 1 mole of butane at 2800 A and about 1.4 moles of butane at 3800 A, by the recombination of methyl and propyl radicals.

Table VI. N' Relative to Ethane

Pressure, mm	N'	Wavelength, A
54[a]	1.06	2800
54	1.48	3800
101	1.30	3800

[a] Average of two runs.

From the data the average value of α_T at room temperature in the ketene–propane system is $\alpha_T = 0.20$ at 2800 A and $\alpha_T = 0.77$ at 3800 A. These values are higher than 0.17 at 2800 A and 0.60 at 3800 A for the ketene-*trans*-2-butene system.

The relative rates of abstraction by triplet methylenes for secondary and primary hydrogen of propane may be evaluated from the yields of 2,3-dimethylbutene, 2-methylpentane, and n-hexane. The ratio of abstraction of a secondary hydrogen to abstraction of a primary hydrogen is found to be 14:1 at 2800 and 3800 A. This value is only approximate since the yield of n-hexane is small. The value 14 per bond agrees well with the value of 11 per bond found in diazomethane–propane photolysis by Whitten and Rabinovitch.[23]

The relative rates of insertion of singlet methylene into primary and secondary C–H bonds of propane may be evaluated. From the data of Table II, the values of N', and the ratio $n\text{-}C_4H_{10}/i\text{-}C_4H_{10} = 0.22$ for butane formed from triplet methylene, we have at 27° $k_{21}/k_{22} = 2.6$ at 2800 A and 0.80 at 3800 A.

Relative insertion rates are dependent on wavelength. The increase in the ratio of n-butane to isobutane with temperature indicates that attack of methylene on primary C–H bonds requires a higher activation energy than the attack on secondary C–H bonds. Singlet

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(22) J. C. J. Thynne, *Trans. Faraday Soc.*, **58**, 1394 (1962).

(23) G. Z. Whitten and B. S. Rabinovitch, *J. Phys. Chem.*, **69**, 4348 (1965).

methylenes formed at short wavelengths possess higher energies than at long wavelengths. A wavelength dependence of the relative insertion rates of singlet methylenes for secondary and primary C–H bonds would be expected.

Since there are six primary and two secondary C–H bonds in propane, the ideal statistical ratio of *n*-butane to isobutane should be 3:1 in the ketene–propane system. The attack of secondary C–H bonds is, however, favored for both singlet and triplet methylene.

The over-all ratios of *n*-butane to isobutane have been found to be 1.93 at 2800 A and 0.37 at 3800 A. The value 1.93 at 2800 A is in good agreement with the value of 1.73 at 3130 A of Frey and Kistiakowsky[24] and 1.8 at 3100 A of Knox and Trotman-Dickenson.[25]

The over-all ratio of *n*-butane to isobutane can be calculated from the fraction of singlet and of triplet methylenes, the relative rate of insertion of singlet methylene and the ratio $n\text{-}C_4H_{10}/i\text{-}C_4H_{10} = 0.22$ due to triplet methylene. The calculations give the over-all ratio of *n*-butane to isobutane to be 2.1 at 2800 A and 0.35 at 3800 A. These two calculated values agree well with the experimental values of 1.93 and 0.37. The data and calculations are self-consistent.

Discussion of the Ketene–Benzene System

In photolysis of ketene with benzene in the vapor phase in a Pyrex cell, Terao and Shida[26] found the major products to be 1,3,5-cycloheptatriene (CHT) and toluene (T). The relative yields are independent of pressure and are not affected by the addition of oxygen or nitric oxide. Since no toluene was formed in the photolysis of diazomethane with benzene in the liquid phase,[27] they suggested a reaction of singlet methylenes with benzene to form an unstable intermediate norcaradiene which rapidly isomerizes to cycloheptatriene and toluene. They did not take account of a possible reaction of triplet methylenes with benzene.

The present experimental results indicate that both singlet and triplet methylene react with benzene to produce cycloheptatriene and toluene. Reaction of triplet methylenes with benzene may not be ignored. Since no toluene was found in diazomethane photolysis with benzene in the liquid phase, insertion of singlet methylene into C–H bonds of benzene must be slow if it occurs at all. Abstraction of hydrogen from benzene by triplet methylenes also must be very slow and is neglected since no biphenyl has been observed.

