

[CONTRIBUTED FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Photolysis of the Aliphatic Aldehydes. V. Acrolein

BY FRANCIS E. BLACET, GEORGE H. FIELDING AND JACK G. ROOF

The pronounced variations which are evident in the near ultraviolet absorption spectra of the unsaturated aliphatic aldehydes¹ have led the authors to believe that a detailed study of the photolysis of these compounds might give evidence which would be very useful in the interpretation of absorption by complex molecules. Contrary to what might have been predicted by comparison with the saturated aliphatic aldehydes,² a study of crotonaldehyde has shown that this substance neither decomposes nor polymerizes at an appreciable rate at room temperature under the influence of ultraviolet light.³

Thompson and Linnett⁴ have reported that, although the apparent quantum efficiency of acrolein photodecomposition is likewise very low, the efficiency of polymerization varied from 0.39 at λ 3665 to 2.3 at λ 3135 Å. In view of the fact that both λ 3665 and λ 3135 are in the region of definitely discontinuous absorption of acrolein, it has seemed profitable to extend this study over a wider spectral range and with a somewhat different experimental approach to the problem.

Experimental Method

Since the apparatus used in this investigation has been described in a previous publication,³ only a brief statement regarding it will be given here. The silica reaction cell was 20 cm. in length, 3 cm. in diameter and had plane 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 other than fused quartz, Pyrex glass and mercury. By means of a differential gage, pressure changes in the thermostated reaction cell of 0.01 mm. could be detected. Monochromatic light was obtained from a crystal quartz monochromator and a high pressure mercury arc. The intensity of radiation was measured by means of a calibrated thermopile and galvanometer system. All experiments were made at 30°.

The method used in purifying the acrolein has been described,¹ boiling range, 53.0–53.2°.

(1) Blacet, Young and Roof, *THIS JOURNAL*, **59**, 608 (1937).

(2) Leighton and Blacet, *ibid.*, **54**, 3165 (1932); **55**, 1766 (1933); Leermakers, *ibid.*, **56**, 1537 (1934); Leighton, Levanas, Blacet and Rowe, *ibid.*, **59**, 1843 (1937).

(3) Blacet and Roof, *ibid.*, **58**, 73 (1936).

(4) Thompson and Linnett, *J. Chem. Soc.*, 1452 (1935).

Experimental Results

Decomposition.—Investigations designed to determine the rate of both photochemical decomposition and polymerization were carried out at λ 3660, 3130, 3020, 2804, 2654 and 2537 Å. Although the experimental method is sufficiently accurate to detect a decomposition quantum yield (Φ_d) of 0.04 based upon the volume of carbon monoxide produced in the reaction, at none of these wave lengths could sufficient gaseous products be obtained in a reasonable length of time to give measurable values of yields. In this respect our results differ from those reported by Thompson and Linnett.⁴ These authors have reported a Φ_d value of 0.01 for λ 3665 and 0.15 at λ 3135. However, by using the complete radiation of the mercury arc placed near the reaction cell, small amounts of gas were obtained which would not liquefy at the temperature of a solid carbon dioxide–acetone refrigerant. The composition of this gas appeared to vary with the pressure in the reaction cell during an exposure, and with the temperature of the trap during the removal of gas for analysis. Also, it is most probable that the composition of this gas would vary with the wave lengths employed.

Exposures in which the irradiated gas was at 200 mm. initial pressure and during which considerable polymer collected in the reaction cell gave an average analysis by micro methods⁵ of 91% CO, 6% unsaturated hydrocarbons, and 3% H₂ for the gas which would not condense in a trap cooled with solid carbon dioxide. In view of the above-mentioned variables, these results are in substantial agreement with an average analysis of 95.5% CO, 1.3% ethylene and 3.2% residue reported by Thompson and Linnett.

Polymerization.—The polymer produced a continuous, translucent deposit on the walls of the reaction cell. This film was much thicker on the lower portion of the cell. The common organic solvents, as well as dioxane and ethylene glycol monomethyl ether, were not appreciably effective in dissolving this residue although the last-named compound did gradually loosen the coating from the walls. Raised to 300° the solid did not melt

(5) Blacet and MacDonald, *Ind. Eng. Chem., Anal. Ed.*, **6**, 334 (1934); *etc.*

but became slightly yellow in color. Higher temperatures caused a gradual charring of the substance.

The rate of apparent polymerization was followed by measuring the pressure decrease in the reaction cell. It was discovered that under the experimental conditions employed there was a definite induction period for the polymerization reaction. This is clearly shown in Fig. 1 in which the pressure decrease in the system expressed in millimeters of mercury is plotted against time in hours. In this case the total acrolein pressure in the system was 200 mm. and the illuminating source was λ 2654. It will be observed that only after one hour of illumination was there an appreciable pressure change in the system and not until about two and one-half hours had elapsed did the rate of change approach a constant value. To check upon the possibility of a dark reaction having been initiated by the irradiation, the shutter in the optical train was closed for two different intervals during the run. As shown by the corresponding flat portions of the curve, there was no dark reaction. Furthermore, it can be seen that upon again opening the shutter the photopolymerization began at approximately the same steady rate which it had attained previously.

