

Fig. 1.—An Arrhenius plot of the rate function theoretically equal to  $k_1 k_6^{1/2} / k_8$ . The data are from the selective photolyses of azomethane at 3660 Å. in *n*-butyraldehyde-azomethane mixtures.

we assume  $k_6 = k_8 = 2.2 \times 10^{13}$  cc./mole-sec.<sup>16</sup> we estimate

$$k_1 \cong 2.8_6 \times 10^{15} e^{-84.9/RT} \text{ sec.}^{-1}$$

Our estimate of  $E_1 \cong 34.9$  kcal./mole is in serious disagreement with the first estimates of this quantity ( $E_1 \cong 19\text{--}21$  kcal./mole). However, it is likely that the accuracy of the previous estimates is low.<sup>9</sup> The results of the present work should be considerably more reliable since the interpretation of the data is much less uncertain in this case.

**Kinetic Estimates of the Enthalpy and Entropy Change of Reaction 1:  $n\text{-C}_3\text{H}_7 \rightarrow \text{CH}_3 + \text{C}_2\text{H}_4$ .**—The thermodynamic quantities related to (1) can

(16) A. Shepp, *J. Chem. Phys.*, **24**, 939 (1956).

be derived from these results and those of Brinton<sup>6</sup> which relate to the reverse of reaction 1,  $\text{CH}_3 + \text{C}_2\text{H}_4 \rightarrow n\text{-C}_3\text{H}_7$ . He finds  $k_{-1}/k_6^{1/2} = 3.3 \times 10^{-7} e^{-8.66/RT}$  (cc./mole-sec.)<sup>1/2</sup>. Changing the units to moles-cc.-sec. and again using Shepp's value for  $k_6$  we derive

$$k_{-1} \cong 1.20 \times 10^{12} e^{-8.66/RT} \text{ (cc./mole-sec.)}$$

The rate constant which we estimate for the forward reaction 1 appears to be reasonably consistent with Brinton's data for the reverse of (1). The data suggest (for temperatures near 200°)  $\Delta H_1 \cong E_1 - E_{-1} \cong 34.9 - 8.7 \cong 26.2$  kcal./mole;  $\Delta S_1^0 \cong R \ln(A_1/A_{-1}) \cong R \ln(2.85 \times 10^{15}/1.20 \times 10^{12}) \cong 15.4$  e.u. (standard state, 1. mole/cc.). These estimates check well with the values of  $\Delta H_1 \cong 26.4$  kcal./mole and  $\Delta S_1^0 \cong 12.1$  e.u. (25°) calculated from Bryant's thermal data summary and his theoretical estimates of the entropies of the *n*-C<sub>3</sub>H<sub>7</sub> and CH<sub>3</sub> radicals.<sup>7</sup> The observed difference in the experimental and theoretical values for  $\Delta S_1^0$  corresponds to a factor of 5.3 in the ratio of the pre-exponential factors,  $A_1/A_{-1}$ , or about 1.7 kcal./mole in the difference  $E_1 - E_{-1}$ . Thus the divergence from "theory" is well within the experimental error and the simplifications involved in this comparison.

From our estimate of  $\Delta H_1$  and standard enthalpy for methane, ethane and ethylene, it can be shown that  $D_{\text{CH}_3\text{-H}} - D_{n\text{-C}_3\text{H}_7\text{-H}} \cong 6.8$  kcal./mole. If we assume with Bryant<sup>7</sup> that  $D_{\text{CH}_3\text{-H}} = 102.0$ , then we estimate that  $D_{n\text{-C}_3\text{H}_7\text{-H}} \cong 95.2$  kcal./mole.

We may conclude that the kinetic data for  $k_1$  reported in this work reaffirm our faith in the thermal estimates of  $\Delta H_1$  and establish the inaccuracy of the previous "low" kinetic estimates of  $E_1$  and  $\Delta H_1$ .

