

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 α -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 γ -carbon by the carbonyl group. While this hypothesis has several attractive features, the opposite effects that addition of carbon dioxide has on Φ_{pentenal} and Φ_{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 Φ_{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 β -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.⁸ 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 Φ_{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 Miller⁴ shows that Φ_{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.

Acknowledgment.—The author wishes to thank Professor W. Albert Noyes, Jr., for advice and encouragement during the course of this work.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

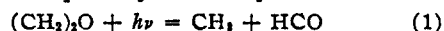
Photochemical and Free Radical Decompositions of Oxetane¹

BY J. D. MARGERUM,² J. N. PITTS, JR., J. G. RUTGERS AND S. SEARLES

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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 iso-octane 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 C_2H_4 , CO, H_2 and CH_2O . 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 Noyes³ postulated that the principal primary process for the vapor phase photolysis of ethylene oxide is

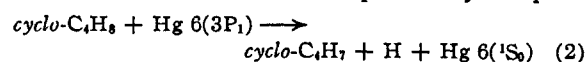


(1) (a) Abstracted in part from a dissertation submitted in June, 1958, to the Graduate School of Northwestern University by J. David Margerum in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) This work was supported by the Atomic Energy Commission: Project No. 4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

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(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,⁴ 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).

(b) the direct intramolecular rearrangement into C_2H_4 and CH_2O , which have been reported as the products from the thermal decomposition of oxetane in the 420–460° range.⁵

The photochemical studies reported here consisted in the analysis of the decomposition products from the photolyses of oxetane and of two substituted oxetanes which afforded a means of observing the effect of unsymmetrical substitution on the mode of photodecomposition. The results observed in the photolyses above 100° suggested that in this system free radicals were produced which in turn initiated some thermal decomposition of oxetane. In their study of the thermal decomposition of oxetane in the 420–460° range Bittker and Walters⁵ postulated that a small part of the decomposition was the result of a free radical attack. Direct evidence for such a free radical initiated, thermal decomposition in the 120–154° range is given here.

Experimental

Materials.—Oxetane (trimethylene oxide) was prepared and initially purified by the method of Searles.⁶ It was further purified by successive treatment with dry KOH, sodium metal, fractional distillation and vacuum distillation, in the manner described by Bittker.⁸ The fractional distillation was carried out using a Piro-Glover spinning band column at a reflux ratio of 50:1. It was vacuum distilled from a bath held at –80° and the center cut of this distillation was stored in a sample tube at –80°. The purified sample gave n_D^{25} of 1.3899, in good agreement with reported values.^{6,7} The infrared spectrum agreed well with that reported by Barrow and Searles.⁸ The mass spectrum showed only the expected peaks and no peaks higher than 58.

2,2-Dimethyloxetane (1,1-dimethyltrimethylene oxide) was prepared and initially purified as described by Bennett and Philip.⁹ It was further purified on a vacuum line by successive treatment with anhydrous $CaSO_4$ at 25° for 12 hr., with anhydrous KOH pellets at 0° for 6 hr. and with clean sodium metal at 0° for 8 hr. During these steps it was warmed to room temperature, then cooled to –80° and outgassed several times. Finally it was thoroughly outgassed at –80°, vacuum distilled from a bath held at –64° into a sample tube and stored at –80°. The purified sample was checked for purity by its infrared spectrum,⁸ by its mass spectrum (which showed no significant peaks higher than the parent peak of 86) and by its ultraviolet spectrum, Fig. 1.

2-Phenyloxetane (1-phenyltrimethylene oxide) was prepared and initially purified as described by Searles, Pollart and Lutz.¹⁰ It was further purified on a vacuum line by drying with anhydrous $CaSO_4$ at 25° for 12 hr. and vacuum distillation. Although it has a low vapor pressure at room temperature, it was vacuum distilled from a bath at 25° and the center cut was stored in a sample tube at –80°. The infrared spectrum showed good agreement with that reported by Barrow and Searles.⁸

