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The Photochemical Stability of Crotonaldehyde

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The homologous series of saturated aliphatic aldehydes has been the subject of extensive photochemical study in the last few years.[1] The object has been not only to determine the mechanism of the reactions produced by light, but also to ascertain to what extent the present interpretations of absorption spectra are borne out by actual photochemical results. These compounds have a common region of electronic absorption attributed to the carbonyl group, which has a maximum at approximately 2800 Å. The absorption in each case is reported to be sharply discontinuous on the long wave length side, then diffuse, and finally continuous at short wave lengths.[2] The prediction has been made that in the region of sharp bands an activated molecule is produced which possibly would not dissociate; in the diffuse or predissociation region some decomposition probably would occur; and in the continuous region decomposition must occur.[1a,g,3] These predictions have been shown to be approximately correct for acetaldehyde, propionaldehyde and normal- and iso-butyraldehyde studied in the vapor phase.[1h] Although some decomposition was found throughout the region of absorption attributed to the carbonyl group, in general the quantum yield was less in the region of banded absorption than in the continuum. Likewise, polymerization was found to vary with wave length.

Except for a complete shift of several hundred Ångström units toward the red, the absorption spectrum of crotonaldehyde resembles markedly that of acetaldehyde. This spectrum, which is to be published in another article, shows discrete bands beginning at λ 3800 Å. and continuing to λ 3245. At this point the bands begin to fade and from λ 3090 to the end of this region, approximately 2600 Å., the absorption is apparently continuous. At λ 2550 a second region of absorption begins and extends into the Schumann region. This absorption is continuous and again by analogy to the saturated aldehydes, may be attributed to an electronic transition in the hydrocarbon end of the molecule.[4]

Leighton and Blacet have presented evidence of the formation of free radicals in the decomposition of the saturated aliphatic aldehydes. The prospect of obtaining further evidence in this regard as well as the possibility of additional correlation of spectral and photochemical data made the photochemical study of crotonaldehyde in the vapor phase seem very desirable.

Experimental Procedure

In general, the apparatus was similar to that previously described.[1h] The light source, except for one experiment, was a high pressure mercury arc of the type perfected by G. S. Forbes and his associates. The monochromator consisted of two cylindrical 30° crystal quartz half prisms and two crystalline lenses, all of which were 10 cm. in diameter. One-half of this monochromator was of right handed and the other half of left handed quartz.[5] A thermopile and galvanometer system, calibrated by means of lamps provided by the Bureau of Standards, was used to measure the intensity of radiant energy.

The absorption cell was 20 cm. in length, 3 cm. in diameter and had plain parallel windows fused on the ends. The gaseous system was arranged so that the aldehyde vapors at no time came in contact with any substances except fused quartz, Pyrex glass and mercury. By means of a differential gage, pressure changes in the reaction cell of 0.01 mm. could be detected. By determining the pressure change in the thermostated system and determining the products of decomposition, quantum yields of both decomposition and polymerization could be obtained. The method of study was sufficiently sensitive so that quantum yields of 0.04 or more for either type of reaction could be measured without difficulty for the weak lines of the source, while for the strong lines values as low as 0.01 could be detected. In all of the experiments carried out in this study, the pressure of the crotonaldehyde was approximately 38 mm. After irradiation, the excess aldehyde was condensed in a trap surrounded with an alcohol and carbon dioxide bath so that the postulated decomposition products of carbon monoxide, hydrogen and hydrocarbons could be removed by means of a Toepler pump.

The crotonaldehyde, a product of the Niacet Chemical Corporation, was further purified by fractionation and

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(1) (a) V. Henri, *Trans. Faraday Soc.*, **25**, 765 (1929); (b) Bowen and Watts, *J. Chem. Soc.*, **129**, 1607 (1926); (c) J. H. C. Smith, *Carnegie Inst. Reports*, **27**, 178 (1928); (d) Norrish and Griffiths, *J. Chem. Soc.*, 2829 (1928); (e) Kirkbride and Norrish, *Trans. Faraday Soc.*, **27**, 404 (1931); (f) Norrish and Kirkbride, *J. Chem. Soc.*, **135**, 1518 (1932); (g) Herzberg, *Trans. Faraday Soc.*, **27**, 378 (1931); (h) Leighton and Blacet, THIS JOURNAL, **54**, 3165 (1932); **55**, 1766 (1933); *et cetera.*

(2) Henri and Schou, *Z. Physik*, **49**, 774 (1928).

