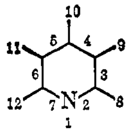
$$\Phi_4 = \frac{1}{\sqrt{12}}(2\psi_1 - \psi_2 - \psi_3 + 2\psi_4 - \psi_5 - \psi_6) \qquad (22)$$

$$\Phi_5 = \frac{1}{2}(\psi_2 - \psi_3 + \psi_5 - \psi_6) \qquad (23)$$

$$\Phi_6 = \frac{1}{\sqrt{6}}(\psi_1 - \psi_2 + \psi_3 - \psi_4 + \psi_5 - \psi_6) \qquad (24)$$

bonds have the same form as (19) and (24) except the ψ's are homopolar localized C–H bonding orbitals. The individual ψ's are given by eq 7.

Below are listed the symmetry MO's for the σ framework of pyridine together with the bonds they refer to; see V.



V

$$\Phi_1 = \psi_1 \qquad \sigma\text{ (N lone pair)} \qquad (25)$$

$$\left.\begin{aligned}\Phi_2 &= \frac{1}{\sqrt{2}}(\psi_2 + \psi_7) \qquad (26)\\ \Phi_3 &= \frac{1}{\sqrt{2}}(\psi_2 - \psi_7) \qquad (27)\end{aligned}\right\}\ \sigma(\mathrm{C}_\alpha\text{–}\mathrm{N})$$

$$\left.\begin{aligned}\Phi_4 &= \frac{1}{\sqrt{2}}(\psi_3 + \psi_6) \qquad (28)\\ \Phi_5 &= \frac{1}{\sqrt{2}}(\psi_3 - \psi_6) \qquad (29)\end{aligned}\right\}\ \sigma(\mathrm{C}_\alpha\text{–}\mathrm{C}_\beta)$$

$$\left.\begin{aligned}\Phi_6 &= \frac{1}{\sqrt{2}}(\psi_4 + \psi_5) \qquad (30)\\ \Phi_7 &= \frac{1}{\sqrt{2}}(\psi_4 - \psi_5) \qquad (31)\end{aligned}\right\}\ \sigma(\mathrm{C}_\beta\text{–}\mathrm{C}_\gamma)$$

$$\left.\begin{aligned}\Phi_8 &= \frac{1}{\sqrt{2}}(\psi_8 + \psi_{12}) \qquad (32)\\ \Phi_9 &= \frac{1}{\sqrt{2}}(\psi_8 - \psi_{12}) \qquad (33)\end{aligned}\right\}\ \sigma(\mathrm{C}_\alpha\text{–}\mathrm{H}_\alpha)$$

$$\left.\begin{aligned}\Phi_{10} &= \frac{1}{\sqrt{2}}(\psi_9 + \psi_{11}) \qquad (34)\\ \Phi_{11} &= \frac{1}{\sqrt{2}}(\psi_9 - \psi_{11}) \qquad (35)\end{aligned}\right\}\ \sigma(\mathrm{C}_\alpha\text{–}\mathrm{H}_\beta)$$

$$\Phi_{12} = \psi_{10} \qquad \sigma(\mathrm{C}_\gamma\text{–}\mathrm{H}_\gamma) \qquad (36)$$

The procedure for calculating $\lambda_{\mathrm{NC}_\alpha}$ is now given.

The σ-electron density on nitrogen is obtained from eq 25–27. Both ψ_2 and ψ_7, given by eq 7, contain ϕ_N; in both cases the coefficient of ϕ_N is $(1/\sqrt{2})(1 + \lambda_{\mathrm{NC}})^{1/2}$. Summing the electron density on nitrogen

$$\begin{aligned} q_{\mathrm{N}\sigma} &= 1 + 4[{}^1/_2(1 + \lambda_{\mathrm{NC}\alpha})] \\ &= 3 + 2\lambda_{\mathrm{NC}\alpha} \end{aligned}$$

Since the σ core of nitrogen in pyridine is four electrons, the charge is $4 - q = 1 - 2\lambda_{\mathrm{NC}\alpha}$. This charge is equated to the Del Ré charge on nitrogen to give for $\lambda_{\mathrm{NC}\alpha}$, +0.07.

Benzene Photosensitization and Direct Photolysis of Cyclobutanone and Cyclobutanone-2-*t* in the Gas Phase[1]

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Abstract: The fluorescence of the $^1\mathrm{B}_{2u}$-state benzene is quenched by cyclobutanone with a quenching cross section ($\pi\sigma^2$) of 4 Å², and this singlet energy transfer produces an excited singlet cyclobutanone which subsequently decomposes to yield primarily ethylene (plus ketene). On the other hand, the $^3\mathrm{B}_{1u}$-state benzene transfers its electronic energy to cyclobutanone with a quenching cross section ($\pi\sigma^2$) of 1 Å² to produce an intermediate which subsequently decomposes to yield a vibrationally excited cyclopropane (plus CO). The yield of cyclopropane is lowered by the addition of *cis*-2-butene which is a quencher of the triplet benzene, and therefore it is proposed that cyclopropane is a characteristic decomposition product of a triplet cyclobutanone. Sensitization quantum yields have been determined, and they are near unity. The comparison of the decomposition product distribution in the benzene-photosensitized samples with that observed at varying excitation energies (wavelength) in the direct photolysis of cyclobutanone indicates that, on the average, about 96 kcal/mole of excitation energy is delivered to cyclobutanone in the singlet energy transfer while about 80–85 kcal/mole of excitation energy is delivered to cyclobutanone in the triplet energy transfer.

The photochemistry of cyclobutanone in the gas phase has been the subject of several investigations. It was first shown in 1942 that photochemically excited cyclobutanone molecules decompose by two primary processes to yield C_2H_4 and CH_2CO (60%) or C_3H_6 and CO (40%),[2a] and only in the later work to

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follow were the quantum yields of these products determined at wavelengths of 3130 and 2654 Å and in the temperature range of 100–300°.[2b] On the basis of the observed pressure dependence and wavelength dependence of the C_3 product yields, it was recently established that propylene is not a primary photodecomposition product but rather the unimolecular decomposition product of the vibrationally excited cyclopropane resulting from the photodecomposition of cyclobutanone.[3,4] Only a small amount of an unidentified photoisomer, which might be 3-butenal, has been found with a quantum yield less than 0.004 in the photolysis of cyclobutanone at 3130 Å,[5] although appreciable amounts of isomeric aldehydes have been found in the photolysis of other cyclic ketones.[6]

In our preliminary report,[7] the involvement of singlet and triplet intermediates in the photodissociation of cyclobutanone has been demonstrated by the mechanistic diagnosis using the benzene photosensitization method.[8–10] In this paper, the detailed study of the mechanistic diagnosis by the fluoresence quenching and the triplet product quenching, the energetics of the intermolecular excitation transfer, the quantum efficiencies for the sensitized decomposition by the singlet and the triplet energy transfer, and the sensitization cross sections will be described. The usefulness of the benzene photosensitization technique in the mechanistic diagnosis of the photochemical reactions in the gas phase will also be examined. In this tracer work relatively more accurate quantum yield data have been obtained than were possible with the benzene photosensitization study of cyclopentanone and cyclopentanone-2-*t*,[8] since cyclobutanone-2-*t* gives mostly volatile hydrocarbon products upon photodecomposition.

Experimental Section

Cyclobutanone (CB) obtained from Chemical Procurement Laboratories, Inc. was used after degassing *in vacuo* but without further purification. An impurity whose retention time was identical with that of methyl ethyl ketone on a Carbowax 20M gas chromatographic column at 60° was present in 0.7%, and another impurity with a longer retention time than methyl ethyl ketone but with a shorter retention time than cyclobutanone was present in 0.4%.

Cyclobutanone-2-*t* (CBT) was prepared by a gas chromatographic isotopic exchange technique developed for the exchange preparation of carbonyl compounds deuterated at the α position.[11] KOH (2.7 g) was dissolved in 50 ml of H_2O, and 27 g of Chromosorb W-HMDS (Johns-Manville Products), 30–60 mesh, was mixed with the KOH solution. The mixture was dried using a vacuum rotary evaporator. The KOH-coated Chromosorb was then mixed with an acetone solution of 2.7 g of Carbowax 6000, and then acetone was removed by a rotary evaporator. The dried Chromosorb coated with KOH and Carbowax 6000 was packed into a 0.25-in. o.d., 10-ft stainless steel tubing. This gas chromatographic column was exchange loaded with tritium by injecting 0.5 ml of tritiated water (100 mCi/g specific activity) at 150°. About 50 μl of cyclobutanone was injected each time into this column, and the tritium-labeled cyclobutanone was collected at liquid nitrogen temperature at the outlet of the column. The labeled cyclobutanone was dried with granular Drierite ($CaSO_4$) *in vacuo*, and it was degassed at about −70° *in vacuo*. The gas chromatographic analysis showed that the impurity with its retention time identical with that of methyl ethyl ketone on a Carbowax 20M column was present in 0.3% only and that the second impurity originally present in the unlabeled cyclobutanone disappeared during the exchange labeling. Liquid scintillation counting equipment (Nuclear-Chicago Model 700 Series with Chroma/Cell detector assembly) was used for the measurement of the specific activity of cyclobutanone-2-*t*. The specific activity of CBT was found to be 0.11 ± 0.01 mCi/mmole. The specific activity of the impurity was slightly lower than that of cyclobutanone-2-*t*; 0.3% of macroscopic impurity contained 0.2% of the total tritium.

