I. PHOTOLYSIS OF LOW MOLECULAR WEIGHT OXYGEN COMPOUNDS IN THE FAR ULTRAVIOLET REGION¹

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Received March 11, 1958

A preliminary survey has been made of the far ultraviolet vapor phase photolysis of several low molecular weight alcohols, ethers, ketones and acetaldehyde by identifying the far ultraviolet absorption bands which appear during the process of irradiation. Although the reaction mechanism would be expected to be complex, most of the products which were detectable fit into comparatively simple patterns. Probable primary processes are discussed.

Pitts³ has recently pointed out both the importance of, and the experimental difficulties of, extending photolysis studies into the far ultraviolet. The present study gives some of the qualitative information which should aid in the planning of significant quantitative experiments.

This investigation started with two compounds, diethyl ether and ethanol, which do not absorb below 50,000 cm.⁻¹. No work has been reported on the photolysis of pure diethyl ether and there is only one article on ethanol vapor. In an attempt to distinguish between primary products and secondary products, the problem was expanded to include an investigation of the identified products. By this time the prediction of detectable products had become surprisingly accurate and a number of compounds were investigated to test the generalization which had become apparent.

Experimental

The equipment⁴ consisted of the source, a reaction vessel and a vacuum spectrograph. All optical parts were either calcium or lithium fluoride and a nitrogen atmosphere was maintained in the spaces between the three sections of the equipment. The source, a hydrogen discharge lamp, gave a continuum throughout the visible and ultraviolet to 59,700 cm.⁻¹ and beyond that a closely spaced line spectrum which was cut off at about 66,000 cm.⁻¹ by the particular window used on the lamp. The reaction vessel, which was a 32.5 cm. Pyrex tube, 1.4 cm. in diameter, was contained in a vapor handling system such that a study could be made of either flowing or static vapor samples. Ilford Q 1 and Q 3 spectrographic plates were used.

The combination of lamp intensity, dispersion of the instrument and plate response necessitated an exposure time of 2-3 minutes. All measurements were therefore a kind of integrated record of the compounds present in the absorption tube during a 2 or 3 minute irradiation period. In the photolysis studies, static vapor samples were irradiated for a total time ranging up to a maximum of 21 minutes. The pressures of the initial vapor samples in the absorption tube ranged from 10^{-2} to 1 mm. of mercury. Six exposures were recorded on each photographic plate.

Six exposures were recorded on each photographic plate. For any one plate these exposures were selected from some combination of the following: (1) the flowing vapor at a known pressure, (2) the initial irradiation period of the static vapor sample at the same pressure, (3) later periods of irradiation of the same static vapor sample, and (4) a series of time calibration exposures. The first gave the truest pleture of the spectrum of the compound being studied and in all cases was free from evidence of photochemical reactions taking place. The second showed the emerging pattern which was followed in later exposures. Time calibration exposures, which were made through the evacuated absorption tube, served as a check on the transmission of the cell windows and also as a basis for estimating relative concentrations.

Results

The microphotometer records of each successive exposure recorded the decrease in absorption of the reactant and at the same time the increase in absorption of the photodecomposition products. See Fig. 1. As the photolysis proceeded, the characteristic narrow bands of the reactant receded toward the general continuum of broad bands and the characteristic narrow bands of the products rose above the general absorption curve.

A number of patterns of reaction were observed. Frequently the spectrum of a product appeared readily during the initial period of irradiation but increased only slightly on continued irradiation. In some cases one product appeared during the initial period while another product, which had an equivalent extinction coefficient, required more prolonged irradiation. All narrow bands which appeared during the photolyses have been identified.

Since this method of analysis is extremely insensitive for those compounds having either structureless broad bands or low intensity narrow bands, the experimental results emphasize certain compounds and minimize others. In order to keep the results in perspective, the spectra of a number of compounds have been summarized in Table I, for the region 2000-1500 Å., $(50,000-66,000 \text{ cm}.^{-1})$. The aldehydes and ketones also have low intensity absorption bands in the near ultraviolet region and 2,3-butanedione also absorbs in the visible region. Unless a footnote is given, the description is based upon measurements which have been made in this Laboratory. In general the method is particularly sensitive for detecting those compounds which have π -bands but quite intensitive for saturated compounds.

