produced with and without added diallyl were measured also. The data given in Table IV show that diallyl increases considerably the quantity of hydrogen formed during ten minutes at 555°.

Discussion.—The results indicate that the acceleration resulting from the presence of the products accounts to a considerable extent for the S-shaped nature of the pressure–time curve for the decomposition of cyclopentane. The mechanism by which ethylene, propylene or cyclopentadiene (or their decomposition products) can bring about the increase in rate has not been established from the existing experimental data. Küchler[3e] and Eucken[20] have suggested that the acceleration of the ring cleavage is due to the assistance which propylene renders in the process of transfer of a hydrogen atom from one carbon atom to an adjacent one.

The present work shows that the dehydrogenation portion of the decomposition is increased in the presence of ethylene or propylene. This acceleration and also the shape of the curve showing the amount of cyclopentadiene or hydrogen *vs.* time for the decomposition of pure cyclopentane give evidence that the dehydrogenation of cyclopentane probably does not proceed as a simple first order reaction. On the basis of the hydrogen formed during the early stages of the reaction Küchler[3e] reported that the hydrogen-forming reaction was first order. Moreover, the rate of pressure increase during the induction period in his experiments seems to have been greater than in the present study. In view of these differences during the initial stage, but agreement in the subsequent period, the possibility of the presence of an impurity in the cyclopentane has been given consideration. In the present study samples of cyclopentane from several different sources[21] have been found to give similar results. Although no definite conclusion can be reached, several experimental observations have indicated that at least part of the difference could be explained if the cyclopentane used in the previous study[3e] contained a small amount of cyclopentene.

Since analyses for ethylene and propylene were not performed in the presence of added substances, no direct evidence for the acceleration of the ring cleavage has been obtained in this work. However, the increase in the rate of pressure rise in the presence of propylene appears to be greater than can be accounted for on the basis of the measured increase in the dehydrogenation reaction. This observation gives an indication that the addition of propylene increases the rate of ring cleavage, in agreement with Küchler's experiments; but ethylene appears to be considerably less effective.

Acknowledgment.—We wish to thank Dr. F. L. Mohler and the staff of the Mass Spectrometry Section of the National Bureau of Standards for performing the mass spectrometric analyses.

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[20] Eucken, *Die Chemie*, **56**, 342 (1943).

[21] Mr. H. D. Batha of this Laboratory has observed that the rate of pressure rise during the induction period at 555° for a sample of cyclopentane (99.95%) from the Phillips Petroleum Co. is the same as that for the two kinds of cyclopentane described in the Experimental section.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Vapor-phase Photolysis of Acetone–Iodine Mixtures

BY JAMES N. PITTS, JR.,[1] AND F. E. BLACET

The quantum yield of methyl iodide formation, Φ_{CH_3I}, is temperature dependent and much less than unity in the vapor-phase photolysis of acetone–iodine mixtures at 3130 Å. At constant acetone concentration and 3130 Å., Φ_{CH_3I} increased from 0.12 at 80° to 0.28 at 177°. Φ_{CH_3I} is also a function of wave length, and at 100° it increases from 0.17 at 3130 Å. to 0.50 at 2654 Å. Only small amounts of carbon monoxide and methane were formed, but no ethane was detected. The significance of these results in terms of the various primary processes postulated for acetone photolysis is discussed.

The nature and extent of the primary processes occurring in the vapor phase photolysis of acetone have been the subject of numerous investigations, the results of which have been reviewed by Davis[2] and again critically discussed by Noyes and Dorfman.[3] The latter authors present a mechanism for the photochemical decomposition in the pressure region where wall effects can be neglected. This includes the following primary processes

$$CH_3COCH_3 + h\nu \begin{cases} \longrightarrow CH_3 + CH_3CO & (1) \\ \longrightarrow 2CH_3 + CO & (2) \\ \longrightarrow CH_3COCH_3' & (3) \end{cases}$$

and excludes the concerted intramolecular process (4).