Zone Refined Grade benzene (99.999%) and cyclohexane (99.98%) obtained from Litton Chemicals were used. *cis*-2-Butene, propane, ethylene, and propylene were of Research Grade from Phillips Petroleum. These hydrocarbons were used after degassing at liquid nitrogen temperature *in vacuo* but without further purification.

Two photolysis cells were used: a 91.6-ml cylindrical quartz cell with two flat windows, 50-mm o.d. and 50 mm in length with a small freezing tip at the bottom, and a 528-ml cylindrical Vycor cell with a window blown flat at one end, 50-mm o.d. and about 300 mm in length. A T-shaped quartz fluorescence cell, 65 mm long, with a side arm 25 mm long in the center, had three 25-mm diameter flat end windows made of Suprasil high-purity quartz. Gases were handled on a mercury-free and grease-free vacuum line in a manner described earlier.[8] It was necessary in some cases to add unlabeled hydrocarbon carrier gas to recover quantitatively the entire sample for analysis (see Table II).

All of the photolysis runs were made at room temperature (23–25°). Benzene photosensitization was obtained at 2537 Å using 100-W low-pressure mercury resonance lamps; one was a helical lamp (Hanovia SC-2537) and the other was a grid lamp (Mineralight Model R51, Ultra-Violet Products, Inc.). These two lamps gave almost identical spectral distribution, when the radiations below 2300 Å wavelength were cut out by a Corning CS-7-54 filter and then were approximately collimated for the photolysis runs. The useful intensity of the lamps is estimated to be below 1×10^{16} photons/sec over an area of approximately 12 cm². For direct photolysis at wavelengths other than 2537 Å, a high-intensity monochromator (Bausch and Lomb, Model No. 5, 7.4-mμ/mm dispersion) with a 200-W mercury arc lamp (Osram HBO 200) was used.

Fluorescence excitation at 2537 Å was made with a small mercury resonance lamp (Pen-Ray Model 11, SC-1c, Ultra-Violet Products, Inc.). The radiations below 2300-Å wavelength were cut out by a Corning CS-7-54 filter and the filtered radiations were collimated to about 13-mm diameter before entering the fluorescence cell kept at 23°. The fluorescence emission was monitored using a flat end window photomultiplier tube (EMI 9526 S), a Bausch & Lomb monochromator (Model No. 5), a high-voltage dc power supply (Power Designs, HV-1565), and an "Electrometer" (Keithley, 610 BR).

Analyses of liquid samples (ketones and aldehydes) were made with a WX-filament thermal conductivity detector (Hewlett-Packard gas chromatograph, Model 700) using a 0.25-in. o.d., 15-ft Carbowax 20M column (5.0% on 30–60 mesh Chromosorb G-DMCS AW). Analyses of volatile products, labeled and unlabeled, were made with a conventional radio gas chromatography set-up.[12] Greater than 99% of the observed hydrocarbon products were present as C_2H_3T, C_3H_5T, and c-C_3H_5T, although the analysis of CHTCO was not possible with the existing experimental set-up. Macroscopic (nonradiochemical) product yields were monitored by a thermistor thermal conductivity detector (Microdetector System Model 1000, Carle Instruments), and the radiochemical yields were monitored by a Dyna-Print (EFCO Systems, Inc.). The separation of hydrocarbon products was made at room temperature on a 0.25 in. o.d., 60-ft dimethylsulfolane column (35% by weight on 30–50 mesh Chromosorb P-HMDS).

The quantum counting of the excited benzenes produced in the system was made through the actinometry technique developed by

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Table I. Specific Activities of Decomposition Products (23°)[a]

Sample no.	Gas pressure, mm C_6H_6	Gas pressure, mm CBT	Wave-length, Å	Specific activity, 10^{10} dpm/mole[b] C_2H_3T	Specific activity, 10^{10} dpm/mole[b] C_3H_5T	Specific activity, 10^{10} dpm/mole[b] c-C_3H_5T	SAR[c] (C_2H_3T/c-C_3H_5T)
3	...	10.0	3130	13.0 ± 0.3	21 ± 3	25.4 ± 0.5	0.51 ± 0.02
8	...	11.0	2537	13.2 ± 0.3	22.8 ± 0.5	25.1 ± 0.5	0.53 ± 0.02
9	...	11.0	2537	13.1 ± 0.3	22.9 ± 0.5	25.0 ± 0.5	0.52 ± 0.02
12	2.5	1.0	2537	13.5 ± 1.8	23 ± 7	25.9 ± 0.8	0.54 ± 0.06
17	2.5	1.0	2537	14.3 ± 1.5	24 ± 4	26.3 ± 0.6	0.54 ± 0.06
19	2.5	1.0	2537	...	22 ± 1	25.6 ± 0.7	...
47	2.5	1.0	2537	14.3 ± 0.7	23.6 ± 1.5	25.7 ± 0.6	0.56 ± 0.03
118	2.5	1.0	2537	12.8 ± 0.9	25 ± 5	25.6 ± 1.0	0.50 ± 0.04
Average[d]	2.5	1.0	2537	13.7 ± 0.6	24 ± 3	25.8 ± 0.5	0.53 ± 0.01

[a] The specific activity of CBT has been measured with a liquid scintillation counter, and it is 0.114 ± 0.010 Ci/mole, or (25 ± 2) × 10^{10} dpm/mole. [b] The specific activity of ethylene-*t*, propylene-*t*, and cyclopropane-*t* has been determined through radioactivity measurements coupled with mass peak measurements (area counts measured by a Disc integrator in gas chromatography). The molar responses of ethylene, propylene, and cyclopropane were 0.652, 0.845, and 0.815, respectively, as compared to that of *cis*-2-butene where the thermistor detector was used. [c] It is the specific activity ratio of ethylene-*t* to cyclopropane-*t*. [d] Average of five runs with benzene.

Cundall, *et al.*,[13] and the quantum yield of *trans*-2-butene from *cis*-2-butene by the benzene photosensitization was taken to be 0.33 on the basis of recent measurements.[14] For series of measurements, one or two quantum counting monitor runs were made with benzene pressure identical with that of the samples of interest and *cis*-2-butene pressure of 2.0 mm.

Results

The linear dependence of hydrocarbon yields from the benzene photosensitization (C_2H_3T, C_3H_5T, and c-C_3H_5T) with respect to irradiation time was obtained within the limit of the over-all experimental error (~5%) for a series of runs in which the pressures of benzene and cyclobutanone-2-*t* (CBT) were maintained at 2.5 and 1.0 mm, respectively, and the intensity of the photochemical lamp was held constant. For example, the total volatile product yield for the longest irradiated sample (60 min) was 5%, and the time-average rate of the cyclopropane-*t* formation for the 60-min irradiation was 0.95 ± 0.03 as compared to that for the 1-min irradiation of 1.00.

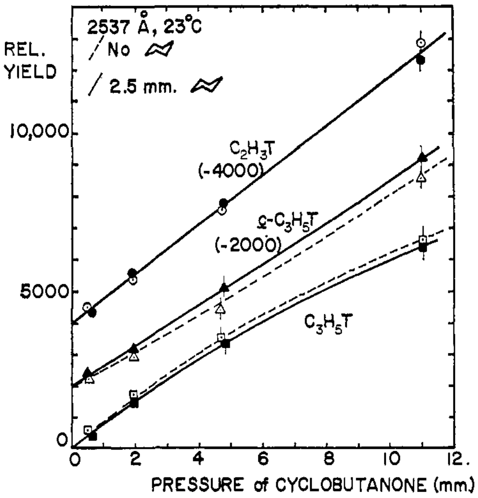

Figure 1. Relative yields of C_2H_3T, C_3H_5T, and c-C_3H_5T in the absence (broken line) and in the presence (solid line, 2.5 mm) of cyclohexane, expressed in arbitrary units, *vs.* pressure of cyclobutanone in mm at a constant light intensity, 23°, and 2537 Å.

The molar extinction coefficient of benzene at 2537 Å is about 80 as compared to 7 for that of cyclobutanone at 2537 Å,[1,15] and the light absorption by cyclobutanone is not negligible compared to that by benzene under typical experimental conditions of this work. Therefore, it is necessary to subtract the contribution of product yields obtained through the direct photolysis of cyclobutanone from the observed product yields, in order to evaluate the product yields attributable to the benzene photosensitization. For this purpose, the yields of hydrocarbon products were measured for specified conditions of time and lamp intensity of 2537 Å, and the relative yields of three products are shown as a function of cyclobutanone pressure in Figure 1. The yields in the presence of 2.5 mm of cyclohexane were also measured, since cyclohexane can be assumed to have an ability approximately equal to that of benzene in removing the excess vibrational energy of the excited singlet molecule, as has been shown for the case of the singlet excited benzene.[9,15] There is no apparent effect of cyclohexane on the C_2H_3T yield, but there is definitely an increase of the cyclopropane-*t* by collisional stabilization at the expense of the propylene-*t* yield, as expected from the previous work.[3,4] In evaluating the direct photolysis yields in the benzene photosensitization experiments, the pressure dependent yields obtained with 2.5 mm of cyclohexane were used for the corrections in the 2.5-mm benzene samples. In general, the assumption of Beer's law appears to be valid for the pressure ranges covered in these experiments.