Rough approximations using known or estimated extinction coefficients indicate that during the time of observation, not more than 50% of the reactant disappeared and that the products observed account for 10-50% of the reacting molecules. The experimental results are summarized below. Diethyl ether: ethylene, acetaldehyde and formaldehyde were all produced in significant quantities. See Fig. 1. Dimethyl ether: formaldehyde was produced in significant quantity. On longer exposure a small quantity of ethylene and acetaldehyde were also produced. The appearance of acetaldehyde was more apparent at higher pressures of the ether va-

⁽¹⁾ The spectrographic research program in this Laboratory has received financial support from the Esso Research and Engineering Company and the National Science Foundation (NSF-G752). This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

⁽²⁾ Sinclair Fellow, 1956-1957.

⁽³⁾ J. N. Pitts, J. Chem. Ed., 84, 112 (1957).

⁽⁴⁾ A. J. Harrison, C. L. Gaddis and E. M. Coffin, J. Chem. Phys., 18, 221 (1950).

carbons

FAR ULTRAVIOLET SPECTRA OF THE COMPOUNDS			
Compounds	Regions of ab- sorption max. (cm1 × 10 -3)	Max. molar extinc- tion coef- ficient (× 10 ⁻³)	Spectral character
Water	60	1.5	Broad, structureless
Alkyl alcohols	55	0.1	Broad, structureless
	62 - 66	1	Some structure
Alkyl ethers	52-56	2-3	Pattern of small blunt bands
	57 - 63	4	Some structure
Formaldehyde	57	18	Sharp
	64	23	Sharp
Acetaldehyde	55-60	13	Three main pairs of bands
	60 - 64	24	Diffuse bands
Propionaldehyde	54 - 55		Sharp, narrow
	55 - 58		Low intensity
	59 - 60		Intense, diffuse
Acetone	50 - 55	10	3 main sets of bands
	60 - 65	10	Several bands
2-Butanone	51-55		Diffuse, similar to acetone
	58 - 60		Intense, diffuse
2-Pentanone	51–55		Similar to 2- butanone
	58 - 60		
2,3-Butanedione	57 - 59		Broad, structureless
2,5-Hexanedione	52–55		Similar to other monoketones
	55 - 60		Broad, intense
Ketene ⁵	55 - 59		Several sharp bands
	61-64		Several diffuse bands
Ethylene ⁶	57 - 61	16	6 bands
Carbon monoxide ⁷	50-60		Low intensity
Hydrogen and satd. hydro-			Transparent

TABLE I



Fig. 1.—Microphotometer record showing the photolysis of diethyl ether, at an initial pressure of 0.19 mm. of mercury. Record: — —, the initial 3 min. exposure of the static vapor sample; ——, the second 3 min. exposure; — . _, the sixth 3 min. exposure; . . . , a 3 min. exposure through the evacuated absorption tube. Bands marked A are due to acetaldehyde, F to formaldehyde and E to ethylene. Note that some photolysis occurred during the initial 3 min. exposure.

por. Ethanol: ethylene, acetaldehyde and formaldehyde were all produced in significant quantities. Methanol: formaldehyde was produced in significant quantity. Acetaldehyde could also be detected but in relatively smaller quantity. 1-Propanol: ethylene, propionaldehyde and formaldehyde were all produced in significant quantities. 2-Methyl-2-propanol: acetone was very readily produced. A much smaller quantity of ketene appeared as the irradiation was continued. Acetaldehyde: ketene and acetone were produced. The rate of disappearance of acetaldehyde was rapid but the quantity of acetone produced was small in comparison to the quantity of acetaldehyde decom-posed. Since the extinction coefficients for ketene are not known, it is not possible to estimate quantities, but they appeared to be small. Acetone: ketene was the only detectable product. The quantity produced was much greater than that produced in the photolysis of acetaldehyde. 2-Butanone: ethylene and ketene were produced in significant quantities, and acetaldehyde may have been produced. If it was, the quantity was so small that its identification cannot be considered as definite. 2-Pentanone: ethylene, ketene and acetone were all produced in significant quantities. 2,3-Butanedione: ethylene, ketene and acetone were produced, but the quantities were very small in comparison to the quantity of reactant decomposed. 2,5-Hexanedione: ethylene, ketene and acetone were all produced in significant quantities.