Mallinckrodt "reagent grade" acetone, which was used for photolyses and as an analytical standard, was vacuum distilled into the appropriate reaction cell or gas bulb. Di-*t*-butyl peroxide from Shell Chemical Corp. was vacuum distilled into reaction bulbs for pyrolysis studies. Analytical standards of hydrogen, methane, ethylene, ethane, propylene, propane, isobutylene, 1-butene, 2-butene and *n*-butane were taken from commercial gas cylinders containing high purity gases. When mass spectrometry indicated an im-

purity the gas samples were further purified on the vacuum line with a Ward-LeRoy still.¹¹ Carbon monoxide was prepared in a vacuum line by dropping concd. H_2SO_4 on sodium formate. Carbon dioxide was obtained by vaporizing "Dry Ice" in a vacuum line. A stock solution of formaldehyde was prepared from commercial 37.8% formaldehyde and was standardized with reagent grade sodium sulfite using 1 *N* HCl and thymolphthalein indicator.¹²

Analytical Methods.—Mass spectrometric analyses obtained on a Westinghouse type LV mass spectrometer were used for hydrogen, saturated hydrocarbons, ethylene, isobutylene and acetone. A Blacet-Leighton micro gas analysis apparatus was used for the determination of carbon monoxide, hydrogen and ethylene using absorption beads of Ag_2O ,¹³ $CuO-KOH$ ¹⁴ and mercuric acetate-mercuric nitrate paste,¹⁵ respectively. All gas volumes were measured with the Blacet-Leighton apparatus. Whenever possible, gas samples were split into several portions so that the components could be analyzed independently and by more than one method. Formaldehyde and higher aldehydes were analyzed colorimetrically¹⁶ with a Beckman DU spectrophotometer. Prior to analysis the samples were fractionated on the vacuum line using a modified Ward-LeRoy still in conjunction with a mercury diffusion pump and a Toepler pump. Usually, H_2 and CO were separated at –200°, ethylene and ethane at –182°, C_2 and C_4 hydrocarbons at –125° and formaldehyde and oxetane were kept in the condensed phase.

Apparatus.—The vapor phase photolyses were carried out in a cylindrical quartz reaction cell 8" long and 2" outside diameter, which was mounted in an aluminum block furnace inside an air-thermostated chamber. The furnace was controlled by a Brown potentiometer circuit to within $\pm 1^\circ$ of the desired temperature. A side arm connected the reaction cell to a trap, which in turn led through Stock valves to a Ward-LeRoy still and then to the vacuum pumpout system. To avoid polymerization of formaldehyde on the grease, ordinary stopcocks were not used. In the vapor phase photolysis of the oxetanes a Hanovia type 8A1 mercury arc, mounted in a water-cooled shield, was used with a 5 mm. diaphragm as an approximate point source of light. This was focused into a nearly parallel beam by a 4" focal length quartz lens. The arc was approximately 6" from the front of the reaction cell. The mercury arc was corrected for aging on the basis of the amount of ethylene produced from 6 hr. of oxetane photolysis at 25°. Runs at higher temperatures were alternated with photolyses at 25°. At each temperature the vapor pressure was adjusted to give a constant concentration (5.13×10^{-3} mole/liter) of fresh sample for each photolysis. Photolyses were carried to 0.3% decomposition.

Acetone photolyses were carried out in the same reaction cell, but a Hanovia type A mercury arc was used in conjunction with a Farrand Model 300 UV monochromator to isolate the 3130 Å. mercury line. The arc was placed immediately in front of a water-cooled entrance slit of the monochromator. Light from the exit slit was focused by the 4" focal length lens into a slightly divergent beam through the reaction cell and onto a RCA 935 phototube. Relative light intensities were measured with an Aminco microphotometer unit No. 10-210. Linearity of current versus light intensity was checked with standard glass filters. Pure acetone vapor at 154° was used as an actinometer.

For liquid phase photolyses cylindrical quartz reaction cells of 10 mm. path length were used. One of these had a volume of 12 ml. and the other one held 5 ml. Each of these was connected, through a hollow bore stopcock, to a much larger trap which was used on the vacuum line to help separate gaseous reaction products from the solvent. Irradiations were done with a Hanovia type S-100 mercury arc, a diaphragm, a 1" path-length filter cell filled with the same solvent used in the reaction cell and a fan to keep the latter at room temperature. The photolyses were carried to 2% decomposition at a concentration of 0.24 mole/liter.

(5) (a) D. A. Bittker and W. D. Walters, *THIS JOURNAL*, **77**, 1429 (1955); (b) D. A. Bittker, *Doctorate Dissertation*, Univ. of Rochester, N. Y., 1952.