The only important reaction should be addition of both singlet and triplet methylenes to the "double" bonds of benzene to form an unstable intermediate norcaradiene which isomerizes to cycloheptatriene and to toluene as Terao and Shida suggested for singlet methylene. Here we only consider the reaction of methylenes with benzene.

$$^1CH_2 \text{ or } ^3CH_2 + C_6H_6 = \text{norcaradiene} \quad (25)$$

$$\text{norcaradiene} + M = \text{cycloheptatriene} + M \quad (26)$$

$$= C_6H_5CH_3 + M \quad (27)$$

By simple kinetic treatment we have

$$\frac{[\text{CHT}]}{[\text{CHT}] + [\text{T}]} = \frac{k_{26}}{k_{26} + k_{27}} \quad (28)$$

Equation 28 requires that the relative yields of cycloheptatriene and toluene be independent of pressure. The data in Table IV indicate that this is true at 3030 A and at 3650 A. At 2520 A and at $\lambda > 2900$ (Pyrex filter) anomalies may be due to the secondary photochemical isomerization of cycloheptatriene after it is formed. 1,3,5-Cycloheptatriene absorbs in the region from 3300 to 2250 A, and the photochemical isomerization gives toluene as a major product and bicyclo[3.2.0]-hepta-2,5-diene as a minor product.[28]

The secondary photochemical isomerization has been proved at wavelengths longer than 2900 A due to the increase in relative toluene yield with increase in light intensity and with time of irradiation. The yield of toluene is generally higher at 2520 A than at 2537 A (Table V). The intensity at 2520 A was higher by a factor of about 10 than at 2537 A.

An activation energy seems to be required for the formation of toluene. Both singlet and triplet methylenes seem to give both products.

After absorbing a quantum at 2520 A the excited singlet benzene molecule may fluoresce, may cross over to triplet state, or do something else. When ketene is present excited benzene molecules may transfer energy to ketene.

$$C_6H_6 + h\nu = {}^1B_{2u} \quad (29)$$

$$^1B_{2u} = C_6H_6 + h\nu' \quad (30)$$

$$^1B_{2u} = {}^3B_{1u} \quad (31)$$

$$^1B_{2u} = \text{something else} \quad (32)$$

$$^1B_{2u} + K = C_6H_6 + {}^1K \quad (33)$$

$$^3B_{1u} + K = C_6H_6 + {}^3K \quad (34)$$

Here $^1B_{2u}$, $^3B_{1u}$, K, ^1K, and ^3K denote excited singlet and triplet benzene and normal, excited singlet, and triplet ketene, respectively.

If ketene quenches benzene emission from the $^1B_{2u}$ state one may write

$$\frac{Q_0}{Q_K} = 1 + \frac{k_{33}[K]}{k_{30} + k_{31} + k_{32}} = 1 + k_{33}\tau[K] \quad (35)$$

where k_{33} is the rate constant of the quenching step (33) and $\tau = 1/(k_{30} + k_{31} + k_{32})$, the mean lifetime of $^1B_{2u}$ benzene in the absence of ketene.

The value of τ is 5.9×10^{-7} sec[15] provided one assumes the lifetime measured by Donovan and Duncan to be the true rather than the radiative lifetime. Thus, $k_{33}\tau = 4.49 \times 10^3$ l. mole^{-1} and $k_{33} = 7.6 \times 10^9$ l. mole^{-1} sec^{-1}. This corresponds to an effective cross section for quenching of 1.5×10^{-16} cm^2. One might use the value $Q_0 = 0.18$[29] to obtain $k_{33} = 4.2 \times 10^{10}$ l. mole^{-1} if the mean lifetime measured by Donovan and Ducan is considered to be a radiative lifetime.

Singlet benzene molecules upon collision with ketene molecules should give excited singlet ketene molecules which would dissociate into singlet methylenes. Con-

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[24] H. M. Frey and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **79**, 6379 (1957).

[25] J. H. Knox and A. F. Trotman-Dickenson, *Chem. Ind.* (London), 268 (1957).

[26] T. Terao and S. Shida, *Bull. Chem. Soc. Japan*, 37, 687 (1964).

[27] W. von Doering and L. H. Knox, *J. Am. Chem. Soc.*, **72**, 2305 (1950).

[28] For a brief review see ref 3, pp 606, 665.

[29] W. A. Noyes, Jr., W. A. Mulac, and D. A. Harter, *J. Chem. Phys.*, **44**, 2100 (1966).

versely, triplet benzene molecules should give triplet methylenes.

Since $^1CH_2$ and $^3CH_2$ apparently yield the same products upon reaction with benzene, it will be necessary to use other reactions to determine the ratio [$^1B_{2u}$]/[$^3B_{1u}$].

If propane is added to the ketene–benzene system in a region where absorption is almost solely by the benzene, one can assume that $^1CH_2$ and $^3CH_2$ react with the propane by their previously discussed reactions 21–24. It is now possible to use ratios of certain products, particularly [n-C_4H_{10}]/[i-C_4H_{10}], which are closely related to the fraction of triplet methylenes to determine the ratio [$^1B_{2u}$]/[$^3B_{1u}$].

