data on the photolysis of acetone in the presence of O^{18}-enriched oxygen can be interpreted[24] to yield $E_{20} - E_{22} \sim 9$ kcal. mole^{-1} with log $A_{20}/A_{22} \sim 19.1$ when concentrations are expressed in molecule/ml.

Hence at oxygen pressures of 1 mm. or higher it is unlikely that much of the carbon monoxide is formed by decomposition of the acetyl radical. It seems more probable that a substantial portion of the carbon monoxide arises from attack on formaldehyde (reactions 27, 28 and 29). The methyl radicals formed by reaction 20 eventually will be oxidized to methoxy radicals.[16,21] These methoxy radicals and those formed by reaction 22 will form methanol and formaldehyde by reactions similar to those suggested for the disappearance of ethoxy radicals. Acetic acid is likely to be formed from the acetyl radical as well. No mechanism for its formation is proposed since only a few approximate estimations of the amounts of the acid were made.

According to the mechanism proposed for the disappearance of the acetyl radicals the ratios CO/CO_2 and CH_3OH/CO_2 should be independent of exposure for a given temperature and azoethane and oxygen pressure. This is observed, as is illustrated in Fig. 4. The product ratio of carbon monoxide falls rapidly for conversions greater than 12%, probably because hydrogen abstraction from ethanol and methanol compete with the hydrogen abstraction from formaldehyde. This may be the explanation of the observed decrease in the product ratios of the alcohols at highest conversion (Table I).

From the foregoing discussion it may be deduced that the total amount of acetaldehyde formed will be equal to the sum of the estimated amounts of acetaldehyde, carbon dioxide, acetic acid and the amount of carbon monoxide formed by reaction 20. At oxygen pressures greater than 0.1 mm. the amount of carbon monoxide formed by reaction 20 is small relative to the amount of carbon dioxide (< 5%) and can be neglected[24]; the amount of acetic acid is negligible in low conversion experiments also. Thus under these conditions the total amount of acetaldehyde formed will be nearly equal to the sum of the amounts of acetaldehyde and carbon dioxide determined, as was assumed earlier.

The formation of C_1-products at rather low conversions indicates that hydrogen abstraction from acetaldehyde is easier than from azoethane. This implies that the concentration of $C_2H_5N_2C_2H_4$ radicals, and hence the rate of formation of nitrous oxide, ethylene and secondary nitrogen, should decrease with increasing exposure until acetaldehyde concentration reaches a steady value. These effects are indeed observed as shown in Table I.

In over-all summary it is clear that the gross general features of the photo-oxidation can be explained by the type of mechanism proposed. Much remains to be done to improve the quantitative reliability of the data, especially at low conversion and low oxygen pressure, before detailed consideration can be given to the interaction of ethyl radicals with oxygen.

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[24] H. Cerfontain, J. M. Vaerman and K. O. Kutschke, unpublished work.

[CONTRIBUTION FROM DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF ROCHESTER, ROCHESTER 20, N. Y., AND UNIVERSITY OF DELAWARE, NEWARK, DEL.]

A Comparison of the Radiolysis and Photolysis of Cyclopentanone

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The major products of the γ-ray radiolysis of cyclopentanone are reported as hydrogen, carbon monoxide, ethylene and an oil. Yields of carbon monoxide and ethylene are uncertain because of secondary reactions setting in at about 0.001% conversion of the parent compound, but the hydrogen yield is constant with dose at $G(H_2) = 0.67$. The oil product has been characterized as having a molecular weight of about 200 and retains much of the parent cyclopentanone character. The gas phase radiolysis qualitatively resembles the liquid phase radiolysis. A comparison is given between the radiolysis and photolysis of cyclopentanone which points up the need for shorter wave length photolysis studies of this system.

The investigation reported here on the radiolysis of oxygen-free liquid and gaseous cyclopentanone by cobalt-60 γ-radiation was prompted by photochemical investigations of the same compound.[2,3] Srinivasan[3] suggested that the photolyzed gaseous system at 3130 Å. contained no detectable free radicals. The pressure and wave length dependence of the ratio of the photolysis products 4-pentenal: CO was attributed to the collisional deactivation of a vibrationally excited upper singlet electronic state. At high pressures the quantum yield of 4-pentenal was increased at the expense of the carbon monoxide yield, presumably the result of an internal isomerization in the ground vibrational state of of the excited electronic state. Photolysis of pure liquid cyclopentanone was used by Srinivasan to prepare 4-pentenal for identification purposes, but the quantum yield was not measured nor were quantum yields of other products measured.

According to the current theories of radiation chemistry, radiolysis presumably results in the

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[2] (a) S. W. Benson and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **64**, 80 (1942); (b) F. E. Blacet and H. Miller, *ibid.*, **79**, 4327 (1958).