(6) S. Searles, *THIS JOURNAL*, **73**, 124 (1951).

(7) C. O. Derick and D. W. Bissell, *ibid.*, **38**, 2478 (1916).

(8) G. M. Barrow and S. Searles, *ibid.*, **75**, 1175 (1953).

(9) G. M. Bennett and W. G. Philip, *J. Chem. Soc.*, 1938 (1928).

(10) S. Searles, K. A. Pollart and E. F. Lutz, *THIS JOURNAL*, **79**, 948 (1957).

(11) D. J. LeRoy, *Can. J. Research*, **B28**, 492 (1950).

(12) J. F. Walker, "Formaldehyde," 2nd Ed., Reinhold Publ. Corp. New York, N. Y., 1953, p. 382.

(13) F. E. Blacet, G. D. MacDonald and P. A. Leighton, *Ind. Eng. Chem., Anal. Ed.*, **6**, 262 (1933).

(14) F. E. Blacet and G. D. MacDonald, *ibid.*, **6**, 334 (1934).

(15) R. Pyke, A. Kahn and D. J. LeRoy, *ibid.*, **19**, 65 (1947).

(16) D. Matsukawa, *J. Biochem. (Tokyo)*, **30**, 386 (1939).

Photolysis of oxetane at -196° was carried out in the 8' path-length cell that was used for the vapor phase studies, except that it was placed in a vertical position with the lower 4' immersed in a Dewar flask filled with liquid nitrogen. The sample was introduced from the vacuum line, was condensed on the bottom window by a -80° bath and then solidified to a film at -196° . A Hanovia type S-100 arc placed near the top window of the cell was used to irradiate downward on the sample film for a period of 9 hr.

Pyrolyses of di-*t*-butyl peroxide were conducted in 1-liter Pyrex glass bulbs placed in an analytical oven which controlled the temperature to within $\pm 1^{\circ}$. The glass bulbs were spherical in shape, with a freeze out tube on one end and a stopcock lubricated with silicone grease on the opposite end. Reactants were introduced into the bulb from the vacuum line and were allowed to stand for several hours at room temperature prior to pyrolysis.

The ultraviolet absorption spectra for oxetane and 2,2-dimethyloxetane are shown in Fig. 1. Their absorption maxima are in the vacuum ultraviolet region, at 1830 and 1735 Å., respectively. It is of interest to note that the dimethyl substitution appears to have the unusual effect of shifting the absorption maxima to a shorter rather than to a longer wave length. The data below 2050 Å. were plotted from readings taken every 10 Å. with a vacuum ultraviolet spectrophotometer with a spectral slit width of 5.1 Å. Basically the instrument used is the one described by Jones and Taylor,¹⁷ using thin window fused-silica cells of 0.177 mm. path length. The data above 2050 Å. were plotted from readings taken every 50 Å. in 10 mm. quartz cells on a Beckman DU spectrophotometer specially converted to give accurate readings down to 1920 Å.¹⁸

Results

The products from the photolysis of oxetane vapor at room temperature are shown in Table I.

TABLE I

PHOTOLYSES OF OXETANES WITH AN UNFILTERED MERCURY ARC^a

Compound	$\text{H}_2\text{C}-\text{CH}_2$ $\text{H}_2\text{C}-\text{O}$ Vapor	$\text{H}_2\text{C}-\text{C}(\text{CH}_3)_2$ $\text{H}_2\text{C}-\text{O}$ Vapor	$\text{H}_2\text{C}-\text{CHC}_6\text{H}_5$ $\text{H}_2\text{C}-\text{O}$ Isooctane soln.
State	Vapor	Vapor	Isooctane soln.
Temp., °C.	25	28	26
Concn. (moles/l.)	5.13×10^{-3}	5.46×10^{-3}	0.27
% decomposition	0.31	0.27	3.3
Products (expressed in μmoles per 6 hr. of irradiation)			
Ethylene	6.47	2.60	3.45
Isobutylene	..	2.17	..
Formaldehyde	4.00	p	12.2
Acetone	..	0.7 ^b	..
Hydrogen	0.67	.5	0.34
Carbon monoxide	.52	.6	0.5
Methane	.031	.6	..
Ethane	.024	.41	..

^a p = Present, in same order of magnitude as C_4H_8 .

^b Separation incomplete.