Measurements of the specific activities of the reactants and the products often provide vital information concerning the mass balance for the reaction, if a radioactive tracer technique is employed in the chemical investigation. In the photolysis of a low specific activity CBT (0.11 mCi/mmole), it is expected that the specific activities of CBT, C_3H_5T, and c-C_3H_5T are identical and those of C_2H_3T and CHTCO are one-half of the specific activity of the CBT, if no tritium isotope effect were

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(13) (a) R. B. Cundall, F. J. Fletcher, and D. G. Milne, *Trans. Faraday Soc.*, **60**, 1146 (1964); (b) R. B. Cundall and A. S. Davies, *ibid.*, **62**, 1151 (1966). These authors reported the quantum yield of *trans*-2-butene from *cis*-2-butene as 0.36 and the *trans*/*cis* branching ratio of 1.37 at 2537 Å.

(14) W. A. Noyes, Jr., and D. A. Harter, *J. Chem. Phys.*, **46**, 674 (1967). In this work, the wavelength dependence of the *trans*-2-butene quantum yields has been determined. We have chosen this value to be 0.33 as a reasonable interpolated value at 2537 Å, using the *trans*/*cis* branching ratio of 1.02 as measured in our laboratory; see G. A. Haninger, Jr., and E. K. C. Lee, *J. Phys. Chem.*, **71**, 3104 (1967).

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Table II. Product Distribution from Cyclobutanone Decomposition by Benzene Photosensitization (2537 Å and 23°)

Sample no.[a]	Sample gas pressures, mm C_6H_6	CBT	C_3H_6	Irradiation time, min	Analysis carrier gas
B 68	2.47	11.0	0.17	1.00	...
A 123	2.55	11.0	...	10.0	...
C 168	2.47	11.0	...	10.0	C_2H_4
C 167	2.53	5.9	...	10.0	C_2H_4
B 66	2.47	5.0	0.17	1.00	...
A 122	2.50	4.6	...	10.0	...
D 135	2.49	3.1	...	10.0	C_3H_8
C 165	2.47	2.5	...	10.0	C_2H_4
B 65	2.47	2.0	0.18	1.00	...
A 120	2.57	1.8	...	10.0	...
D 134	2.60	1.0	...	10.0	C_3H_8
C 164	2.47	0.73	...	10.0	C_2H_4
D 131	2.51	0.65	...	10.0	C_3H_8
D 132	2.47	0.51	...	10.0	C_3H_8
A 119	2.47	0.50	...	10.0	...
B 63	2.56	0.49	0.16	1.00	...
E 99	1.15	0.42	...	10.0	...
E 111	1.18	0.26	...	10.0	...
E 110	1.18	0.175	...	10.0	...
E 95	1.15	0.105	...	10.0	...
E 96	1.13	0.080	...	10.0	...
E 108	1.18	0.065	...	11.0	...
E 98	1.15	0.055	...	10.0	...
E 107	1.18	0.050	...	10.0	...

Sample no.[a]	Obsd activity yield (10^3 counts)[b] C_2H_4	C_3H_6	c-C_3H_6	Sensitization yield (10^3 counts)[c] C_2H_4	C_3H_6	c-C_3H_6	Sensitization quantum yield (Φ)[d] C_2H_4	C_3H_6	c-C_3H_6
B 68	3.84	1.15	5.41	2.80	0.39	4.56	0.39	0.030	0.32
A 123	5.48	1.92	8.65	3.72	0.62	7.21	0.30	0.028	0.30
C 168	5.56	1.67	7.68	3.95	0.49	6.36	0.36	0.025	0.30
C 167	4.51	1.44	8.56	3.65	0.72	7.85	9.32	0.036	0.36
B 66	2.56	0.92	5.47	2.08	0.51	5.08	0.29	0.039	0.36
A 122	3.76	1.34	9.27	3.02	0.69	8.67	0.25	0.031	0.37
D 135	3.20	1.12	9.59	2.72	0.68	9.20	0.23	0.032	0.40
C 165	2.94	0.90	9.34	2.57	0.53	9.03	0.23	0.027	0.42
B 65	1.54	0.60	5.70	1.35	0.42	5.55	0.19	0.032	0.39
A 120	2.28	9.90	11.03	1.99	0.62	10.80	0.157	0.029	0.45
D 134	1.65	0.66	11.28	1.49	0.51	11.15	0.122	0.024	0.47
C 164	1.23	0.57	10.37	1.12	0.46	10.28	0.101	0.024	0.48
D 131	1.20	0.47	11.09	1.10	0.36	11.01	0.092	0.017	0.48
D 132	0.94	0.38	10.38	0.86	0.29	10.32	0.074	0.014	0.46
A 119	0.95	0.49	10.66	0.87	0.40	10.59	0.072	0.019	0.45
B 63	0.56	0.26	4.35	0.51	0.21	4.31	0.069	0.016	0.30
E 99	1.36	0.80	15.20	1.14	0.56	15.06	0.070	0.020	0.48
E 111	0.86	0.56	13.42	0.74	0.43	13.34	0.050	0.016	0.47
E 110	0.58	0.42	11.76	0.50	0.33	11.71	0.034	0.013	0.41
E 95	0.48	0.36	10.61	0.43	0.30	10.58	0.026	0.010	0.34
E 96	0.30	0.30	9.17	0.26	0.25	9.14	0.016	0.009	0.30
E 108	0.32	0.20	8.51	0.29	0.17	8.49	0.018	0.006	0.27
E 98	0.23	0.22	7.55	0.20	0.19	7.53	0.012	0.007	0.24
E 107	0.16	0.19	6.78	0.14	0.16	6.76	0.010	0.006	0.24

[a] A quartz cell with 91.6-ml volume was used in series A–D, while a Vycor cell with 528-ml volume was used in series E. [b] Unit count corresponds to 0.83 dpm, and the following statistical errors result in the activity measurements: 9000 ± 100, 4000 ± 70, 1000 ± 40, 500 ± 30, and 200 ± 30. [c] The sensitization yield is obtained by subtracting the direct photolysis yield contribution as obtained from calibration runs in which benzene was absent but otherwise the same. The errors in the sensitization yield are slightly greater than those shown in footnote *b*: 9000 ± 120, 4000 ± 100, 1000 ± 50, and 200 ± 40. [d] The sensitization quantum yields were calculated on the basis of the quantum yield of *trans*-2-butene as being 0.33 in the benzene-photosensitized *cis–trans* isomerization of *cis*-2-butene. The nonradiochemical value of quantum yield was calculated by the appropriate use of the sensitization activity yield, the corresponding specific activity of each component, and the degree of *cis–trans* isomerization of *cis*-2-butene observed in the actinometry runs which had been sandwiched between series of samples. Unit quantum yield of cyclopropane-*t* corresponds to the following average value for each series of runs: (A) 23,800 counts; (B) 14,200 counts; (C) 21,400 counts; (D) 23,500 counts; (E) 30,200 counts. These values simply indicate the variations in the photon flux, photolysis time, benzene pressure, and volume of the cell.

assumed as a first approximation. Table I shows the values of specific activities of three hydrocarbon products resulting from the decomposition of the excited CBT molecules produced in the direct photolysis at 3130 and 2537 Å, as well as in the benzene photosensitization at 2537 Å. In general, the specific activity measurements for the benzene photosensitization samples were not as accurate as those obtained for the direct photolysis samples, since the conversion was lower in the former than in the latter, and the average of five runs was tabulated for the former. It is clear that the observed specific activities are equal to the expected, first approximation value within the experimental error.

For the mechanistic diagnosis of the cyclobutanone photodecomposition, a test similar to that employed for the study of the cyclopentanone was used.[7,8] Product

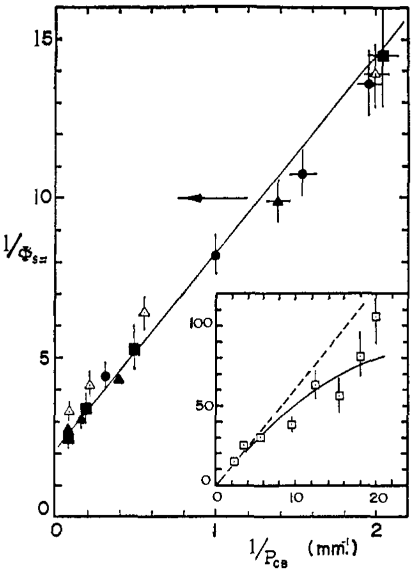

Figure 2. The reciprocal of the benzene photosensitization quantum yield of ethylene as a singlet product *vs.* the reciprocal of cyclobutanone pressure in mm^{-1}: series A, with no carrier for analysis and no additive gas (△); series B, with C_3H_6 as additive (■); series C, with C_2H_4 as carrier (▲); series D, with C_3H_8 as carrier (●); and series E, with no carrier and no additive (□). $P(C_6H_6)$ for series A–D is 2.5 mm and that for series E is 1.2 mm at 23°.