Discussion

Generalizations.--Most of the observed products can be summarized by three empirical rules. In stating these, there is no intent to imply the mechanism by which the products are formed. They simply give an easy way of summarizing a number of details. The photolysis of all the compounds which had two adjacent carbon atoms, other than a carbonyl carbon atom, led to the formation of ethylene

$$\begin{array}{c} H H & H H \\ \downarrow & \downarrow \\ H - C - C - H + h_{\nu} \longrightarrow H - C = C - H + ? \quad (I) \\ \downarrow & \downarrow \\ R' R \end{array}$$

where R' may be a hydroxy group, an alkoxy group or a carbonyl group and R may be a hydrogen, an alkyl group or a group containing a carbonyl group. The photolysis of alcohols and ethers led to the formation of aldehydes or ketones

$$\begin{array}{c} \mathbf{R} & \mathbf{R} \\ \mathbf{R} - \mathbf{C} - \mathbf{O} + h_{\nu} \longrightarrow \mathbf{R} - \mathbf{C} = \mathbf{O} + ? \qquad (\mathrm{II}) \\ \mathbf{R} & \mathbf{R} \end{array}$$

where R may be a hydrogen atom or an alkyl group. Acetaldehyde and all of the ketones reacted to form ketene

$$\begin{array}{c} H & H \\ H - C - C = 0 + h_{\nu} \longrightarrow H - C = C = 0 + ? (III) \\ \downarrow \\ R & R \end{array}$$

(6) V. J. Hammond and W. C. Price, Trans. Faraday Sor., 51, 605 (1955)

(7) D. N. Read, Phys. Rev., 46, 571 (1934).

⁽⁵⁾ W. C. Price, J. P. Teegan and A. D. Walsh, J. Chem. Soc., 920 (1951).

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where R is a hydrogen atom, an alkyl group or a more complicated group which may contain a second carbonyl group.

The above three statements include all of the observed products with the exception of acetaldehyde from dimethyl ether⁺ and methanol^{*}; ethylene from dimethyl ether⁺ and 2,3-butanedione^{*}; acetone from acetaldehyde^{*}, 2-pentanone, 2,3-butanedione^{*} and 2,5-hexanedione; and ketene from 2-methyl-2propanol^{+.8}

The generalizations may reflect the fundamental nature of the process. On the other hand they may be the consequence of the selectivity of the method of detection.

Although the present study can give no direct information as to the formation of carbon monoxide, its formation is so probable that a fourth reaction should be added to the above list.

$$\begin{array}{ccc} R-C = 0 + h\nu \longrightarrow CO + ? & (IV) \\ P \end{array}$$

Compounds which do not absorb below 50,000 cm.⁻¹: the region of 50,000-60,000 cm.⁻¹ corresponds to 143–189 kcal. per mole. These energies are sufficient to break any bond in the molecule or to break two bonds providing the energy is properly distributed. If transfer of energy by collision is neglected, probable types of primary reaction are

$$Reactant + h\nu \longrightarrow R' + R''$$
(1)

where \mathbf{R}' and \mathbf{R}'' are two radicals which result from breaking any bond in the molecule

$$Reactant + h\nu \longrightarrow R' + M + R'' \qquad (2)$$

where R' and R" are two radicals which are formed by breaking two single bonds and M is a molecule which in its ground state contains a new π -bond. and

Reactant
$$+ h\nu \longrightarrow M_1 + M_2$$
 (3)

where M_1 and M_2 are stable molecules, one of which contains a new π -bond. For any one reactant several primary processes of any one of these three types could conceivably take place.

Since the free radicals produced by process (1) have unusually high energies, the rate of decomposition would be much greater than that usually observed and the rate of combination reactions which are not followed by decomposition would be much less than that which is usually encountered. Process (1) followed by the decomposition of one radical, $\mathbb{R}'' \to \mathbf{M} + \mathbb{R}'''$, approaches process (2) as the life time of \mathbb{R}'' approaches zero. This two step process will be designated as (2').