These products were observed when less than 1% was decomposed. In photolyses carried out from 5 to 20% decomposition the same products were observed, accompanied by small amounts of propane, *n*-butane and unidentified compounds with molecular weights higher than 58. Altogether these latter products never contributed more than 1% of the total decomposition products. Quali-

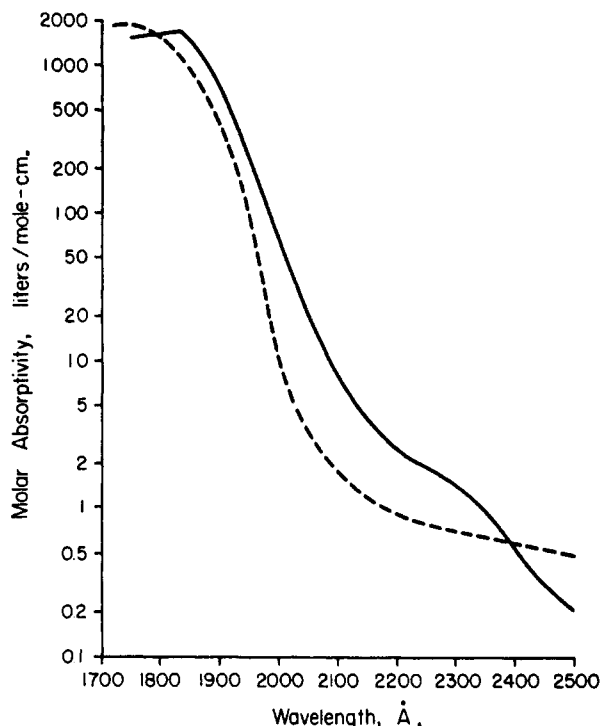


Fig. 1.—Ultraviolet absorption spectra of oxetane (solid line) and 2,2-dimethyloxetane (broken line) in *n*-heptane solution; the molar absorptivity is on a logarithmic scale.

tative tests showed that even at low per cent. decomposition the secondary photolysis of formaldehyde, yielding CO and H_2 ,^{19,20} was a complicating feature of the photolysis system. (Two tests were used. Both showed a decrease in the $\text{CO}/\text{C}_2\text{H}_4$ ratio, because the amount of formaldehyde photolysis was decreased. In one test oxetane vapor was pumped over KOH pellets during the photolysis. In the other test formaldehyde vapor was used as a filter for the irradiation from the mercury arc.) Secondary photolysis was always significant because the mercury lines in the 1900 Å. region, which were responsible for the oxetane photolysis, were very weak compared with the near-ultraviolet mercury lines which decomposed the formaldehyde. This was shown by a photolysis of oxetane using a Corning glass No. 9863 as a filter, which reduced the products to 0.7% of the amount obtained without using it. This filter cut off radiation below 2280 Å. but transmitted most of the near ultraviolet radiation. It was calculated that at least 94% of the decomposition from unfiltered radiation was due to the weak mercury lines below 2380 Å., namely, 2002, 1973, 1942 and 1849 Å. Since oxygen absorbs appreciably at 1849 Å., the other three mercury lines may have accounted for most of the decomposition.

The results from the vapor phase photolysis of 2,2-dimethyloxetane are given in Table I. The conditions were nearly equivalent to the 25° photolyses of oxetane, although the secondary photolysis of acetone as well as formaldehyde further com-

(17) L. C. Jones, Jr., and L. W. Taylor, *Anal. Chem.*, **27**, 228 (1955).

(18) L. W. Taylor and L. C. Jones, Jr., *ibid.*, **28**, 1706 (1956).

(19) J. G. Calvert and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 176 (1951).

(20) E. I. Akeroyd and R. G. W. Norrish, *J. Chem. Soc.*, 890 (1936).

plicated the system. The dimethyl derivative has a lower absorptivity between 2400 and 1785 Å. than does oxetane (see Fig. 1). This, rather than a lower quantum yield, could account for the slower photolysis rate of the dimethyloxetane.

Products from 2-phenyloxetane photolysis are shown in Table I. This system differed from the vapor photolysis systems in absorption spectra, concentration and per cent. decomposition.