**Acknowledgments.**—The authors gratefully acknowledge the financial support received from the United States Public Health Service, National Institutes of Health, Bethesda, Md., and the communication with Dr. A. F. Trotman-Dickenson who has allowed us reference to his preliminary results before publication.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

## Photoisomerization Processes in Cyclic Ketones. I. Cyclopentanone and Cyclopentanone-2,2,5,5-*d*<sub>4</sub><sup>1</sup>

BY R. SRINIVASAN

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4-Pentenal has been identified as one of the products of the vapor phase photolysis of cyclopentanone at 3130 Å. Quantum yields for the formation of 4-pentenal have been obtained at various temperatures and in the presence of added oxygen and carbon dioxide. The photolysis of cyclopentanone-2,2,5,5-*d*<sub>4</sub> has been found to give tetradeutero-4-pentenal, the structure of which is most probably CD<sub>2</sub>=CHCH<sub>2</sub>CD<sub>2</sub>CHO. On the basis of these results, it is deduced that the photoisomerization of cyclopentanone to 4-pentenal involves a direct transfer of a hydrogen atom from a β-carbon to the carbonyl group in an excited state of the ketone molecule.

### Introduction

The vapor phase photolysis of cyclopentanone has been investigated by Saltmarsh and Norrish,<sup>2</sup>

by Benson and Kistiakowsky<sup>3</sup> and more recently by Blacet and Miller.<sup>4</sup> The products of photolysis are carbon monoxide, ethylene, cyclobutane and

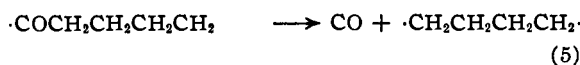
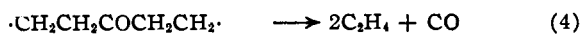
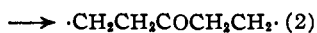
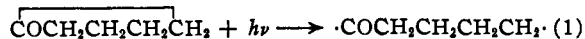
(1) This research was supported in part by contract AF18(600) 1528 with the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command. Reproduction in whole or in part is permitted for any purpose by the United States Government.

(2) O. D. Saltmarsh and R. G. W. Norrish, *J. Chem. Soc.*, 455 (1935).

(3) S. W. Benson and G. B. Kistiakowsky, *THIS JOURNAL*, **64**, 80 (1942).

(4) F. E. Blacet and A. Miller, *ibid.*, **79**, 4327 (1957).

possibly a polymer. These products could be explained by the steps<sup>4</sup>



The present study was undertaken to see if in addition to these products which can be explained on the basis of a primary split to give diradicals, there are other product(s) that are formed by a direct rearrangement. In the case of straight-chain ketones with radicals having  $\gamma$ -carbon atoms and at least one hydrogen atom on the  $\gamma$ -carbon, a rearrangement process is known to occur (type II process) in addition to a free radical split (type I process).<sup>5</sup> The type II process generally gives a methyl ketone<sup>6</sup> and an olefin, both of which usually have appreciably lower boiling points than the starting material. It was suspected that in the case of cyclopentanone any photo-rearrangement process would lead to an isomeric product, which would be difficult to isolate on the basis of its volatility. Therefore, use was made of gas chromatography, which had not been applied previously to the study of the photochemistry of cyclopentanone, to look for the hypothetical product.

### Experimental

Cyclopentanone was a "research" grade sample supplied by K. and K. Labs. Its vapor chromatogram showed no impurities. It was further distilled twice from bulb to bulb *in vacuo* and stored at Dry Ice temperature. Cyclopentanone-2,2,5,5-*d*<sub>4</sub> was prepared by the method of Streitwieser, *et al.*<sup>7</sup> The purity of the sample so made was checked by vapor chromatography and found to be at least 97%. Its mass spectrum showed the following distribution pattern (mass 88 = 100) 89—6.0; 87—32.4; 86—5.9; 85—0.7; 84—0.09. The infrared spectrum showed that the medium strong peak at 1407  $\text{cm}^{-1}$  in cyclopentanone due to the two methylene groups adjacent to the carbonyl was totally absent.

Oxygen was prepared by heating potassium permanganate crystals and passing the gas through a trap cooled in liquid nitrogen. Carbon dioxide supplied by Airco was used without purification.