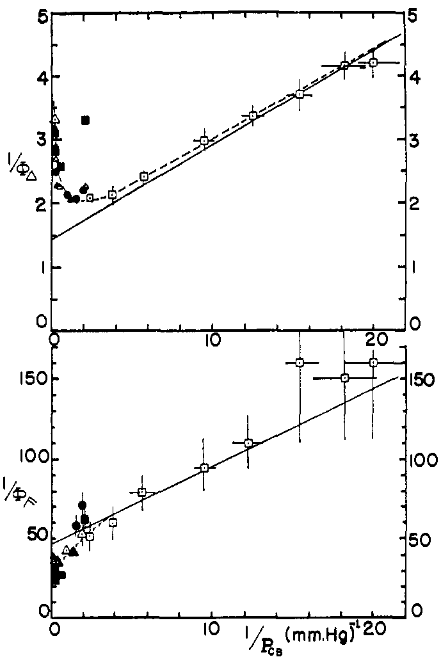

Figure 3. The reciprocal of the benzene photosensitization quantum yield of cyclopropane *vs.* the reciprocal of cyclobutanone pressure in mm^{-1} (upper part). The reciprocal of the benzene photosensitization quantum yield of propylene *vs.* the reciprocal of cyclobutanone pressure in mm^{-1} (lower part). The symbols used here for various experimental conditions are identical with those in Figure 2.

distribution from the benzene-photosensitized decomposition of cyclobutanone at 2537 Å is tabulated in Table II. In series A–D, benzene pressure was held at 2.5 mm, while CBT pressure was made to vary between 0.49 and 11.0 mm. In series E, benzene pressure was held at 1.2 mm, while CBT pressure was made to vary between 0.42 and 0.050 mm. It can be seen from the results tabulated in Table II that the direct photolysis yields of labeled product diminish substantially as the CBT pressure is reduced, and the magnitude of the uncertainty in the sensitized quantum yield is indicated in the Stern–Volmer plots (Figures 2 and 3).

In order to confirm the singlet sensitization from which C_2H_3T is produced, the quenching of the fluorescence of benzene ($^1B_{2u}$) by cyclobutanone was studied, and the results are shown in Table III. It is seen that the fluorescence is quenched in increasing degree with the increasing pressure of cyclobutanone. Assuming the proportionality between the photocurrent due to the emission and the intensity of the benzene fluorescence emission, i_0/i can be equated to f_0/f, where i_0 and i are the net photocurrent due to the observation of benzene emission in the absence and in the presence of cyclobutanone, respectively, and f_0 and f are the corresponding benzene fluorescence yields.

It can be shown that the yield of C_2H_3T in the benzene-photosensitized samples is not affected by the addition of *cis*-2-butene, but the yields of C_3H_5T and *c*-C_3H_5T are gradually lowered by the addition of *cis*-2-butene in increasing amounts. This product quenching by *cis*-2-butene[10,13,14] is an indication of the triplet benzene sensitization of the CBT, and the pertinent results are tabulated in Table IV.

The wavelength dependence of product distribution in the direct photolysis is shown in Table V. Except for two samples all the measurements were made at relatively constant pressure (9.5–11.0 mm of CB), since the ratio of C_3H_6 to *c*-C_3H_6 is pressure dependent as well. This ratio increases with the decrease in the wavelengths of excitation, as expected. The results obtained from the benzene photosensitization in the presence of 11 mm of cyclohexane are shown in Table VI, which will be useful later for the excitation energy calculation.

Discussion

A. Singlet Sensitization. The $^1B_{2u}$ benzene possesses about 4 kcal/mole of excess vibrational energy when it is produced by absorption of the 2537-Å Hg resonance line, and it relaxes quickly to its ground vibrational state by collisional deactivation processes.[16] These two initial photophysical processes can be expressed as

$$C_6H_6 + h\nu\ (2537\ \text{Å}) \longrightarrow {}^1C_6H_6^* \qquad (1a)$$

$$^1C_6H_6^* + M \longrightarrow {}^1C_6H_6 + M \qquad (1b)$$

where superscript 1 denotes the electronic multiplicity of the excited singlet benzene, the asterisk indicates that the excited benzene has some vibrational excitation energy (4 kcal/mole), and M denotes the collisional deactivator which removes the vibrational energy of the excited singlet benzene.

Three unimolecular and two bimolecular processes shown below adequately describe the fate of the $^1C_6H_6$

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(16) The intensity of a resonance fluorescence line of benzene at 2617 Å is less than 4% of the total emission intensity of 0.5 mm of benzene pressure, and it is further reduced to 1% of the total if 5 mm of cyclohexane is added. This observation is consistent with the result obtained by Kistiakowsky and Parmenter,[15] and for all practical purposes this singlet benzene responsible for the photosensitization at 2537 Å is in its ground vibrational state (E = 109 kcal/mole), since only 11 collisions with the ground-state benzene are required to remove the excess vibrational energy of the singlet benzene: M. Stockburger, paper presented at the International Conference on Photochemistry, Munich, Germany, Sept 6–9, 1967.

Table III. Quenching of Benzene Fluorescence by Cyclobutanone[a]

Gas pressure (mm)				
C_6H_6	2.5	2.5	2.5	2.5
Cyclobutanone	1.0	2.1	3.0	4.0
i_0 (10^{-9} A)[b]	2.29	2.27	2.29	2.27
i (10^{-9} A)[c]	1.72	1.36	1.13	0.97
i_0/i	1.33 ± 0.04	1.67 ± 0.05	2.02 ± 0.06	2.34 ± 0.08

[a] Benzene fluorescence was excited by the 2537-Å mercury resonance line at 23°, and the fluorescence emission bands were viewed at 280 mμ with a 15-mμ spectral band width. The dark current of the photomultiplier was 0.080 × 10^{-9} A at 500 V. [b] $i_0 = i_{\text{obsd}} - i_{\text{dark}} - i_{\text{cell}}$, where i_{obsd} is the observed photomultiplier current with benzene alone in the cell, i_{dark} is the photomultiplier dark current, and i_{cell} (0.10 × 10^{-9} A) is the net observed photocurrent with an empty cell, which arises from the scattered radiation due to the weak fluorescence of the high-purity quartz cell material. Thus i_0 is the photocurrent due to the benzene emission. [c] $i = i'_{\text{obsd}} - i_{\text{dark}} - i_{\text{cell}}$, where i'_{obsd} is the observed photomultiplier current with both benzene and cyclobutanone in the cell and i_{dark} and i_{cell} are the same as in footnote *b*. Thus i is the photomultiplier current due to the benzene emission in the presence of cyclobutanone.

Table IV. Quenching of the Triplet Energy Transfer (Benzene to Cyclobutanone) by *cis*-2-Butene[a]

Sample no.	137	138	139	140	141
Gas pressure, mm					
C_6H_6	1.18	1.18	1.20	1.17	1.19
CBT	0.436	0.444	0.444	0.444	0.436
cis-C_4H_8	0	0.070	0.200	0.423	0.94
Irrad time, min	20	60	60	60	60
Obsd activity (10^3 counts)					
C_2H_3T	2.68	7.53	7.50	7.34	7.15
C_3H_5T	1.51	3.80	3.68	3.29	2.92
c-C_3H_5T	27.00	49.75	32.39	20.85	13.28
Obsd isomers (10^3 area counts)					
cis	...	111.0	319.5	683.0	1508.0
trans	...	3.33	6.28	8.03	10.77
Sensitized activity yields (10^3 counts)[b]					
C_2H_3T	6.83	6.32	6.29	6.13	5.94
C_3H_5T	3.22	2.49	2.37	1.98	1.61
c-C_3H_5T	80.25	48.44	31.64	20.10	12.53
Triplet yield of *c*-C_3H_5T (10^3 counts)[c]	76.8 ± 1.4	45.6 ± 1.1	28.2 ± 1.1	16.7 ± 1.0	9.13 ± 1.0
$(\Phi_{T\Delta})_0/(\Phi_{T\Delta})$[d]	(1.00)	1.68 ± 0.06	2.72 ± 0.14	4.6 ± 0.3	8.4 ± 1.0
Sensitized *trans*-2-C_4H_8 yields (10^3 counts)[e]	...	3.20 ± 0.30	5.84 ± 0.30	6.76 ± 0.30	8.00 ± 0.40

[a] A 528-ml Vycor cell was used for irradiation at 2537 Å. [b] This is the normalized sensitization activity yield for 60 min, 1.20 mm of C_6H_6, and 0.44 mm of cyclobutanone-*t*. For this normalized condition, the contribution from the direct photolysis has been estimated as follows: C_2H_3T, 1210 ± 200; C_3H_5T, 1310 ± 200; and *c*-C_3H_5T, 750 ± 200. [c] The singlet sensitization yield of 3400 counts has been subtracted from the sensitization activity yield to obtain the triplet sensitization yield of *c*-C_3H_5T (see Table VII). [d] This ratio is obtained by dividing the triplet sensitization yield of sample no. 137 by that of other samples, and it represents the inverse of the relative triplet quantum yield of *c*-C_3H_5T for each sample as compared to the unquenched sample (no. 137). [e] The sensitization yield of *trans*-2-butene is obtained after correcting for the initial impurity level of *trans*-2-butene in *cis*-2-butene (0.20%) and for a small fraction of *trans*-2-butene which had undergone *trans*-to-*cis* isomerization during the photolysis period.