Table II and Fig. 2 show that while virtually the same products were obtained from oxetane photolysis

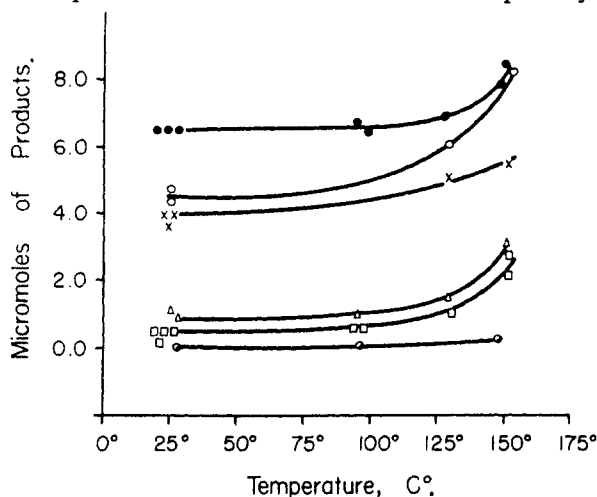


Fig. 2.—Rates of formation of products from oxetane vapor photolyses, given in micromoles of products formed per 6 hr. of irradiation (at each temperature the concentration of oxetane was 5.13×10^{-3} mole/liter): ●, C_2H_4 ; ○, $CH_2O + CO$; X, CH_2O ; Δ, H_2 ; □, CO ; ○, $CH_4 + C_2H_6$.

ses under various conditions of temperature or state, the ratio of these products did vary. In aqueous solution secondary photolysis of formaldehyde contributed least to the products, presumably because it is in equilibrium with its hydrate and does not photolyze as readily. On the other hand, as the temperature of the vapor phase photolyses increased the amounts of carbon monoxide and hydrogen increased, and the amount of CH_2O plus CO approached the amount of C_2H_4 . This is attributed to increased decomposition of the formyl radicals which were formed from formaldehyde photolysis¹⁹



The relative rates of formation of products from oxetane vapor photolyses are shown as a function of temperature in Fig. 2. The rates were nearly constant up to 100° and then increased rapidly, which suggested that a free radical reaction contributed to the formation of the products above 100°. Although hydrogen atoms and formyl radicals were believed to be responsible for initiating a free radical decomposition of oxetane above 100°, it was more convenient to use CH_3 radicals to study this decomposition. Table III shows the results from the formation of methyl radicals in the presence of excess oxetane. Besides CH_4 and C_2H_6 none of the products are found from just the photolysis of acetone²¹ (except CO) or

(21) W. Davis, Jr., *Chem. Revs.*, **40**, 201 (1947).

TABLE II EFFECT OF ENVIRONMENT ON THE PHOTOLYSIS OF OXETANE ^a				
State	Vapor	Isooctane soln.	Aqueous soln.	Solid
Temp., °C.	25	27	27	-196
Products (expressed in relation to each 100 μmoles of C_2H_4 produced)				
Ethylene	100	100	100	100
Formaldehyde	62	p	p	p
Hydrogen	10	4.4	1.5	9.2
Carbon monoxide	8.0	3.8	0.7	8
Methane	0.48	0.1	.07	0.3
Ethane	.377	1
Carbon dioxide7	...

^a p = present, in the same order of magnitude as C_2H_4 .

TABLE III
PRODUCTS FROM METHYL RADICAL ATTACK ON OXETANE VAPOR

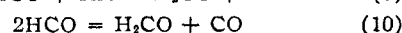
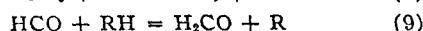
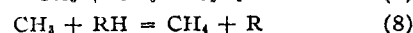
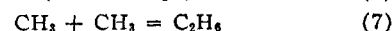
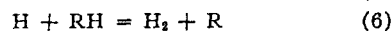
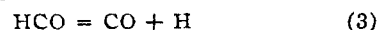
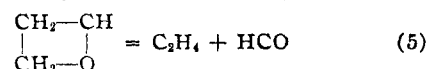
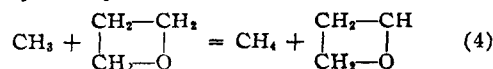
Source of CH ₃	3130 Å. photolysis of acetone	Pyrolysis of di- <i>t</i> -butyl peroxide	
Temp., °C.	154	150	120
Oxetane pressure, mm.	98.6	46	44
Ratio: oxetane/ source material	11/1	107/1	12/1
Period of run, hr.	7.67	4.0	118.7
Max. amt. CH ₃ formed (μmoles)	21	43	376
Amt. of CH ₃ found (μmoles)	15.4	21.2	197
Other products	Quantum yield ^a	Amt. formed per 100 μmoles of CH ₄	
Ethane	0.13	9	17 14
Ethylene	0.64	43	35 7
Formaldehyde	w	w	3 1
Hydrogen	0.25	17	12 2
Carbon monoxide ^b	.29 (1.00)	20 (68)	23 6
C ₂ , C ₄ hydrocar- bons	.02	1	6 2
Higher aldehydes	w