Photolyses were carried out in a water-jacketed quartz cell 20.0 cm. long and 3.9 cm. in dia. The light source was a Hanovia S-100 mercury arc lamp filtered by 2 mm. of Corning 0-53 glass. The useful radiation was essentially the group of lines at 3130 Å. The intensity of the light as determined by a diethyl ketone actinometer at 95° ( $\Phi_{\text{CO}} \sim 1$ ) was  $1.2 \times 10^{16}$  quanta/sec. The extent of the photolysis was always less than 3%. In view of the difficulties reported by Dunn and Kutschke<sup>8</sup> in studying the effect of oxygen on the photolysis of cyclohexanone, the runs in the presence of oxygen (and blanks) were conducted in a Pyrex bulb in the center of which a collimated and filtered beam of light was passed.

(5) This classification is due to C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1935).

(6) Unless the parent ketone is substituted at both  $\alpha$ -carbons.

(7) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *THIS JOURNAL*, **80**, 2326 (1958).

(8) J. R. Dunn and K. O. Kutschke, *Can. J. Chem.*, **33**, 725 (1954).

### Results

Vapor phase photolysis gave carbon monoxide, ethylene, cyclobutane and an unknown product A. A was characterized by its retention time in a gas chromatographic column and its mass spectrum. A sufficient amount of A could not be prepared by vapor phase photolysis to obtain a satisfactory infrared spectrum, but as a dilute solution in chloroform, A showed peaks at 1720 and possibly 910 and 990  $\text{cm}^{-1}$ . Photolysis of cyclopentanone in the liquid phase also gave rise to A. A pure sample of A was prepared in this manner in sufficient quantity to obtain a good infrared spectrum and to prepare a 2,4-dinitrophenylhydrazine derivative. The infrared spectrum (in chloroform) showed peaks at 1720 (C=O), 1641, 990 and 910 ( $\text{CH}_2=\text{C}-$ ), 2680, 2800 (aldehydic C-H) and 1408 ( $-\text{CH}_2-$  adjacent to C=O). The melting point of the 2,4-DNP derivative was 116° (m.p. of 2,4-DNP of 4-pentenal is 116–117.5°,<sup>9</sup> 120°<sup>10</sup>). From this evidence it was concluded that A is 4-pentenal.<sup>11</sup>

Analysis of the products was confined to carbon monoxide and 4-pentenal in most cases. A few runs in which ethylene and cyclobutane were separated and measured essentially confirmed the result of Blacet and Miller<sup>4</sup> that at 3130 Å. and below 125°  $\Phi_{\text{CO}} = \Phi_{\text{C}_2\text{H}_4} + \Phi_{\text{C}_4\text{H}_8}/2$ . 4-Pentenal was separated from the undecomposed cyclopentanone by means of gas chromatography (using a Perkin-Elmer Vapor Fractometer Model 154) and estimated by the area of the trace made by the recorder under standard conditions, and by mass spectrometric analysis using a Consolidated Engineering Co. type 21-620 mass spectrometer.

Quantum yields for the production of carbon monoxide and 4-pentenal are given in Table I. The absorption spectrum of cyclopentanone shows a steep rise in the region of 3130 Å. Since the mercury line which is the source of radiation is actually a triplet, to use a single absorption coefficient corresponding to the wave length of 3130 Å. is only an approximation. Therefore, the absolute values of the quantum yields are probably less accurate than the relative values.

TABLE I  
QUANTUM YIELDS OF CO AND 4-PENTENAL IN PHOTOLYSIS OF CYCLOPENTANONE

Pressure, mm.	Temp., °C.	Time, min.	$\Phi_{\text{CO}}$	$\Phi_{\text{pentenal}}$	Remarks
2.4	1.2	60	0.11	0.049	
11.5	26.7	60	.12	.056	
11.5	40.1	60	.13	.052	
11.8	55.2	60	.14	.045	
11.8	75.1	60	.16	.042	
12.0	94.0	56	.18	< .04 <sup>a</sup>	
12.3 <sup>b</sup>	26.0	840	.. <sup>c</sup>	.063	$P_{\text{O}_2} = 18.7$ mm.
11.7	26.8	60	.09	.12	$P_{\text{CO}_2} = 27.5$ mm.

<sup>a</sup> Interference from unknown product. <sup>b</sup> Pyrex bulb with Pyrex filter. <sup>c</sup> Not determined.

The quantum yield for the production of 4-pentenal is roughly half of that for carbon monoxide at room temperature. At higher temperatures 4-

(9) H. P. Thomas and C. L. Wilson, *THIS JOURNAL*, **73**, 4804 (1951).