(3) R. Mecke, *Trans. Faraday Soc.*, **27**, 359 (1931).

(4) (a) Henri and Wurmser, *Compt. rend.*, **156**, 230 (1913); (b) Henri and Bielecki, *ibid.*, **155**, 456 (1912).

(5) The authors are indebted to the National Research Council for a Grant-in-Aid to cover the cost of the monochromator and of the high sensitivity galvanometer used in this work.

drying with anhydrous copper sulfate. The final fraction had a boiling range of 102.4–102.6° and a density (d^{25}_4), corrected to vacuum, of 0.8495. The sample was introduced into the system by two successive low temperature vacuum distillations. Special precautions were taken to eliminate all traces of oxygen from the apparatus by flushing, and then evacuating, several times with nitrogen.

Experimental Results

The following lines of the mercury arc were used as sources: 3660, 3130, 3020, 2804, 2654, 2537 and 2399 Å. The first five of these lines fall in the region of absorption ascribed to the carbonyl group, while the last two are in the region where the excitation is considered to occur in the hydrocarbon part of the molecule.

Contrary to what one would predict by analogy to the saturated aldehydes, in no case could decomposition of crotonaldehyde be detected. This was true even when the full radiation of the mercury arc was used for several hours.

Only at λ 3660 could a pressure decrease due to polymerization be observed. The quantum yield, based upon the number of molecules disappearing from the system per quantum absorbed, was estimated to be 0.02. A solid was formed on the walls of the reaction cell. If the assumption is made that this was a trimer, only one quantum out of every 150 absorbed was effective in causing polymerization. It is possible that a corresponding amount of polymerization occurred at other wave lengths used in this study, but because the intensity of the source in each case was small compared to that of λ 3660, a measurable pressure change was not obtained during an exposure of five or six hours. Upon using the full intensity of the arc, a pressure decrease was observed which corresponded approximately to that found at λ 3660.

In order to determine the effect of activated mercury vapor on crotonaldehyde an argon–mercury lamp which is known to emit about 88% of its radiation as the 2537 resonance line[6] was substituted for the high pressure arc which does not give this resonance line. Although about 80% of this energy went to form activated mercury atoms in the reaction cell, the photochemical results were precisely the same as before, *i. e.*, no decomposition and no measurable polymerization.

No fluorescence in the visible region could be observed at any of the wave lengths listed above. This is true even at very low pressures and even though some of the mercury lines fall in the region of sharp absorption bands.

The observation was made that the oxidation by oxygen of crotonaldehyde in the vapor phase, in the system herein described, is a photochemical reaction and does not progress at a measurable rate in the dark. Between two and three molecules of aldehyde reacted per molecule of oxygen. Using λ 3130 as the energy source and partial pressures of oxygen and aldehyde of 1 mm. and 38 mm., respectively, the quantum yield based upon the molecules of aldehyde reacting was of the order of 0.2 to 0.3. Additional studies of this reaction will be made.

Discussion of Results

The accepted interpretation of continuous absorption in the gaseous phase is based largely on the study of diatomic molecules. The theory may be extended with caution to more complex molecules if one makes the reservation that a spectrum which appears to be continuous may or may not be so in fact.[7] In molecules where there are several possible types of vibration each with its many energy states, a broadening of absorption bands may occur under the influence of impacts which could give a transfer to the neighboring states with a high yield. Hence it is conceivable that although the molecules are still in the excited state, the usual experimental methods will not give discontinuity in absorption. However, studies at very low pressures should bring out the discrete structure.

If only activated molecules are produced in the region of absorption between λ 3800 and 2600 Å., the failure of crotonaldehyde to decompose may be understood. The almost complete lack of polymerization is in accord with the known chemical facts in regard to this compound.[8] It is probable that excitation in the carbonyl group is followed rapidly in this case by an energy shift to other modes of vibration. Therefore, since polymerization of the aldehydes involves the carbonyl group, a low rate of this reaction would be expected. The conjugated double bonds may play an important part in stabilizing this molecule. The fact that fluorescence was not observed in the visible region does not signify that this phe-

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[6] Leighton and Leighton, *J. Chem. Ed.*, **12**, 139 (1935).