^a From acetone photolysis assuming a quantum yield of 2.00 for CH_3 . ^b Numbers in parentheses are for CO produced from acetone photolysis. w = Present, as indicated by a weak qualitative test.

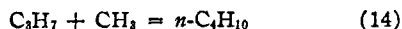
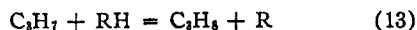
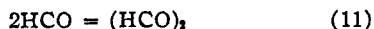
the pyrolysis of di-*t*-butyl peroxide.²² Therefore these products must be attributed to the induced decomposition of oxetane, which by itself is stable in the same temperature range.

Discussion of Results

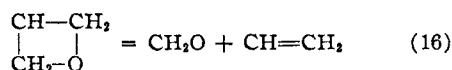
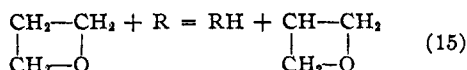
Free Radical Initiated Decomposition of Oxetane.—The reactions (4) to (14) afford an adequate mechanism to explain the major sources of the observed products in the decomposition of oxetane, caused by methyl radical attack.



(22) J. H. Raley, F. F. Rust and W. E. Vaughan, *THIS JOURNAL*, **70**, 88, 1336, 2768 (1948).



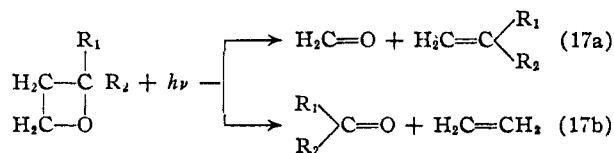
The RH in these equations refers to oxetane and other compounds with abstractable hydrogen in the systems, such as acetone or the peroxide. Equations 4, 5 and 3 have been suggested by Bittker and Walters⁵ as a possible mechanism for free radical initiated decomposition of oxetane which occurred in their pyrolysis studies in the 420–460° range. They also suggested equations (15) and (16) as a possible mechanism.



In the lower temperature range studied here, the small amount of formaldehyde found and the absence of propylene and 1,4-butadiene indicate that reaction 16 did not occur to an appreciable extent.

For each C_2H_4 molecule formed *via* reaction 5 a free radical is produced (HCO or H) which presumably can initiate decomposition analogous to CH_3 radicals in reaction 4, causing a chain reaction. However, the quantum yield of C_2H_4 in the acetone photolysis experiment was only 0.6, and about 13% of the methyl radicals did not result in gaseous products. This indicates either (a) that free radicals added to oxetane to give a relatively stable open chain radical $\text{R}(\text{C}_3\text{H}_6\text{O})$, or (b) that $\text{C}_3\text{H}_5\text{O}$ radicals (with cyclic or open chain structures) from oxetane were somewhat stable and combined with radicals to form $\text{R}(\text{C}_3\text{H}_5\text{O})$ compounds. These suggestions are consistent with the observation that at lower temperatures there was a decreased yield of gaseous products from free radical attack.

Intramolecular Photolysis Mechanism.—The photodecomposition products (except traces of CH_4 and C_2H_6) for the three oxetanes are consistent with general equation 17, which indicates that direct intramolecular rearrangements could be the main primary process in their photolyses. In