(10) C. D. Hurd and M. A. Pollack, *ibid.*, **60**, 1905 (1938).

(11) M. S. Kharasch, J. Kuderna and W. Nudenberg, *J. Org. Chem.*, **18**, 1225 (1953), have reported that 4-pentenal is formed as one of the products in the photolysis of a solution of cyclopentanone in octene-1.

pentenal becomes less important, for even though  $\Phi_{\text{pentenal}}$  decreases only slowly with rising temperature,  $\Phi_{\text{CO}}$  increases rapidly. At 75° and above the presence of a new compound in the products interfered with the separation of 4-pentenal by gas chromatography. This compound had a prominent peak at mass 78, but it was not identified as it was formed only in small quantities, relative to 4-pentenal, even at 94°. It is likely that this compound is one of the products of step 6 in the reaction scheme of Blacet and Miller.

Decrease of pressure appears to cause  $\Phi_{\text{pentenal}}$  to decrease although this effect could not be studied precisely, as the vapor pressure of cyclopentanone at 25.7° is only 12.0 mm.<sup>3</sup> The addition of 18.7 mm. of oxygen does not inhibit the formation of 4-pentenal. In fact  $\Phi_{\text{pentenal}}$  shows a slight increase on adding oxygen. That this effect could be due to quenching of an electronically excited ketone molecule from a high to lower vibrational levels is shown by the addition of carbon dioxide, when  $\Phi_{\text{pentenal}}$  shows a marked increase. At the same time  $\Phi_{\text{CO}}$  is diminished. A similar effect with respect to  $\Phi_{\text{CO}}$  has been reported by Dunn and Kutschke<sup>8</sup> in the photolysis of cyclohexanone.

TABLE II

MASS SPECTRA OF 4-PENTENAL AND 4-PENTENAL-*d*<sub>4</sub>

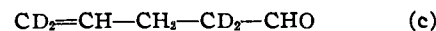
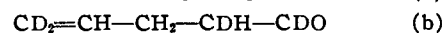
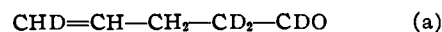
Peak heights for *m/e* values from 16 to 19 have not been reported due to uncertainty caused by the background noise.

<i>m/e</i>	Peak height		<i>m/e</i>	A C <sub>5</sub> H <sub>8</sub> O	B C <sub>5</sub> H <sub>4</sub> D <sub>4</sub> O
	A C <sub>5</sub> H <sub>8</sub> O	B C <sub>5</sub> H <sub>4</sub> D <sub>4</sub> O			
12	1.8	2.5	51	8.6	5.8
13	3.6	1.7	52	2.0	8.2
14	11.3	4.7	53	24.3	7.0
15	28.4	8.1	54	5.9	6.2
25	4.1	1.9	55	154.0	22.2
26	35.1	10.2	56	78.4	89.6
27	181.1	40.9	57	16.2	54.5
28	100	100	58		146.1
29	216.2	187.0	59		127.9
30	6.3	113.6	60		45.5
31	8.1	104.5	61		3.9
32		100.6	65	2.8	
33		23.0	66	4.7	
37	7.7	5.3	67	2.3	2.3
38	13.5	10.1	68		4.3
39	113.4	26.0	69	16.2	5.8
40	18.0	79.2	70	1.4	8.2
41	143.2	76.6	71		14.4
42	62.2	57.2	72		6.2
43	38.7	159.7	83	37.0	
44	10.4	120.8	84	21.6	
45	2.0	44.2	85		5.4
46		17.5	86		20.6
47		3.1	87		26.5
49	2.5		88		24.2
50	8.6	3.1			