The low pressure of the sample would have tended to favor decomposition reactions in the vapor phase and reactions at the wall. The small diameter of this reaction vessel would also tend to accentuate the latter.

The same principal products were detected in the photolysis of an alcohol and the corresponding ether: ethanol and diethyl ether gave ethylene (see empirical rule I), acetaldehyde and formaldehyde (see empirical rule II); methanol and dimethyl ether

(8) Of these, products marked * were found in relatively small amounts; products marked * appeared only on prolonged irradiation and in small amounts.

gave formaldehyde (II) and smaller quantitites of acetaldehyde. Using radiation up to 55,000 cm.⁻¹. Patat and Hoch⁹ obtained acetaldehyde and hydrogen as the photolysis products of ethanol vapor, and formaldehyde and hydrogen as photolysis products of methanol vapor. On the basis of a parahydrogen method of detecting hydrogen atoms they concluded that intramolecular reactions were involved (process 3). In an attempt to determine whether the ethylene and formaldehyde found in the present work were due to the second electronic transition of ethanol, an oxygen filter was introduced to cut off the region of the second band. The rate of photolysis was decreased but in so far as it is possible to tell by inspection the relative quantities of the three products were not changed.

Since the ethylene and acetaldehyde formed in the photolysis of the dimethyl ether did not appear until a rather high concentration of formaldehyde had been produced, it seems probable that these products are the result of a free radical mechanism which involves formaldehyde. This also seems to be true for the formation of acetaldehyde from methanol. In both cases, the quantity of formaldehyde seemed to approach a maximum value during the irradiation.

1-Propanol reacted in a similar manner to give ethylene (I), propionaldehyde (II) and formaldehyde (II). It would be interesting to know whether the ethylene contains carbons 1 and 2, or 2 and 3. Not enough is known about the spectrum of propylene to conclude that it was not produced.

2-Methyl-2-propanol.—Since the ketene most probably resulted from the photolysis of acetone, the direct photolysis of this tertiary alcohol seems to have followed the usual pattern—the single product, acetone (II), being the result of the symmetry of the alcohol. The spectrum of 2-methyl-1-propene has too little structure to determine its presence or absence as a product.

Compounds which also absorb below 50,000 $cm.^{-1}$: for a substance which has four absorption bands with extinction coefficients of 10, 100, 1000 and 10,000, the relative number of molecules undergoing the four transitions, in an infinitely thin sample, would be approximately 1, 10, 100 and 1000, respectively. Strictly speaking, oscillator strengths should be compared, the light source should be of uniform intensity at the four wave lengths and the quantity of material in the light path should be small enough to not drastically reduce the light intensity. For an infinitely thick sample, where all of the light at these wave lengths is absorbed, the relative number of molecules undergoing the four transitions would be approximately 1, 1, 1 and 1. Many of the compounds studied have molar extinction coefficients of the order of 10 or less below 50,000 cm.⁻¹, as compared to coefficients of the order of 10² to 10⁴ in the far ultraviolet. This, coupled with the small quantity of material in the light path, minimized the number of electronic transitions produced by the low frequency region of the source. Unless fluorescence was markedly different in the two regions, the observed photolysis was therefore due for the most part to the

(9) F. Patat and H. Hoch, Z. Elektrochem., 41, 494 (1935).

high frequency portion of the source band. Although many of the observed products are also produced in the near ultraviolet by well known mechanisms, the authors are inclined to believe that the same processes are not necessarily involved in the far ultraviolet region.

Acetaldehyde.¹⁰—The relatively small amounts of detectable products may be due to the formation of methane and carbon monoxide (IV, 3). This intramolecular reaction has been shown to be increasingly important at higher frequencies in the near ultraviolet. The small quantity of acetone probably indicates that a free radical mechanism is also involved. The relative quantity of ketene is too high to have resulted from the photolysis of acetone. Any number of mechanisms could account for the ketene: a free radical reaction or any one of processes 2, 2' or 3. Formaldehyde and 2,3-butanedione were not detected. The first is significant since formaldehyde has such a characteristic pattern of high intensity absorption bands. On the basis of the literature, it had been expected that 2,3-butanedione¹¹ could have been detected but preliminary measurements in this Laboratory indicated that this compound does not have intense narrow absorption bands and it is doubtful that it could have been detected. It is also doubtful if it would have been produced under the existing energy conditions.