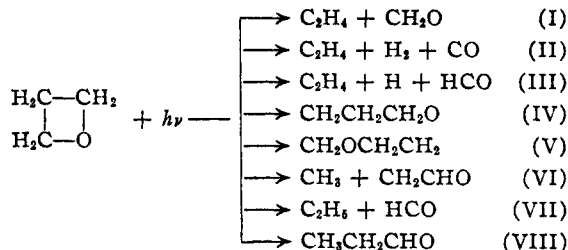


oxetane photolyses the minor products, H_2 and CO, can be attributed to secondary photolysis of formaldehyde. Similarly H_2 , CO, CH_4 and C_2H_6 are attributable to the secondary photolysis of both formaldehyde and acetone in the 2,2-dimethyloxetane photolysis. The minor products from 2-phenyloxetane photolysis were also H_2 and CO, produced secondarily from formaldehyde. According to equation 17 the latter photolysis also should have produced benzaldehyde and styrene as major products. They were not detected by infrared analysis in the large excess of solvent and undecomposed 2-phenyloxetane. However, they

would be expected to have undergone secondary photochemical reactions such as polymerization and back reactions. The latter would correspond to reactions of the type reported by Büchi, Inman and Lipinsky,²³ who found that 2-methyl-2-butene combined with aldehydes in the presence of ultraviolet light to form substituted oxetanes. It is of considerable interest to note that the photochemical decompositions of oxetanes are essentially the reverse of the photochemical syntheses found by Büchi, *et al.*

The unsymmetrically substituted dimethyloxetane split about equally into the products indicated by 17a and 17b. The ratio of isobutylene to ethylene was 0.85/1, indicating that the methyl substituents did not have a large effect on the direction of the intramolecular split. Although many secondary reactions undoubtedly occurred in the photolysis of 2-phenyloxetane, the large 3.5/1 ratio of formaldehyde to ethylene indicates that intramolecular split 17a probably was favored over 17b.

Possible Primary Processes of Oxetane Photolysis.—The reactions given below all have some basis for being considered as primary processes for the photolysis of oxetane. Reaction I corresponds to the general intramolecular mechanism postulated in equation 17. Secondary photolysis of CH_2O produced some H_2 and CO; however, this has not been demonstrated to be their only source. Therefore, processes II and III are postulated as possible sources of these products. The observation that CO and H_2 accounted for less than 2% of the photolysis products in aqueous solution indicates that II and III are, at most, only minor processes compared to I. However, the initial step might be the



formation of a biradical, as in IV and V, which could break up to yield the observed products. If a biradical were formed, it would be highly energetic since the radiation absorbed corresponds to 143 kcal./mole or greater, while the C–O bond of oxetane has been estimated to be 75 kcal./mole.⁶ The following points indicate that if biradicals are formed they are quite unstable and probably decompose into ethylene and formaldehyde before they have an opportunity to undergo other reactions: (a) the rate of formation of ethylene in the vapor phase photolyses (Fig. 2) was nearly constant between 25 and 100° whereas biradicals undergoing a significant number of collisions would not be expected to break up quantitatively into C_2H_4 and CH_2O at a rate independent of temperature over this range, (b) photolyses in solutions seemed to proceed by the same mechanism as in the vapor phase, although reactive biradicals might be expected to abstract hydrogen atoms from the sol-

(23) G. Büchi, C. G. Inman and E. S. Lipinsky, *THIS JOURNAL*, **70**, 4327 (1954).

vent, particularly in water solutions where the basic oxygen of the ether²⁴ would be hydrogen bonded to water molecules and (c) photolysis at -196° gave the same products as the vapor phase photolyses, whereas at low temperatures a biradical might be expected to undergo reactions other than a thermal decomposition into C_2H_4 and CH_2O .

Processes VI, VII and VIII are all analogous to the type of photodecomposition that Gomer and Noyes³ postulated for ethylene oxide, equation 1. These reactions are postulated as very minor primary processes, which could account for the formation of CH_4 , C_2H_6 and traces of other hydrocarbons. Analyses did not identify propionaldehyde as a photolysis product, but it would be expected to undergo secondary photolysis that would lead to

(24) H. S. Gutowsky, R. L. Rutledge, M. Tamres and S. Searles, *THIS JOURNAL*, **76**, 4242 (1954).

the formation of H_2 , CO , CH_2O and C_2H_4 as well as C_2H_6 and CH_4 ,²⁵ although in different ratios than were found for these products in the oxetane photolyses. Another source of ethane could be from ethyl radicals resulting from the reaction of ethylene with hydrogen atoms produced by the secondary photolysis of CH_2O .

These studies have indicated that intramolecular primary process I accounts, directly or indirectly, for about 98% of the products of oxetane photolysis. The high energy of the absorbed radiation in the 2000 Å. region suggests that the quantum yield of this decomposition into C_2H_4 and CH_2O might be near unity, in which case oxetane would be valuable as a sensitive and convenient chemical actinometer.