Vapor phase photolysis of cyclopentanone-2,2,5,5-*d*<sub>4</sub> gave carbon monoxide, C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>, cyclobutane-*d*<sub>4</sub> and a product B. B had the same retention time on a chromatographic column as 4-pentenal under standard conditions, and it was characterized by its mass spectrum. In Table II the mass spectra of 4-pentenal and B are compared. These spectra

were obtained under identical operating conditions, using about equal pressures of the two compounds. B is obviously 4-pentenal with four deuterium atoms replacing four hydrogen atoms. The mass spectra indicate that (a) relative to the parent peaks at 84 and 88, the peak at 28 has not changed significantly; (b) evidently the peak at 27 in 4-pentenal has shifted to 29 in the case of the deuterated compound. On comparing the mass spectra of 4-pentenal, 3-butenal<sup>12</sup> and 5-hexenal, it seemed likely that the peak at 27 is due to the fragment CH<sub>2</sub>=CH— and that in the deuterated pentenal, this group has two deuterium atoms and one hydrogen atom; (c) if the peak at 69 in 4-pentenal is due to the loss of a methyl, presumably by a preliminary rearrangement of 4-pentenal to 3-pentenal, then the shift of this peak to 71 in the deuterated compound also indicates the presence of two D atoms on the two end carbons.

Further evidence for the location of the deuterium atoms in B was obtained from its infrared spectrum. For this purpose cyclopentanone-2,2,5,5-*d*<sub>4</sub> was photolyzed as a thin liquid film. The deuterated pentenal that was formed was separated from the unreacted ketone by gas chromatography. The identity of the product obtained by vapor phase photolysis to the product of the liquid phase photolysis was established by mass spectrometry.<sup>13</sup> The infrared spectrum of B in chloroform showed peaks at 1725 (C=O), 2700 and 2800 (aldehydic C-H, unchanged from 4-pentenal) and no absorption in the vicinity of 1640, 990 and 910 cm.<sup>-1</sup>. The moderately strong peak in 4-pentenal at 1408 cm.<sup>-1</sup> was wholly absent. On the basis of the mass spectrum and infrared spectrum of B, it was not possible to locate the deuterium atoms in it incontrovertibly. Hence the evidence was used to decide among three structures that were considered probable, on the basis of assumed mechanisms for the photoisomerization. These were



(a) was eliminated on the grounds that in this structure there is only one D atom on the two end carbons, and there is a D atom on the carbonyl group. The latter consideration eliminated (b) also. (c) appeared to fit all the available information on the structure of tetradeuteriopentenal, and in the absence of any conflicting evidence this was taken to be the correct structure.

## Discussion

The photoisomerization of cyclopentanone to 4-pentenal<sup>14</sup> conceivably can occur in several ways.

(12) Mass spectrum No. 1974 in the tables kindly supplied by Celanese Corporation of America, Clarkwood, Texas.

(13) No evidence has been found in this Laboratory to indicate that exchange between deuterated compounds and the column material used occurs to an appreciable extent.

(14) Formally, this rearrangement is similar to the process  $\text{C}_5\text{H}_8\text{O} \xrightarrow{h\nu} \text{C}_2\text{H}_2\text{CHO} + \text{C}_2\text{H}_4$  which was postulated by Norrish and Appleyard (*J. Chem. Soc.*, 874 (1934)). Such a process was classified by Bamford and Norrish (*ibid.*, 1504 (1935)) as a type III process. Since there appears to be no type II process in the photochemistry of cyclopentanone, this classification need not be adopted here.

Of these mechanisms, those that postulate the synthesis of 4-pentenal from smaller radical fragments are ruled out by the non-inhibition of the process by oxygen. Mechanisms which predict the shift of a hydrogen atom to the carbonyl group from one of the  $\alpha$ -carbon atoms would not be in agreement with the results obtained with cyclopentanone- $d_4$ . A further possibility that may be considered is that 4-pentenal is formed from the diradical  $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}\cdot$  by an internal abstraction of a hydrogen from the  $\gamma$ -carbon by the carbonyl group. While this hypothesis has several attractive features, the opposite effects that addition of carbon dioxide has on  $\Phi_{\text{pentenal}}$  and  $\Phi_{\text{CO}}$  makes it unlikely that these two products would originate from the same intermediate diradical. It would be even harder to explain the small increase in  $\Phi_{\text{pentenal}}$  on adding oxygen.

On the basis of the present work one is led to conclude that the transfer of a hydrogen atom from the  $\beta$ -carbon to the carbonyl group occurs directly, in an excited cyclopentanone molecule even before the ring structure is disrupted. It does not appear possible to prove this rigorously in cyclopentanone itself. By studying the photochemistry of a substituted cyclopentanone where isomerization would lead to a substituted pentenal, if it is found that one geometric isomer of the product is formed exclusively, this may be taken as evidence that hydrogen transfer occurs before the ring structure breaks up. Such studies are now in progress.