At 2800 A in ketene–propane mixtures one finds [n-C_4H_{10}]/[i-C_4H_{10}] = 1.93 and α_T is 0.20. At 3800 A the figures are 0.37 and $\alpha_T = 0.77$. From the data one can make a plot of [n-C_4H_{10}]/[i-C_4H_{10}] *vs.* α_T.

At constant total pressure the fraction of triplet methylenes may increase as the mole fraction of ketene decreases in the ketene–benzene–propane system since the ratio [n-C_4H_{10}]/[i-C_4H_{10}] goes down at 2520 A (where ketene does not absorb). The limiting ratio is 0.30. This gives 0.87 for the fraction of triplet methylenes.

The fluorescent yield of benzene is 0.18,[29] and at zero ketene pressure 0.82 is the fraction of benzene molecules free to engage in other processes. If the fraction of $^3CH_2$ is equated to the fraction of $^3B_{1u}$ radicals, one obtains $0.82 \times 0.87 = 0.71$ as the apparent quantum yield of triplet benzene. This figure is based on data from the ketene–propane system.

The value 0.71 agrees as well as could be expected with the values obtained by the method of Cundall, *et al.*,[30] and by the use of biacetyl.[31] In a forthcoming article C. Burton and the senior author have reviewed data on triplet benzene formation in the gas phase at about 2530–2590 A and conclude that 0.72 ± 0.07 is about the best value based on presently available information.

These calculations are not stressed but are presented as interesting support for the order of magnitude of the yield of triplet benzene.

(30) R. B. Cundall and A. S. Davis, *Trans. Faraday Soc.*, **62**, 1151 (1966); W. A. Noyes, Jr., and D. A. Harter, *J. Chem. Phys.*, **46**, 674 (1967).

(31) *Cf.* W. A. Noyes, Jr., and I. Unger, *Pure Appl. Chem.*, **9**, 461 (1964).

Mechanistic Consequences of Curved Stern–Volmer Plots. The Photolysis of Cyclobutanone

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Abstract: Mechanistic determinations of photochemical mechanisms are often based on a steady-state analysis of a simplified mechanism, which then often predicts straight-line behavior for reciprocal pressure plots, etc. For the special case of fluorescence processes this leads to the well-known Stern–Volmer plots. If one of the steps of this mechanism involves an energy-dependent rate constant, then such a quasi-Stern–Volmer plot may no longer be linear and hence is not useful as a test of the mechanism, let alone give numerical values for the individual constants of the mechanism. Conversely, however, a linear Stern–Volmer plot is no guarantee against these complications since the pressure curvature may set in at pressures higher than investigated. This complication is extremely severe in the present example and has its origin in the spread in internal energy of one of the intermediates as the result of strong photopartitioning, even though the irradiation was carried out with monochromatic light. For nonfiltered photo-experiments one would expect this complication to be aggravated. The mechanism of the photolysis of cyclobutanone is considered in light of this complication, forcing one to perform more elaborate experiments to elucidate the nature of the primary steps. It is shown here that propylene is not formed in a primary process anywhere within the first absorption band of cyclobutanone. Although this has been suggested before, the conclusion was based on inadequate evidence. A simple quasi-Stern–Volmer plot would easily have led one to the opposite conclusion.

Mechanistic analyses of photochemical systems frequently employ pressure plots of the observed species as a means of interpreting the mechanism. These analyses implicitly assume that the reactive species can be divided into reactive and unreactive states only. In particular, such a two-level mechanism yields a linear plot if relative concentrations are appropriately plotted against reciprocal pressures, the Stern–Volmer plot, in the case of a quenching process. If such a plot has pronounced curvature, this can be attributed to a variety of causes,[2] hence making any mechanistic conclusions difficult at best. The opposite has, however, not been clearly emphasized; that is, even linear (or nearly linear) plots may not be a sufficient guarantee against this type complication, hence invalidating conclusions based on this apparently linear plot. One should probably look for special features of a mechanism before accepting results derivable from a linear Stern–Volmer plot. The photolysis of cyclobutanone

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(1) (a) Abstracted from the Ph.D. thesis of R. J. Campbell; (b) Alfred P. Sloan Research Fellow; (c) National Science Foundation Undergraduate Participant.

(2) H. M. Frey and I. D. R. Stevens, *J. Chem. Soc.*, 4700 (1964); T. F. Thomas and C. Steel, *J. Am. Chem. Soc.*, **87**, 5290 (1965).