(25) F. E. Blacet and J. N. Pitts, Jr., *ibid.*, **74**, 3382 (1952).

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The Effect of Surface Oxidation on the Voltammetric Behavior of Platinum Electrodes. The Electroreduction of Iodate

BY FRED C. ANSON

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Chronopotentiograms of iodate ion reduction at platinum electrodes show that the iodate reduction proceeds much more reversibly at oxidized than at reduced electrodes. The reduction of the platinum oxides on the surface of an oxidized platinum electrode appears to catalyze the reduction of iodate ion. In solutions of pH 1 and below the cathodic reduction of iodate to iodide at unoxidized electrodes proceeds by means of iodine as an intermediate.

A platinum electrode which has been oxidized has a coating of PtO and PtO_2 on its surface¹ and displays quite different voltammetric behavior than for an unoxidized electrode.² This study delineates the way in which the oxidation of a platinum electrode influences the reduction of iodate ion at its surface.

The polarographic behavior of iodate ion at mercury electrodes is well known³ but the only previous report of iodate ion reduction at platinum electrodes was made by Shain⁴ who observed a reduction wave at a (presumably unoxidized) rotating platinum electrode in $5F H_2SO_4$.

In the present study the reduction of iodate ion at reduced and oxidized platinum electrodes was investigated with the chronopotentiometric technique.⁵ The experiments show that the reduction of iodate ion occurs very close to the potential where hydrogen ions are reduced at *unoxidized* electrodes in neutral or moderately acid solutions. However, at *oxidized* electrodes the reduction of iodate occurs at potentials from 200 to 600 millivolts more positive (oxidizing). This decrease in overvoltage apparently is due to a catalysis of

iodate reduction when it is accompanied by the reduction of the oxide film on an oxidized platinum electrode.

Experimental

The experimental arrangement for the chronopotentiometric measurements was identical to the one previously described.^{2c} A Varian model G-10 recorder with a 10 millivolt intrinsic range and a 1 second full scale deflection time was used.

The bright platinum electrode employed had an area of 7.3 cm^2 per side.

The auxiliary electrode was a platinum wire immersed in a sample of the test solution in a glass tube terminating in a sintered glass disc. The extent of electrode oxidation was determined as previously^{1,2c} by stirring the electrode free of the oxygen formed during oxidation, allowing the solution to become quiescent, passing a constant cathodic current through the electrode and measuring the cathodic transition time for the reduction of the platinum oxides.

Oxidation of the platinum electrode while in the test solution was accomplished by passing an anodic current of *ca.* 25 milliamperes through the electrode for 5 seconds. Earlier experiments¹ have shown that the surface of a platinum electrode can be oxidized to a rather reproducible maximum extent after which all of the current goes toward oxidizing water. The completely oxidized electrode contained 1.3×10^{-3} microequivalent of platinum oxides per cm^2 .

The area of the gold electrode which was used was 6.5 cm^2 per side. In contrast to platinum there appeared to be no well-defined upper limit for the extent to which the gold electrode could be anodically oxidized in 0.1 *M* sulfuric acid.

The current-voltage curves were obtained with an "Auto-graph" X-Y recorder model G-3 (F. L. Mosely Co., Pasadena, Calif.). The polarizing voltage was obtained from a 1000 ohm Helipot potentiometer driven by a synchronous motor.

All measurements were made in oxygen-free solutions.

(1) F. C. Anson and J. J. Lingane, *THIS JOURNAL*, **79**, 4901 (1957).
(2) See, for instance: (a) S. S. Lord and L. B. Rogers, *Anal. Chem.*, **26**, 284 (1954); (b) I. M. Kolthoff and N. Tanaka, *ibid.*, **26**, 632 (1954); (c) F. C. Anson and J. J. Lingane, *THIS JOURNAL*, **79**, 1015 (1957); (d) I. M. Kolthoff and E. R. Nightingale, *Anal. Chim. Acta*, **17**, 329 (1957).

(3) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Pub., Inc., New York, N. Y., 1952, p. 574-575.

(4) I. Shain, *Anal. Chem.*, **26**, 281 (1954).

(5) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Pub., Inc., New York, N. Y., 1954, Chapt. 8.