Dunn and Kutschke found that the products arising through a diradical intermediate from the photolysis of cyclohexanone are formed even in the presence of 10 mm. of oxygen.<sup>8</sup> This suggests that the electronic state involved in the formation of the diradical is an upper singlet in cyclohexanone. Extending this idea to cyclopentanone, it is possible to explain the effect of added oxygen and carbon dioxide by assuming that the vibrational level of the cyclopentanone molecule in the upper singlet state would determine whether it should form a diradical and then give carbon monoxide, or rearrange to 4-pentenal. Since the vibrational energy can be removed by collision, increasing the total pressure at constant temperature should favor the formation of pentenal at the expense of carbon monoxide. This is found to be so. Similarly, the decrease in  $\Phi_{\text{pentenal}}$  with rising temperature can be wholly accounted for by the decrease in concentration of the ketone, since these runs were made at about equal pressures. The work of Blacet and Miller<sup>4</sup> shows that  $\Phi_{\text{CO}}$  increases with decreasing wave length, which supports this general picture. The detailed mechanism of the primary processes in this system is under investigation at present.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

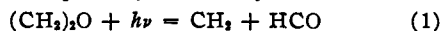
## Photochemical and Free Radical Decompositions of Oxetane<sup>1</sup>

BY J. D. MARGERUM,<sup>2</sup> J. N. PITTS, JR., J. G. RUTGERS AND S. SEARLES

RECEIVED JULY 23, 1958

Studies on three oxetanes show that the photolytic products are consistent with intramolecular rearrangement mechanisms as the main photochemical primary processes. Vapor phase photolyses indicate that oxetane splits into ethylene and formaldehyde, while 2,2-dimethyloxetane rearranges by two paths into both ethylene plus acetone and formaldehyde plus isobutylene. Products from 2-phenyloxetane photolysis in isoctane solution include ethylene and formaldehyde, indicating that it also decomposes *via* two paths of intramolecular rearrangement. The possibility of biradical formation prior to intramolecular rearrangement is investigated by measuring the relative rates of formation of photo-decomposition products of oxetane vapor between 25 and 154° and by observing its photolytic products in solution and as a solid. No evidence was found for the existence of a stable biradical. It is shown that methyl radical attack on oxetane vapor in the 120 to 154° range initiates its decomposition into  $\text{C}_2\text{H}_4$ , CO,  $\text{H}_2$  and  $\text{CH}_2\text{O}$ . These products are consistent with a mechanism of decomposition wherein a radical abstracts hydrogen from oxetane and the resultant radical decomposes into ethylene and a formyl radical.

These studies of several oxetanes were undertaken mainly as a means of investigating their primary photochemical processes. To date only one other cyclic ether, ethylene oxide, has been studied photochemically. Gomer and Noyes<sup>3</sup> postulated that the principal primary process for the vapor phase photolysis of ethylene oxide is

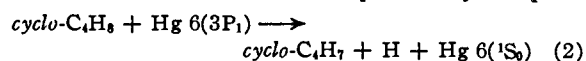


(1) (a) Abstracted in part from a dissertation submitted in June, 1958, to the Graduate School of Northwestern University by J. David Margerum in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) This work was supported by the Atomic Energy Commission: Project No. 4 of Contract AT (11-1)-89.

(2) Address communications to: J. David Margerum, Pioneering Research Division, Quartermaster Research and Engineering Center, Natick, Massachusetts.

(3) R. Gomer and W. A. Noyes, Jr., *THIS JOURNAL*, **72**, 101 (1950).

The photochemistry of another four-membered ring, cyclobutane, has been studied by Kantro and Gunning,<sup>4</sup> who investigated the mercury sensitized decomposition with 2537 Å. radiation. They postulated that the main primary process in this system involved the formation of a cyclic, free radical. Besides the possibility of photo-



decompositions analogous to equations 1 and 2, the structure of oxetane suggested as other possible primary processes (a) the breaking of a carbon-oxygen bond to form a biradical,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\cdot$ , and

(4) D. L. Kantro and R. E. Gunning, *J. Chem. Phys.*, **21**, 1797 (1953).