[3] (a) R. Srinivasan, *ibid.*, **81**, 1546 (1959); (b) **83**, 4344 (1961); (c) **83**, 4348 (1961).

production of excited vibrational and electronic states in addition to ionic species. It is therefore of interest to compare the radiation chemistry of cyclopentanone with this interesting photochemical behavior.

The major products of the radiolysis of liquid cyclopentanone are CO, H_2, C_2H_4 and a relatively non-volatile oil. Tentative *G*-values (no. of molecules formed per 100 e.v. energy absorbed) listed in Table I are based on initial slope data. This is necessary because of the secondary product reactions which become significant at about 0.001% (10^{18} e.v./g.) conversion of cyclopentanone to products.

TABLE I

$G(CO) \cong 1.5^a$	$G(H_2) = 0.67 \pm 0.05$
$G(C_2H_4) \cong 0.3^a$	$G(\text{oil}) \cong 1^b$

[a] Initial slope data. [b] Rough estimate based on an average molecule wt. of 200.

The hydrogen yield is linear with dose and invariant with increased temperature (100° *vs.* 25°), whereas both the CO and C_2H_4 yields are sensitive functions of dose and increase with increased temperature.

The rate of production of CO from liquid cyclopentanone decreases with increased dose and is accompanied by a corresponding increase in the rate of production of ethylene with increasing dose. It is believed that both CO and C_2H_4 act as radical scavengers since addition of small amounts of these gases to the pure liquid before irradiation causes a change in the initial *G*-values of other products. The effect is most striking in the case where the prior addition of 400 mm. of CO to the liquid results in a zero ethylene yield. Ausloos[4] has postulated that carbon monoxide is a radical scavenger and Back[5] has shown the effect of small amounts of ethylene in promoting a secondary scavenging reaction at very low percentage conversion in the radiolysis of hydrocarbons.

When oxygen, iodine or cyclohexene is added to the liquid before irradiation the yields of C_2H_4 and H_2 are decreased and the yield of CO is increased slightly.

From spectral data on the radiolytic oil product, much of the parent cyclopentanone character is probably retained in the oil. Most of the deuterium in the oil product from radiolyzed 2,2,5,5-cyclopentanone-d_4 is contained in methylene groups α to a carbonyl group. It also appears from the molecular weight of the oil and mass balance considerations that entire unfragmented cyclopentanone molecules have been incorporated into the oil. No liquid products other than the oil have been found in the irradiated liquid. Integral C_2H_4 yields are less than integral CO yields so that in the absence of other identifiable liquid or gaseous products it is likely that the oil has also incorporated in it $-CH_2CH_2-$ fragments.

Radiolysis of cyclopentanone vapor produces qualitatively the same major gaseous products as obtained in the liquid phase, namely CO, H_2 and C_2H_4. No significant amounts of other low molecular weight products have been observed. Again the *G*-values are dose dependent and no accurate values of the initial slopes are available because of the small amount of gaseous products available. Qualitatively *G*(CO) is again greater than either $G(C_2H_4)$ or $G(H_2)$. No polymeric product has been observed because of the small vapor pressure of cyclopentanone (12 mm. at 25°) and the relatively inefficient absorption of cobalt 60 γ-radiation in the vapor phase. Further irradiations are being carried on larger samples with longer irradiation times in order to isolate and characterize other products.

Comparison of our results with photochemical studies reveal these differences: 1. Liquid and gas phase photolysis at 3130 Å. produces 4-pentenal. None has been observed either in vapor or liquid phase radiolysis. 2. No free radicals are detectable in the vapor phase photolysis. There are many indications that free radicals are present in the liquid phase radiolysis and probably are also present in the vapor phase radiolysis. 3. No significant amount of cyclobutane is present in the radiolysis but is a major product in the photolysis. 4. No hydrogen is present in the photolysis at 3130 Å. but is a major product in radiolysis. Several investigations,[6,a,b] however, have shown that photolytic molecular detachment of hydrogen from hydrocarbons is possible at 1470 Å. 5. An oil is present and characterized in the radiolysis but no polymer has been isolated and identified in the photolysis at 3130 Å. However, Blacet and Miller[2b] reported a "light yellow, non-volatile residue which became evident in the reaction cell after several runs, *especially* at the *shorter wave lengths*" (emphasis added) in the vapor phase photolysis.

From these results it would appear that if an electronically excited state of cyclopentanone is responsible for any of the radiolysis products it is unlikely that this state is identical with that obtained in the 3130°Å. photolysis. If electronic excitation is indeed important in the radiolysis of cyclopentanone the photochemical evidence indicates that photolysis experiments at shorter wave lengths[2b,6a,b] may allow closer correlations between the photochemistry and radiation chemistry of cyclopentanone. Such experiments are now in progress in this Laboratory.

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