[7] (a) Bonhoeffer and Harteck, "Grundlagen der Photochemie," Theodor Steinkopff, Dresden, Germany, 1933, p. 53; (b) Franck, Sponer and Teller, *Z. physik. Chem.*, **B18**, 88 (1932).

[8] James B. Conant, "The Chemistry of Organic Compounds," The Macmillan Co., New York, N. Y., 1933, p. 297.

nomenon does not occur. With many energy levels present in the molecule it may be that the reradiation takes place in small units and a search in the infra-red would reveal fluorescence bands.

An alternate and doubtless more acceptable approach to the problem of correlating the photochemical stability and the absorption spectrum of crotonaldehyde would be to use the above explanation for those wave lengths where the absorption is obviously banded and attempt to find a reason why dissociation products were not obtained below λ 3090. The general mechanism for the dissociation of an aldehyde in the continuum associated with the carbonyl group has been given in a previous publication.[1h] It is as follows

$$\begin{array}{rcll} \mathrm{RHCO} + h\nu & \longrightarrow & \mathrm{R} + \mathrm{HCO} & (1) \\ \mathrm{R} + \mathrm{HCO} & \longrightarrow & \mathrm{RH} + \mathrm{CO} & (2) \\ \mathrm{R} + \mathrm{R} + \mathrm{M} & \longrightarrow & \mathrm{R_2} + \mathrm{M} & (3) \\ \mathrm{HCO} + \mathrm{HCO} & \longrightarrow & \mathrm{H_2} + 2\mathrm{CO} & (4) \\ \mathrm{R} + \mathrm{HCO} + \mathrm{M} & \longrightarrow & \mathrm{RHCO} + \mathrm{M} & (5) \end{array}$$

As the aldehyde becomes more complex, the need for the third body, M, diminishes and Reactions 3 and 5 tend to become bimolecular. If the energy of activation of Reaction 5 is small compared with Reactions 2, 3 and 4, the reversal reaction would predominate and the net result from irradiation would be no decomposition, although the primary process is dissociation and is represented by a continuous absorption spectrum. This mechanism suggests a high temperature coefficient for the dissociation processes due to a greater probability of Reactions 2, 3 and 4 taking place as the temperature is increased. Accordingly, irradiation at elevated temperatures may be expected to give decomposition products.

The concept of a predominating reverse reaction appears to be a very useful one. It serves to explain the fact that the quantum yields of decomposition for the higher saturated aldehydes are considerably less than unity in the continuous region of absorption, and that the numerical values of those yields decrease with increase in molecular weight. It appears to offer a more direct and plausible reason for the low quantum yield of acetone than the mechanism recently proposed by Norrish, Crone and Saltmarsh.[9] Finally, it may be used to explain the "thermal absorption" referred to by Henri.[4] This phenomenon, which may be defined as continuous absorption by the vapor without decomposition, is exhibited by the aliphatic aldehydes in the extreme ultraviolet, by the saturated and unsaturated alcohols and doubtless by many other compounds.

Crotonaldehyde may be thought of as displaying this type of mechanism in two regions of electronic excitation. The 3020, 2804 and 2654 lines of the mercury arc fall in the first of these and the 2537 and 2399 in the second. Both the primary process and the subsequent reactions are most certainly different in the two regions, but the principle of a rapid reverse reaction may be applied in each case.

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Summary

The effect of monochromatic ultraviolet radiation upon crotonaldehyde in the vapor phase has been described. Although the lines of the mercury arc which were used as light sources cover at least three types of absorption, no decomposition and no appreciable polymerization was found to occur. These results are contrary to the predictions which may be made by comparison with corresponding saturated aldehydes. The system of conjugated double bonds appears to contribute greatly to the photochemical stability of the molecule.

The concept of a predominating reverse reaction is presented as an explanation of the failure to obtain products of dissociation in the region in which absorption is apparently continuous.

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(9) Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1463 (1934).