Acetone.^{10,12}—The near ultraviolet photolysis of acetone proceeds entirely by a free radical mechanism which is largely initiated by dissociation to give methyl and acetyl radicals. On the basis of the increased yield of hydrogen obtained by Manning¹³ using an aluminum spark and fluorite windows, dissociation to hydrogen and acetonyl radicals is believed to be increasingly important at higher wave numbers. However, Howe and Noves14 found no hydrogen at low pressures and 1900 Å. and concluded that decomposition proceeded almost entirely by an intramolecular dissociation to ethane and carbon monoxide (IV, 3). It is probably sig-nificant that 2-butanone, 2,5-hexanedione and acetaldehyde were not detected in the present work. The spectra of the first two are similar to that of acetone but the maxima fall at different wave lengths and any appreciable concentration of either should have been detected. The absence of acetaldehyde probably eliminates one means of formation of ketene: the disproportionation of two acetyl radicals. The intramolecular reaction of Howe and Noves¹⁴ is consistent with the relative low concentration of detectable products.

(10) The photolysis of acetaldehyde has been extensively studied in the near ultraviolet. Only one reference is given below. E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. I, Reinhold Publ. Corp., New York, N. Y., 1954.

(11) V. R. Ells, J. Am. Chem. Soc., 60, 1864 (1938),

(12) The photolysis of acetone has been extensively studied in the near ultraviolet. Only one reference is given below. W. A. Noyes, Jr., G. B. Porter and J. E. Jolley, Chem. Revs., 56, 49 (1956).

(13) W. M. Manning, J. Am. Chem. Soc., 56, 2589 (1934).
(14) J. P. Howe and W. A. Noyes, Jr., *ibid.*, 58, 1404 (1936).

Since the situation becomes so complex and consequently even more speculative only a few comments are made about the higher molecular weight ketones.

2-Butanone.—The formation of ethylene is in keeping with (I) but the absence of a significant quantity of acetaldehyde indicates that the reaction did not proceed by 3. It is doubtful that the ethylene was formed by the photolysis of ketene since ethylene was not detected as a product in the photolysis of either acetone or acetaldehyde. In both of the latter a comparable quantity of ketene was produced.

2-Pentanone.—The formation of ethylene (I) and acetone is consistent with the near ultraviolet intramolecular reactions 3 of aldehydes and ketones which contain a γ -carbon atom.¹

2,5-Hexanedione.-The rate of photolysis and the quantities of detectable products were similar to that of 2-pentanone. Ethylene is consistent with (I) but acetone is an anomaly unless a combination of (I) and (IV) is considered, possibly as a single intramolecular reaction.

2,3-Butanedione.—On the basis of iodine inhibited vapor phase studies in the near ultraviolet, Bell and Blacet¹⁵ suggested that, in addition to the free radical mechanism, some acetone and carbon monoxide were formed by an intramolecular process (IV, 3) and that this process became increasingly significant at higher wave numbers The rapid photolysis and the small quantities of detectable products obtained in the present work may indicate that other intramolecular processes, such as a direct decomposition to ethane and carbon monoxide, are involved. The formation of ethylene is not consistent with either the free radical mechanisms¹⁰ proposed for the near ultraviolet, or the results obtained with other compounds in the far ultraviolet where two adjacent carbon atoms other than the carbonyl carbon seem to have been a necessary condition for the formation of ethylene. Its presence here suggests a unique reaction of the conjugated system or an impurity in the sample. The latter seems improbable since all of the samples were fractionated in a Fenske column, the boiling point checked well with the reported value and a gas chromatogaphic analysis indicated a single component

At this preliminary stage in the investigation, no conclusions can be drawn but it seems probable that processes 2, 2' and 3, particularly 2 and 2' are more important in this region than in the near ultraviolet. An effort should be made to extend the work. More restricted energy sources are possible although high intensity monochromatic sources are not available. By combining mass spectrometer and gas chromatographic analyses with a quantitative study of absorption spectra it should be possible to obtain the quantitative data necessary to establish the mechanisms involved.

(15) W. E. Bell and F. E. Blacet, ibid., 76, 5332 (1954).