Table V. Wavelength Dependence of Product Distribution in the Direct Photolysis (23°)

		Photolysis[a]		Observed activity (10^3 counts)[c]			Ratios[d]	
Sample	Cyclobutanone, mm	Wavelength, Å[b]	Time, min	C_2H_3T	C_3H_5T	*c*-C_3H_5T	C_3H_6/*c*-C_3H_6	(C_3H_6 + *c*-C_3H_6)/C_2H_4
142	10.8	3180	30	142.6	6.05	105.6	0.063 ± 0.002	0.41 ± 0.01
143	11.0	3180	10	47.7	1.67	36.0	0.051 ± 0.002	0.41 ± 0.01
2	9.5	3130	30	83.3	3.51	60.4	0.064 ± 0.002	0.40 ± 0.01
3	10.0	3130	30	49.6	1.86	37.3	0.055 ± 0.002	0.42 ± 0.01
182	4.2	3130	15	13.4	1.01	11.4	0.10 ± 0.01	0.49 ± 0.02
185	4.2	3130	10	47.1	4.00	36.4	0.12 ± 0.01	0.45 ± 0.02
144	11.0	2800	30	14.2	4.56	12.2	0.41 ± 0.01	0.63 ± 0.01
145	11.0	2800	30	13.9	4.65	12.5	0.41 ± 0.01	0.66 ± 0.01
8	11.0	2537	60	159.4	113.4	115.3	1.08 ± 0.01	0.78 ± 0.01
9	11.0	2537	60	156.7	112.5	113.3	1.09 ± 0.01	0.79 ± 0.01
147	11.0	2480	..	17.7	17.4	11.9	1.60 ± 0.03	0.92 ± 0.02
156	11.0	2480	30	2.90	2.96	1.95	1.61 ± 0.03	0.94 ± 0.02

[a] A quartz cell with 91.6-ml volume was used. [b] Wavelength accuracy is about 60 Å (spectral slit width), except at 2537 Å. [c] Unit count corresponds to 0.83 dpm. [d] This nonradiochemical ratio was calculated from the relative amounts of each macroscopic component, and the latter was obtained by dividing the observed activity by the specific activity of each component.

Table VI. Triplet Component Yields of Propylene and Cyclopropane in Benzene Photosensitization[a]

Sample no.	175	176
Cyclobutanone, mm	0.105	0.105
Benzene, mm	1.18	1.18
Cyclohexane, mm	11.0	11.0
Obsd yields, counts		
C_2H_3T	670 ± 30	610 ± 30
C_3H_5T	270 ± 30	260 ± 30
c-C_3H_5T	19,750 ± 150	19,700 ± 150
C_2H_3T		
Direct	100 ± 20	100 ± 20
Singlet	570 ± 40	510 ± 40
C_3H_5T		
Direct	80 ± 20	80 ± 20
Singlet	90 ± 20	80 ± 20
Triplet	100 ± 70	100 ± 70
c-C_3H_5T		
Direct	80 ± 20	80 ± 20
Singlet	400 ± 100	360 ± 90
Triplet	19,270 ± 300	19,620 ± 300
$\frac{\text{Triplet } C_3H_6}{\text{Triplet } c\text{-}C_3H_6} = \left(\frac{\Phi_{T\wedge}}{\Phi_{T\Delta}}\right)^b$	0.006 ± 0.004	0.006 ± 0.004

[a] Photolysis was carried out with a Vycor cell (528 ml) at 2537 Å and 23° for 20 min. [b] This nonradiochemical ratio was calculated with the use of known specific activities of each isotopic molecule.

in the system (reactions 2–6), where CB denotes cyclobutanone, and superscript 1 and an asterisk indicate the electronic multiplicity and the vibrational excitation of CB, respectively. The location of the first excited singlet state of cyclobutanone has been estimated to be about 88 kcal/mole above the ground state.[17] Thus the exothermicity of reaction 6 can be estimated to be about 21 kcal/mole. This excited singlet cyclobutanone eventually decomposes to ethylene and ketene, is stabilized by an unknown mechanism, or gives rise to an intermediate (X) which will not yield ethylene and ketene.[18]

(a) fluorescence $^1C_6H_6 \longrightarrow C_6H_6 + h\nu$ (2)
(b) isomer formation $^1C_6H_6 \longrightarrow C_6H_6$ (isomer) (3)
(c) intersystem crossing $^1C_6H_6 \longrightarrow {}^3C_6H_6$ (4)
(d) self-quenching $^1C_6H_6 + C_6H_6 \longrightarrow 2C_6H_6$ (5)
(e) singlet sensitization $^1C_6H_6 + CB \longrightarrow C_6H_6 + {}^1CB^*$ (6)

$$^1CB^* \longrightarrow \begin{cases} C_2H_4 + CH_2CO & (7a) \\ CB & (7b) \\ X & (7c) \end{cases}$$

$$\frac{f_0}{f} = 1 + \frac{k_6}{k_2 + k_3 + k_4 + k_5(C_6H_6)}(CB) \qquad (I)$$

$$\frac{1}{\Phi_{S=}} = \frac{1}{n_{S=}}\left[1 + \frac{k_2 + k_3 + k_4 + k_5(C_6H_6)}{k_6(CB)}\right] \qquad (II)$$

A detailed kinetic analysis of benzene photosensitization system analogous to this system has been described earlier,[8] and only the final result from such analysis will be used here. The two Stern–Volmer formulas (eq I and II) can be used to relate the fluorescence quenching by cyclobutanone and the complementary increase in the ethylene yield quantitatively, where f_0 is the benzene fluorescence yield in the absence of cyclobutanone, f is the benzene fluorescence in the presence of varying amounts of cyclobutanone, $\Phi_{S=}$ is the sensitization quantum yield of ethylene, $n_{S=}$ is the quantum efficiency for producing ethylene (or $\Phi_{S=}$ at infinite pressure of CB), and k's are the respective individual rate constants for the listed processes. The plot of f_0/f as a function of cyclobutanone pressure, from the data in Table III, gives a straight line confirming the Stern–Volmer eq I, indicating that the half-quenching pressure for the $^1B_{2u}$ benzene is 3.0 mm of cyclobutanone. Furthermore, Figure 2 shows that the experimental data on the sensitized quantum yield of ethylene confirm the fit to the Stern–Volmer eq II, indicating that the half-pressure is also 3.0 mm of CB. Therefore the values of singlet quenching constants, $K_S = k_6/k_2 + k_3 + k_4 + k_5(C_6H_6)$, obtained through the use of eq I and II agree very well, and this check provides *sufficient evidence for the proposed singlet energy-transfer mechanism.* The quantum efficiency for ethylene production, $n_{S=}$, is 0.49, and it should be noted in Figure 2 that at a very low pressure of CB the sensitized quantum yield of ethylene is somewhat higher than that expected from the values obtained at higher pressures. This means that there must be an additional source of ethylene, but it is only of minor importance.

If one uses the lifetime of the $^1B_{2u}$ benzene in this system to be 0.59 μsec, $(k_2 + k_3 + k_4)$ being 1.72×10^6/sec,[19] and $k_5 = 4.6 \times 10^{-13}$ cm^3/(molecule sec),[9] the value of k_6 can be calculated to be 1.76×10^{-11} cm^3/(molecule sec). This calculated value of k_6 then yields the "effective" quenching cross section for the singlet energy transfer by reaction 6 to be 1.3 Å^2 or the $\pi\sigma^2$ quenching cross section of 4.0 Å^2 for reaction 6. It is significant to note that almost an identical quenching cross section has been observed for the quenching of the singlet benzene by cyclopentanone,[8] while the quenching cross sections of O_2 and biacetyl are greater than that of cyclobutanone by a factor of only 2.[9]

B. Triplet Sensitization. The quantum yield determination of the intersystem crossing of the $^1B_{2u}$ state benzene to the triplet state benzene *via* reaction 4 has been the subject of several investigations,[9,13,14,20,21] and the best current estimate for this value is 0.72 ± 0.07.[21] The electronic state of benzene which is responsible for the sensitized *cis–trans* isomerization of 2-butenes and for the sensitized phosphorescence emission from biacetyl has been assigned to the $^3B_{1u}$ state benzene.[9,10,13,14]

The disappearance of triplet benzene can be accounted for by the two intersystem crossing processes and one sensitization process (eq 8–10), where superscript 3 denotes the electronic multiplicity, and the asterisk indicates that CB possesses some vibrational excitation

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(17) The short wavelength limit of 3200 Å for the cyclobutanone fluorescence at 77°K in EPA and the longer wavelength limit of the absorption at 3300 Å allow an estimate of 3250 Å for the assignment of 0–0 band of the singlet–singlet n → π* transition.[4a]

(18) N. E. Lee, H. O. Denschlag, and E. K. C. Lee, direct photolysis results obtained in our laboratory, to be published. This work confirms that the first excited singlet cyclobutanone undergoes an internal conversion and the vibrationally excited, ground singlet gives rise to ethylene and ketene upon unimolecular decomposition. Since the rates of the internal conversion and the decomposition are extremely fast compared to the collisional stabilization below 100 mm, reaction 7a is only a simplified mechanism.