$$CH_3COCH_3 + h\nu \longrightarrow C_2H_6 + CO \qquad (4)$$

In addition to these primary processes, Noyes and Dorfman include reaction (5) to account for the fraction, *a*, of the acetyl radicals produced by process (1) that immediately dissociate as a result of excess energy remaining after (1).

$$a\ CH_3CO' \longrightarrow a\ CH_3 + a\ CO \qquad (5)$$

In this investigation acetone–iodine mixtures were irradiated in order to obtain quantitative information as to the extent of processes (1), (2), (4) and (5), and to examine carefully the photolysis products by chemical and mass spectrometric methods.

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[1] Department of Chemistry, Northwestern University, Evanston, Ill.

[2] W. Davis, Jr., *Chem. Revs.*, **40**, 201 (1947).

[3] W. A. Noyes, Jr., and L. M. Dorfman, *J. Chem. Phys.*, **16**, 788 (1948).

Experimental

The experimental techniques employed have been previously described and need not be discussed in detail in this paper.[4,5,6]

The reaction products, together with the unreacted starting materials, were separated at −80° into a gaseous phase and a condensed phase which contained about 98% unreacted acetone and iodine. The non-condensable gases were collected with the aid of a Toepler pump and the carbon monoxide yield was determined with a Blacet–Leighton apparatus for the micro-analysis of gases. Finally the residual gas was analyzed with a Westinghouse Model LV mass spectrometer.

The condensed phase was analyzed by two procedures. In runs 1 and 2 the condensable fractions were first treated with mercury to remove unreacted iodine, then briefly exposed in the vapor state to sulfuric acid to remove the excess acetone and other oxygenated compounds, and finally introduced into the mass spectrometer. After the mass spectrum had been obtained the products were recondensed from the spectrometer and analyzed for total iodide. The condensable fractions from photolyses 3 and 4 were dissolved in carbon tetrachloride and shaken with liquid mercury at room temperature for about 15 minutes and then distilled from the mercury–mercuric iodide residue. The distillate was then equilibrated with 0.001 *N* aqueous potassium hydroxide. Analysis of the organic phase for iodide by a procedure that had been verified using synthetic samples containing known amounts of methyl iodide, provided an estimate of the alkyl iodide yield, and the iodide titer of the aqueous solution gave an estimate of the acetyl iodide present in the condensable fraction that survived the photolysis and subsequent analytical procedure. As an additional check on the distribution of iodide in the system, the interior of the reaction cell was washed with dilute base and the solution analyzed for iodide ion. In Table I are presented the quantitative results obtained in this study.

TABLE I

QUANTUM YIELDS, Φ, OF PRODUCTS, FROM THE PHOTOLYSIS OF ACETONE-IODINE MIXTURES

Photolysis no.		1	2	3	4
Wave length, Å.		2654	3130	3130	3130
Temperature, °C.		100	80	100	177
Acetone pressure, mm		122	111	113	138
Acetone concentration, moles × 10^{-3}/liter		5.25	5.04	4.87	4.92
I_2 pressure, mm.		4.5	2.8	3.8	4.0
I_a, (quanta abs./sec.-ccm.) × 10^{-12}		4.68	6.77	8.14	8.23
Quantum yields, Φ	CH_3I	0.50	0.12	0.17	0.28
	CO	.057	.0015	.003	.014
	CH_4	.004	.000	.000	.006
	C_2H_6	.000	.000	.000	.002

The quantum yield of iodide found in the aqueous phase following the equilibration of the products with the carbon tetrachloride–dilute base mixture was only of the order of 0.01. Somewhat larger quantities of iodide, Φ about 0.01$_6$, were deposited on the walls of the reaction system, but in no case did the yield of iodide ion exceed about one-eighth of the yield of the methyl iodide. Mass spectra of the condensed products in the region from m./e. 60 to m./e. 190 showed no significant peaks above m./e. 142, the parent peak of methyl iodide. These results, however, do not eliminate the possibility of relatively large amounts of acetyl iodide having been formed in the photolyses. Recent tests of the analytical procedure using synthetic samples containing known amounts of acetyl iodide showed that it decomposes readily in the presence of room light and mercury; hence the analysis procedure gave only a lower limit for acetyl iodide formation.