(19) J. W. Donovan and A. B. F. Duncan, *J. Chem. Phys.*, **35**, 1389 (1961). A justification for the use of this value can be found in ref 10.

(20) W. A. Noyes, Jr., and C. S. Burton, paper presented at the International Conference on Photochemistry, Munich, Germany, Sept 6–9, 1967, and references therein.

(21) S.-Y. Ho and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **89**, 5091 (1967).

(a) unimolecular conversion $^3C_6H_6 \longrightarrow C_6H_6$ (8)

(b) self-quenching $^3C_6H_6 + C_6H_6 \longrightarrow 2C_6H_6$ (9)

(c) triplet sensitization $^3C_6H_6 + CB \longrightarrow C_6H_6 + {}^3CB^*$ (10)

energy. The quantum yield for phosphorescence is negligible as compared to the quantum yields of reactions 8 and 9, since the phosphorescence emission due to the triplet benzene in the gas phase has not been observed, and therefore the phosphoresence process in the above mechanism has been omitted. The $^3CB^*$ will eventually disappear by the following unimolecular mechanism

$$^3CB^* \longrightarrow c\text{-}C_3H_6^* + CO \qquad (11a)$$

$$\longrightarrow CB \qquad (11b)$$

where the asterisk indicates some degree of vibrational excitation on the product molecule of cyclopropane since this decomposition reaction (11a) is exothermic by at least 60 kcal/mole. Some of the excited cyclopropanes might have enough vibrational energy, above 65 kcal/mole (the activation energy for the decomposition of cyclopropane), and they will isomerize to propylene unless collisionally stabilized as shown below[4]

$$c\text{-}C_3H_6^* + M \longrightarrow c\text{-}C_3H_6 \quad k_s \qquad (12a)$$

$$c\text{-}C_3H_6^* \longrightarrow C_3H_6 \quad k_d \qquad (12b)$$

where M is the collisional deactivator molecule in the system, k_s is the rate of stabilization (a function of the pressure of M), and k_d is the unimolecular rate constant for isomerization (a function of the energy of c-$C_3H_6^*$).

The expression for the sensitized quantum yield of the sum of the triplet products (c-C_3H_6 and C_3H_6) as a function of the pressure of CB can be expressed in a Stern–Volmer form, as has been shown for the case of the benzene–cyclopentanone system[8]

$$\frac{1}{\Phi_T} = \frac{1}{n_T}\left[1 + \frac{k_2 + k_3 + k_5(C_6H_6) + k_6(CB)}{k_4}\right] \times \left[1 + \frac{k_8 + k_9(C_6H_6)}{k_{10}(CB)}\right] \qquad (III)$$

where Φ_T is the sensitized quantum yield of the triplet products, n_T is the quantum efficiency for the triplet product formation (a measure of $k_{11a}/[k_{11a} + k_{11b}]$), and k's are the appropriate rate constants for the reactions involved. At low pressure of CB, the first bracketed term will be almost independent of the CB pressure, since $k_6(CB)$ will be small compared to $k_2 + k_3 + k_5(C_6H_6)$, and it is the reciprocal of the fraction of the $^1B_{2u}$ which intersystem-crosses; this simplification at low pressure yields a Stern–Volmer relationship for $1/\Phi_T$ *vs.* 1/CB. The triplet quenching constant is $K_T = k_{10}/[k_8 + k_9(C_6H_6)]$, and it is the reciprocal of the half-pressure for the triplet energy transfer. If the total pressure of the gases in the system is approximately constant at low CB pressure to ensure the constancy of the stabilization to the isomerization (k_s/k_d), then the Stern–Volmer relation (eq III) would be obeyed individually by the yield of cyclopropane as well as by that of propylene. For both, the half-quenching pressure (K_T^{-1}) is 0.103 mm of CB as shown in Figure 3. This value of K_T^{-1} and the actual lifetime of the triplet benzene at 2.5 mm of benzene of about 70 μsec[22,23] give the value of $k_{10} = 4.2 \times 10^{-12}$ cm^3/(molecule sec) and the $\pi\sigma^2$ quenching cross section of 1 Å^2 for reaction 10.

The following kinetic data can be obtained in the low CB pressure range. The limiting values of the triplet sensitization quantum yields obtained by the extrapolation to the infinite CB pressure as indicated by solid lines in Figure 3 are $\Phi_{T\triangle}{}^{\infty} = 0.69 \pm 0.05$ for cyclopropane, $\Phi_{T\wedge\!\setminus}{}^{\infty} = 0.022 \pm 0.005$ for propylene, and $\Phi_T{}^{\infty} = \Phi_{\triangle}{}^{\infty} + \Phi_{T\wedge\!\setminus} = 0.71 \pm 0.06$ for the sum of the two. This value of $\Phi_T{}^{\infty} = 0.71$ is in good agreement with the expected value of 0.72 as the upper limit of the triplet sensitization yield.[21] This means that the quantum efficiency value, n_T, is almost unity, and therefore the ^3CB produced by the triplet benzene sensitization yields finally a vibrationally excited cyclopropane (c-$C_3H_6^*$) with almost 99% efficiency.

C. Sensitization above 0.3 mm. Approximately 10% of the $^1B_{2u}$ benzene is removed from the system by quenching with 0.3 mm of CB, and as a result the fraction of the singlet benzene which intersystem-crosses to the triplet state is correspondingly small compared to the fraction in the quencher-free system. Therefore, above 0.3 mm of CB, the diminution of the triplet benzene becomes more serious, and a significant reduction in the triplet-sensitized quantum yield for cyclopropane results, as shown by the steady increase in $1/\Phi_{\triangle}$ values at low 1/(CB) values in Figure 3. The behavior of the triplet-sensitized quantum yield for propylene, on the other hand, is not the same because of the fact that a major fraction of propylene at 1 mm of CB arises from the excited singlet cyclobutanone decomposition, an important complication which will be discussed later in detail. Now, however, attention will be focused on the pressure-dependent behavior of the cyclopropane quantum yield above 0.3 mm of CB. It should also be noted that the triplet-sensitized yield of cyclopropane at lower pressures of CB constitutes 97% of the total triplet-sensitized quantum yield.

The broken line in the upper half of Figure 3 represents the calculated values of the inverse of the sensitized quantum yield of cyclopropane at various values of the inverse of CB pressure, when the following set of values is used with eq III: $n_T = 1.00$, $[k_2 + k_3 + k_5(C_6H_6)]/k_4 = 0.28/0.72 = 0.39$ as a reasonable value,[10,14,24] $[k_8 + k_9(C_6H_6)]/k_{10} = 0.103$ mm $= 3.4 \times 10^{15}$ molecules/cm^3, and $k_6 = 1.76 \times 10^{-11}$ cm^3/(molecule sec). The experimental data fit the calculated curve well up to 2 mm of CB. Beyond this pressure, the observed yields are higher than the calculated yields, although it is not apparent from Figure 3. The degree of this deviation is tabulated in Table VII. $\Phi_{T\triangle}$ is the triplet component of the sensitized cyclopropane quantum yield calculated by the above procedure, and $\Phi_{S\triangle}$ is the additional quantum yield of cyclopropane which cannot be accounted for from reaction 10 alone. This secondary source of cyclopropane is *assumed to arise from the decomposition of the excited*

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[22] C. S. Parmenter and B. L. Ring, *J. Chem. Phys.*, **46**, 1998 (1967). A lifetime of 26 ± 5 μsec at 300°K and 20 mm of benzene was observed.

[23] Preliminary data of C. S. Parmenter and his coworkers at Indiana University, Bloomington, Ind., private communication. A lifetime of 70 ± 20 μsec at 2.0 mm of benzene $(1/k_8 + k_9(C_6H_6))$ is observed.

[24] The choice of this value is based on the assumption that the triplet benzene quantum yield is 0.72,[21] and $[k_2 + k_3 + k_5(C_6H_6)]$ merely represents the sum of all processes which do not lead to the production of the triplet benzene for this calculation only, although this is not explicit in the mathematical expression used above.

Table VII. Evaluation of Triplet and Singlet Components of the Propylene and Cyclopropane Sensitization Quantum Yields[a]

Sample no.	Cyclobutanone, mm	C_3H_6 $\Phi_{T\wedge}$	C_3H_6 $\Phi_{S\wedge}$	c-C_3H_6 $\Phi_{T\triangle}$	c-C_3H_6 $\Phi_{S\triangle}$
A 123	11.0	0.005	0.023 ± 0.004	0.15	0.15 ± 0.02
C 168	11.0	0.005	0.020 ± 0.004	0.15	0.15 ± 0.02
C 167	5.9	0.007	0.029 ± 0.004	0.23	0.13 ± 0.02
A 122	4.6	0.008	0.023 ± 0.004	0.27	0.10 ± 0.02
D 135	3.1	0.010	0.022 ± 0.004	0.33	0.07 ± 0.02
C 165	2.5	0.011	0.017 ± 0.004	0.36	0.06 ± 0.02
A 120	1.8	0.013	0.016 ± 0.004	...	...
D 134	1.0	0.015	0.009 ± 0.003	...	...
C 164	0.73	0.015	0.009 ± 0.003	...	...

[a] Benzene pressures were about 2.5 mm, and the photolyses were carried out at 2537 Å and 23°.

triplet cyclobutanone produced by the intersystem crossing of the singlet cyclobutanone which has been originally produced by singlet sensitization reaction 6. Therefore the precursor of this extra cyclopropane can now be designated as "X" in reaction 7c, which is an excited triplet cyclobutanone. The plot of $1/\Phi_{S\triangle}$ *vs.* $1/P_{CB}$, from the data tabulated in Table VII, gives a straight line confirming a Stern–Volmer relationship, and the half-quenching pressure is 3 ± 1 mm of cyclobutanone as expected from the assumed mechanism (reaction 13),

$$^1CB^* \longrightarrow {}^3CB^{**} \qquad (13)$$

which can now specifically replace reaction 7c; the double asterisk signifies the higher internal excitation energy content of this CB as compared to the $^3CB^*$ produced by reaction 10.

A tabulation of the triplet and singlet components of propylene quantum yields, $\Phi_{T\wedge}$ and $\Phi_{S\wedge}$, respectively, is also shown in Table VII, and an appropriate Stern–Volmer plot of $1/\Phi_{S\wedge}$ *vs.* $1/P_{CB}$ gives the half-quenching pressure of 3 ± 1 mm of cyclobutanone as expected. The accuracy obtained in this case is somewhat better than that for cyclopropane, and $1/\Phi_{\wedge}$ values at large values of CB drop sharply in Figure 3, since $\Phi_{S\wedge} > \Phi_{T\wedge}$.

The fact that the half-quenching pressure of 3 mm of CB for the singlet components of cyclopropane and propylene quantum yields is equal to the singlet half-quenching pressure (K_S^{-1}) for the ethylene formation strongly supports the above suggested intersystem-crossing mechanism (reaction 13). The quantum efficiencies of the product yields by this intersystem crossing are $n_{S\wedge} = 0.04 \pm 0.02$ for propylene and $n_{S\triangle} = 0.17 \pm 0.06$ for cyclopropane, if $1/\Phi_S^{\infty}$ values obtained at infinite pressure of CB by extrapolation are used. Therefore the total cross-over contribution is 0.21 ± 0.08, and this value should be added to the quantum efficiency value for the ethylene production of 0.49 ± 0.04 in order to obtain the total singlet sensitization quantum efficiency, $n_S = n_{S=} + n_{S\wedge} + n_{S\triangle} = 0.70 \pm 0.12$.

D. Triplet Quenching by *cis*-2-Butene. The triplet reactions of interest here are the competitive quenching reactions 10 and 14 and the isomerization reaction 15b, where superscript 3 denotes the electronic multiplicity of the excited species. Possible energy-transfer reactions involving ^3CB and *cis*-2-butene or ^{3}(*cis*-2-butene) and CB were excluded on the basis of the extremely short unimolecular lifetimes of the triplet species and thus the low probability of bimolecular reactions under the present experimental conditions.

$$^3C_6H_6 + CB \longrightarrow C_6H_6 + {}^3CB^* \qquad (10)$$

$$^3C_6H_6 + cis\text{-2-butene} \longrightarrow C_6H_6 + {}^3(cis\text{-2-butene}) \qquad (14)$$

and

$$^3(cis\text{-2-butene}) \longrightarrow \begin{cases} cis\text{-2-butene} & (15a) \\ trans\text{-2-butene} & (15b) \end{cases}$$

The kinetic treatment of competing reactions such as those above can be found elsewhere,[25] and only the pertinent quenching equations will be shown below. The Stern–Volmer equation for the cyclopropane quenching is

$$\frac{(\Phi_{T\triangle})_0}{(\Phi_{T\triangle})} = 1 + \frac{k_{14}(cis\text{-2-butene})}{k_8 + k_9(C_6H_6) + k_{10}(CB)} \qquad (IV)$$

where $(\Phi_{T\triangle})$ and $(\Phi_{T\triangle})_0$ are the triplet components of the cyclopropane quantum yield in the presence and in the absence of *cis*-2-butene, respectively, and, *k*'s denote appropriate rate constants. The Stern–Volmer equation for the rate of *cis–trans* isomerization as a function of *cis*-2-butene pressure is

$$\frac{1}{R_{c\to t}} = \frac{1}{R_{c\to t}^{\infty}}\left[1 + \frac{k_8 + k_9(C_6H_6) + k_{10}(CB)}{k_{14}(cis\text{-2-butene})}\right] \qquad (V)$$

where $R_{c\to t}$ and $R_{c\to t}^{\infty}$ are rates of *cis–trans* isomerization in the presence of a finite amount of the *cis* isomer and in the presence of an infinite amount of the *cis* isomer, respectively, but otherwise under the same experimental condition. The most useful value of $[k_8 + k_9(C_6H_6)]/k_{14}$ is 0.026 ± 0.004 mm at a benzene pressure of 1.2 mm and at 23°.[26] Using this value, $k_{10}/k_{14} = 0.21 \pm 0.03$ is obtained from the cyclopropane quenching data (eq IV) and $k_{10}/k_{14} = 0.21 \pm 0.04$ is obtained from the *cis–trans* isomerization data (eq V). The agreement between the above two values is good within experimental accuracy, and an additional confirmation of the internal consistency for the above values is provided by the following calculation: $[k_8 + k_9(C_6H_6)]/k_{14} = 0.026$ mm[26] divided by $[k_8 + k_9(C_6H_6)]/k_{10} = K_T^{-1} = 0.103$ mm is $k_{10}/k_{14} = 0.26 \pm 0.06$. It is also obvious now why the sensitization quantum yield of cyclopropane for sample B63 is very low (see Table II and Figure 3), since 0.16 mm of propylene added as a quencher of the triplet benzene[25] competes well with 0.49 mm of cyclobutanone.

E. Energetics of the Sensitization Processes. The excited singlet cyclobutanone produced from sensitization reaction 6 ($^1CB^*$) is almost indistinguishable from

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(25) G. A. Haninger, Jr., and E. K. C. Lee, *J. Phys. Chem.*, **71**, 3104 (1967).

(26) E. K. C. Lee, H. O. Denschlag, and G. A. Haninger, Jr., *J. Chem. Phys.*, in press. A preliminary account of this work has already been reported.[25] The value of $k_8 + k_9(C_6H_6)$ is pressure dependent,[22,23] and it is somewhat risky to use the value obtained by Cundall and Milne,[13b] since it not only disagrees with our value but also their earlier measurements[13a,b] cannot be reproduced because of the gas chromatographic analysis problem as indicated in footnote 9 of ref 25. The value for C_6D_6 obtained by P. Sigal (*J. Chem. Phys.*, **46**, 1043 (1967)) cannot be used here, since the lifetime of C_6D_6 has not yet been measured and is likely to be different from that of C_6H_6. Furthermore, the value obtained at 70 mm of benzene pressure by M. Tanaka, T. Terao, and S. Sato (*Bull. Chem. Soc. Japan*, **38**, 1645 (1965)) cannot be used, since their experimental condition is quite different from ours. For these reasons, we have chosen to use our value of 0.026 mm measured for the benzene pressure range of 0.5–5 mm.

the excited singlet cyclobutanone produced with a direct excitation at 3000 Å on the following grounds: (1) the observed singlet sensitization quantum yield of 0.49 ± 0.04 for ethylene is comparable to the direct photolysis quantum yield for ethylene of 0.51 at 3130 Å and 0.53 at 2654 Å;[27] (2) the quantum efficiencies for forming cyclopropane and propylene *via singlet sensitization* are 0.17 ± 0.06 and 0.04 ± 0.02, respectively, while those obtained *in the direct* photolysis are 0.13 and 0.014 at 3130 Å, respectively, and are 0.17 and 0.12, respectively, at 2654 Å;[27] and (3) the total singlet sensitization quantum yield ($C_2 + C_3$) is 0.70 ± 0.12, while that in the direct photolysis is 0.65 at 3130 Å and 0.82 at 2654 Å.[27]

It has been observed by previous investigators[3,4] that the ratio of propylene to cyclopropane increases sharply with the increasing photoexcitation energy in the direct photolysis of CB; this ratio is a measure of decomposition *vs.* stabilization (D/S) and also of the internal energy content of the cyclopropane produced originally in the photodecomposition of CB. The calibration of the D/S values at various photoexcitation energies (and wavelengths), obtained from the direct photolysis data in Table V, is shown as a solid line in Figure 4.