Discussion

The significance of the results in Table I and the supplementary information derived from analyses of the reaction products can be summarized in the following manner:

1.—No ethane was found at 100° at 3130 or 2654 Å., thus the intramolecular process (4) should not be included in a mechanism for acetone photolysis at either wave length. This conclusion is in accord with the results of Gorin,[7] and Benson and Forbes,[8] who irradiated acetone–iodine mixtures at 3130 and 2537 Å., respectively, and with the results of Noyes and Dorfman.[3]

2.—The over-all quantum yield of methyl iodide formation, Φ_{CH_3I}, is temperature dependent at 3130 Å. and rises from 0.12 at 80° to 0.28 at 177°. Since Φ_{CO} was very small at all temperatures, processes (2) and (5) are unimportant at 3130 Å. and thus within experimental error, Φ_{CH_3I} is equal to ϕ_1, the primary yield of (1) in the iodine-inhibited system.

3.—The magnitude of Φ_{CH_3I} shows a marked dependence upon the energy of the quantum absorbed, as Φ_{CH_3I} increases from 0.17 at 3130 Å. and 100° to 0.50 at 2654 Å. at the same temperature. Upon correcting for the formation of methyl radicals by (5) one obtains a value of about 0.44 for ϕ_1 at 2654 Å.

4.—Very small amounts of carbon monoxide were produced in the photolyses at 3130 Å. Φ_{CO} was temperature dependent but the maximum yield was only 0.014 at 177° compared to a value of 0.28 for Φ_{CH_3I}. At 100° Φ_{CO} was also a function of wave length, increasing from 0.003$_5$ at 3130 Å. to 0.057 at 2654 Å.

5.—Under more energetic reaction conditions, iodine apparently was slightly less effective in trapping the methyl radicals produced in the photolysis since traces of methane were formed at the higher temperatures and at the shorter wave length.

The results of this brief investigation are generally in qualitative agreement with the findings of other investigators.[3,7,8] There is, however, a considerable contrast between the absolute quantum yields at 3130 Å. determined by Gorin[7] and those obtained by the authors. As a result of this investigation it is evident that Φ_{CH_3I} at 3130 Å. is not about 0.85 as earlier reported,[7] but instead at constant acetone concentration it is temperature dependent and ranges from 0.12 at 80° to 0.28 at 177°. It is significant that the value of 0.17 obtained for Φ_{CH_3I} at 100° is in excellent agreement with the results of recent work on the iodine inhibited photolysis of acetone by Martin and Sutton.[9] These investigators photolyzed acetone–iodine mixtures under reaction conditions comparable to those employed by Gorin,[7] and the present authors, and utilized a radioactive tracer method for the analysis of the iodides produced.[10]

The observed dependence of ϕ_1 upon temperature at 3130 Å. confirms the prediction of Noyes and Dorfman who suggested[3] that, since the efficiency of

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[4] F. E. Blacet and J. D. Heldman, THIS JOURNAL, **64**, 889 (1942).

[5] F. E. Blacet and J. G. Calvert, *ibid.*, **73**, 667 (1951).

[6] J. N. Pitts, Jr., and F. E. Blacet, *ibid.*, **72**, 2810 (1950).

[7] E. Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

[8] S. W. Benson and G. S. Forbes, THIS JOURNAL, **65**, 1399 (1943).

[9] G. R. Martin and H. C. Sutton, private communication. Their work will be reported in detail in another journal.