A calculation of the excitation energy of the excited singlet cyclobutanone (^{1}CB*) is possible, since the ^{1}CB* intersystem crosses to give the ^{3}CB** *via* reaction 13 which yields the singlet component of cyclopropane and propylene. The ratio of $\Phi_{S\wedge}$ to $\Phi_{S\triangle}$, D/S, for the singlet benzene sensitization is 0.15 for sample A123 and 0.13 for sample C168 (see Table VII), and these values of D/S correspond to an excitation energy of 96 kcal/mole on the direct photolysis calibration line in Figure 4: the region marked with "S" and an arrow pointing left.

Another calculation of this average singlet excitation energy can be made by comparing the ratio of $(\Phi_{S\wedge} + \Phi_{S\triangle})/\Phi_{S=}$, obtained for the *singlet sensitization components* (samples A123 and C168 in Tables II and VII), to the calibration ratio of C_3/C_2 obtained for the direct photolysis at varying wavelengths (Table V). A broken line is drawn through the calibration points for C_3/C_2 in Figure 4, and the average value of $C_3/C_2 = 0.52$ for the singlet sensitization points is marked with "S" and an arrow pointing right, indicating an average excitation energy of 95 kcal/mole. This value is in excellent agreement with the value of 96 kcal/mole obtained from the D/S ratios.

In the case of triplet sensitization, the ratio of $\Phi_{T\wedge}/\Phi_{T\triangle}$ is 0.006 ± 0.004 (see Table VI), and this ratio yields the excitation energy of the ^{3}CB* of 80–85 kcal/mole as indicated by the region labeled "T," if the calibration curve (solid line) is extrapolated to the low-energy region. The experimental accuracy of the D/S ratio is such that 85 kcal/mole is an upper limit, and this upper limit is also set by the energy of the triplet benzene in its ground vibrational state, 84 kcal/mole. The true lower limit of the excitation energy may even be below 80 kcal/mole, since no propylene formation is expected from the decomposition of the excited cyclopropane if the excitation energy is lower than 81 kcal/mole.[28]

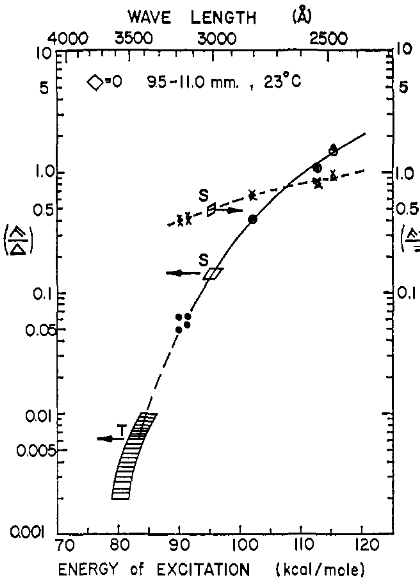

Figure 4. The ratio of propylene quantum yield to cyclopropane quantum yield *vs.* energy of the photoexcitation in kcal/mole (left). The ratio of C_3 (propylene plus cyclopropane) quantum yield to C_2 (ethylene) quantum yield *vs.* energy of the photoexcitation in kcal/mole (right).

It is apparent from the above results that about 13 kcal/mole of energy resides in the benzene molecule after singlet sensitization reaction 6 and about 8 kcal/mole of vibrational excitation is given to the ^{1}CB* in addition to the required electronic excitation energy which is estimated to be about 88 kcal/mole.[17] The total excitation energy of the ^{1}CB* (96 kcal/mole) is slightly lower than that obtained for the excited singlet cyclopentanone produced in the singlet benzene sensitization (99 kcal/mole),[8] but they are almost equal within experimental error. It is most likely that in the triplet benzene sensitization only a few kilocalories/mole of energy resides in the benzene molecule after triplet sensitization reaction 10 and also only a few kilocalories/mole of excess vibrational energy is delivered to the ^{3}CB*, since the triplet energy level of cyclobutanone must lie at 70–80 kcal/mole. It is not possible to obtain more precise information on the energy partitioning now because of the lack of experimental accuracy in the photochemical, spectroscopic, and thermochemical data available to date.

F. Tritium Kinetic Isotope Effect. One of the tritium isotope effects to consider is that due to the extinction coefficient difference between perhydrocyclobutanone (CB) and cyclobutanone-2-*t* (CBT). There is no direct measurement to demonstrate the magnitude of the extinction coefficient difference between them, but the direct photolysis data in Table I strongly imply that it is perhaps less than a few per cent, if no other isotope effect is assumed to be operative in the photodecomposition reactions which yield ethylene and cyclopropane; the specific activity of C_2H_3T is (13.2 ± 0.2) × 10^{10} dpm/mole and that of c-C_3H_5T is (25.1 ± 0.3) × 10^{10} dpm/mole, as an average of samples 8 and 9, while that of CBT is (25 ± 2) × 10^{10} dpm/mole. The specific activity of C_2H_3T is slightly higher than the

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(27) These quantum yields were measured at a pressure range of 100–150 mm of cyclobutanone and at a temperature range of 100–300° by Blacet and Miller.[2]

(28) The activation energy for the isomerization of cyclopropane to propylene is 65 kcal/mole, and the endothermicity of the reaction (cyclobutanone = cyclopropane + CO) is estimated to be about 16 kcal/mole.[3] Therefore, the excitation energy may be below 81 kcal/mole if no propylene is observed in the triplet sensitization.

expected value of 12.6×10^{10} dpm/mole, which is one-half of the specific activity of c-C_3H_5T if no other isotopic fractionation is permitted except for the stoichiometry of reaction 7a. Therefore, there is a slight degree of isotopic fractionation when reactions 6 plus 7a and reactions 10 plus 11a are compared, but the observed difference may well be within the over-all accuracy of the experiment.

A measurable tritium isotope effect observed for the secondary decomposition reaction 12b in which the vibrationally excited c-$C_3H_5T^{**}$ decomposes to C_3H_5T is clearly outside of the experimental error and is significant. This unimolecular isomerization kinetic isotope effect is about 10% in the direct photolysis at 2537 Å (see Table I), favoring the isomerization of c-$C_3H_6^{**}$ by a 10% greater rate constant than of c-$C_3H_5T^{**}$. Exactly the same kinetic isotope effect has been observed in the thermal unimolecular isomerization of c-C_3H_6 and c-C_3H_5T at 500° and 200 mm[29] and in the unimolecular isomerization of the vibrationally excited cyclopropanes produced by the addition of CH_2 and CHT to C_2H_4 at room temperature.[30] Therefore, the present data are in excellent agreement with the data obtained previously from the system of vibrationally excited cyclopropanes.

The tritium isotope effect observed in the benzene photosensitization of CB and CBT (see Table I) is very much like that in the direct photolysis, within the over-all accuracy of the experiment, although the specific activities in the former are slightly greater than those in the latter. As in the case of the benzene photosensitization of cyclopentanone-2-*t*,[8] no large additional isotope effect seems necessary to explain the data for the benzene photosensitization of cyclobutanone-2-*t*. The low degree of tritium isotope effect observed in the benzene photosensitization is an interesting contrast to the large deuterium isotope effect observed in the Hg($^3P_1$) photosensitization of alkanes.[31]

G. Concluding Remarks. Cyclobutanone,[7] cyclopentanone,[8] and cyclohexanone[32] intercept the excited singlet benzene with about equal quenching cross sections ($K_S^{-1} = 3.0$ mm of ketone), while monooolefins do not quench the excited singlet benzene.[26] This observation might be indicative of the simple electronic energy-transfer process operating between the excited singlet benzene and ketones rather than the formation of a long-lived complex between them. This may also be the case for the triplet-energy-transfer processes. In any case, the benzene photosensitization method provides a rich source of information on the vibronic excitation-transfer process.

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The Reactions of Energetic Chlorine Atoms with Methyl Chloride in the Gas Phase[1]

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Abstract: The reactions of energetic chlorine atoms with methyl chloride in the gas phase have been studied in detail, using the technique of nuclear recoil. Both substitution products, Cl for Cl and Cl for H, were observed in yields of 3.1 and 0.7%, respectively, for well-scavenged gaseous samples. The substitution reactions were confirmed as hot, and not thermal, processes by diminishing their yield with helium and neon as inert moderators. Quantitative evaluation of the kinetic theory parameters shows that the α values (moderator efficiencies) of CH_3Cl/Ne/He are in the ratio 3.0/1.0/0.41. The high value for CH_3Cl indicates substantial energy loss in highly inelastic collisions; the "billiard-ball" ratio for Ne/He would be 1.0/0.26. The chemical reactions have been studied using both $Cl^{37}(n,\gamma)Cl^{38}$ and $Ar^{40}(\gamma,p)Cl^{39}$ as the nuclear reaction source, with results in excellent agreement with each other. The absolute yields of the $Cl^{37}(n,\gamma)Cl^{38}$ reaction have been internally monitored with the $Ar^{40}(n,\gamma)Ar^{41}$ reaction. All of the observed reactions can be consistently interpreted as chemical reactions of neutral ground-state chlorine atoms with excess kinetic energy.

Energetic atoms from nuclear recoil provide abundant additional information about the kinetic behavior of atomic species, especially in reactions with covalent molecules, as has already been shown in detail for atomic hydrogen and carbon, and as is now being shown for atomic fluorine.[2–4] The chemistry of energetic

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