[10] R. W. Durham, G. R. Martin and H. C. Sutton, *Nature*, **164**, 1052 (1949).

the fluorescence process at 3130 Å. was a function of temperature,[11] the primary quantum yield of decomposition should also be temperature dependent. With regard to the small magnitude of ϕ_1, at 3130 Å., W. A. Noyes, Jr., has suggested[12] that the low probability of (1) in the iodine-inhibited photolyses does not exclude the possibility that it may be close to unity in the non-inhibited reaction. He pointed out that, if at 3130 Å. "predissociation" occurred from a long-lived excited state of acetone, as the fluorescence data indicate,[11] then iodine might be efficient in deactivating a large fraction of the molecules in this state and thus reduce ϕ_1, to a very low value, or even zero. This reasoning would also lead one to expect a larger value of ϕ_1, at the shorter wave lengths where the fluorescence is very small and the absorption approaches a continuum. This conclusion is also verified by the results of this study since ϕ_1 at 100° rises from 0.17 at 3130 Å. to 0.44 at 2654 Å.

Since only small traces of methane were found it is evident that the iodine vapor was an efficient "trap" for the methyl radicals produced at both 3130 and 2654 Å. The absence of methane also eliminates reaction (6) as a primary process under the reaction conditions employed in this study.

$$CH_3COCH_3 + h\nu \longrightarrow CH_4 + CH_2CO \qquad (6)$$

Several attempts have been made to evaluate the quantity a at various wave lengths. In this study if one assumes that all the carbon monoxide formed at either wave length comes from the so-called "hot atom" dissociation reaction (5) plus the analogous thermal decomposition (7)

$$CH_3CO \longrightarrow CH_3 + CO \qquad (7)$$

one can calculate a value of 0.11 for a at 2654 Å., and a maximum value of 0.02 at 3130 Å. The value at 2654 Å. is compatible with that of 0.22 ± 0.05 calculated for 2537 Å. by Noyes and Dorfman[3] from the results of Benson and Forbes and others. It should be noted that it was not possible to distinguish between the carbon monoxide formed by processes (1) and (5) occurring in rapid succession, and that formed by primary process (2). Therefore, to the extent that (2) occurred, the value for a is too high. It should be noted that process (2) is not appreciable at either wave length. Since several investigators[13,14,15] have shown that Φ_{CO} is unity in the non-inhibited photolysis of acetone at temperatures slightly above 100°, it is evident that the carbon monoxide must come from process (1) followed by reaction (7) and other secondary processes involving free radicals, rather than from primary process (2).

It is impossible to account quantitatively for the fate of the carbonyl part of the molecule since no reproducible, quantitative analytical results for acetyl iodide were obtained. It seems likely that acetyl iodide was formed in the photolyses, but that most of it reacted with mercury and thus did not survive the analytical procedure employed. This reaction between acetyl iodide and mercury in the presence of light may also be responsible for the difficulties other workers have encountered in obtaining consistent analyses for this compound.[8,9] However, regardless of the ultimate fate of the acetyl radicals, the small values for the ratio Φ_{CO}/Φ_{CH_3I} obtained in this research and in the photolysis of methyl ethyl ketone-iodine mixtures[6] are good evidence that in the presence of a free radical inhibitor, such as iodine, the acetyl radical is quite stable at temperatures as high as 177°. Since Φ_{CO} is unity in the non-inhibited photolysis of acetone at temperatures slightly above 100°,[13,14,15] this fact has been taken as being indicative of the instability of the acetyl radical at elevated temperatures.[16] It now seems evident that from 100 to 175° the acetyl radical dissociates readily only in the presence of relatively large concentrations of free radicals, whereas in the absence of such radicals it is quite stable over that temperature range.

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(11) R. E. Hunt and W. A. Noyes, Jr., THIS JOURNAL, **70**, 467 (1948); G. W. Luckey and W. A. Noyes, Jr., *J. Chem. Phys.*, **19**, 227 (1951).

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(13) D. S. Herr and W. A. Noyes, Jr., THIS JOURNAL, **62**, 2052 (1940).

(14) J. A. Leermakers, *ibid.*, **56**, 1899 (1934).

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(16) *Cf.* E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, p. 379 ff.