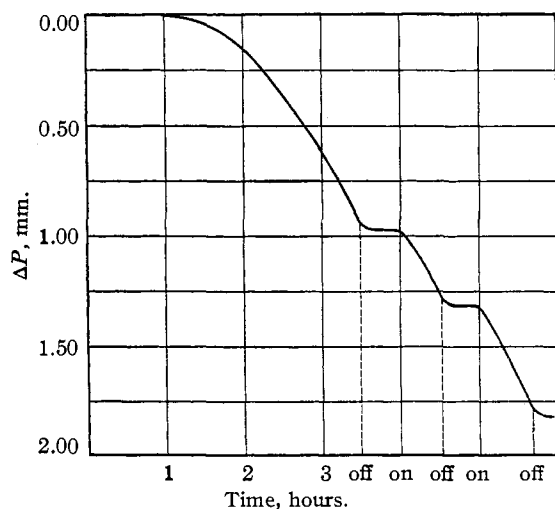


Fig. 1.—Curve showing (1) an induction period and (2) the absence of a dark reaction. The radiation was turned on and off as indicated.

The accumulation of solid polymer in the reaction cell made it difficult to duplicate runs. Hence, a standard procedure was adopted of removing the reaction tube after each run, cleaning it with hot dichromate-sulfuric acid solution and

placing it back in the system after thorough rinsing and drying. Before the acrolein was admitted again, the cell was flushed out with nitrogen and this gas removed by means of a Toepler pump. By following this routine and by operating the mercury arc on a constant amperage, very similar pressure curves could be obtained without difficulty at a given wave length. No attempt was made to study the effect of intensity of radiation on the reaction rate.

It is obvious that because of the induction period, a quantum yield calculated from an overall pressure change in the reaction system would vary with the length of the exposure. Accordingly, a quantum yield, Φ_P , of polymerization was adopted, based upon the rate of pressure change with quanta absorbed after the induction period presumably was finished. It represents the ratio of the number of molecules which disappeared in the system to the number of quanta absorbed in a unit of time during which the pressure was decreasing at a very nearly constant rate. The portion of the rate curves used in this calculation in every case represents approximately the second one-half millimeter pressure decrease in the reaction cell. Values of Φ_P obtained in this way for six different wave lengths are given in Table I. The initial acrolein pressure in each case was approximately 200 mm.

It was of interest to know whether the so-called induction period was reproducible and whether its duration varied over the spectral range studied. In order to make a comparison of runs the segment of the curve used in calculating Φ_P was extended back as a straight line to the ordinate representing zero change in pressure. The abscissa at this point gives an approximate measure of the quanta absorbed in the induction process. Numbers so obtained may be found in Table I. Because of the difficulty in ascertaining the correct slope of the curve segments, and because of minor variations in the curves themselves, there is some difference between values reported for different runs at the same wave length. Nevertheless, the figures indicate a definite trend with respect to wave length.

Only qualitative evidence has been obtained pertaining to the influence of pressure at a given wave length on the factors described above. The data available indicate that quantum yields increase rapidly with pressure in the range of low pressures and then slow down to an approximately

Wave length, Å.	Quanta absorbed in induction process	Quantum yields, Φ_P
2537	2.0×10^{17}	18.5
	1.6×10^{17}	19.5
2654	2.6×10^{17}	19.4
	1.6×10^{17}	18.3
2804	2.7×10^{17}	10.1
	3.2×10^{17}	9.4
3020	44×10^{17}	1.1
	54×10^{17}	0.92
3130	80×10^{17}	.47
	150×10^{17}	.39
	130×10^{17}	.62
3660	220×10^{17}	.27
	300×10^{17}	.40

steadily increase for pressures between 100 and 250 mm. The number of quanta absorbed during induction appears to be independent of pressure.

In agreement with the findings of Thompson and Linnett⁴ no fluorescence of the acrolein vapor was observed.

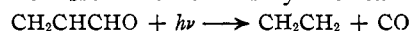
Discussion of Results

The Polymerization Process.—By an inspection of Fig. 2 it can be seen that there is a definite correlation between the character of molecular absorption and the observed quantum yield of polymerization. Irradiation by wave lengths which fall in the region of markedly discontinuous absorption gives a low quantum yield but, as the absorption becomes more diffuse, approaching shorter wave lengths, the efficiency of the reaction increases very rapidly and then appears to reach a constant value in the continuum. The absorption spectrum which was taken in this Laboratory¹ indicates that continuous absorption begins at a wave length somewhat longer than λ 2804. However, since Φ_P is far from its maximum value at λ 2804, it may be that absorption is still somewhat diffuse at this wave length in spite of the seemingly smooth slope of the log ϵ curve.

In the region of banded absorption it may be postulated that polymerization results from the interaction of activated and normal molecules. However, at the shorter wave lengths, where quantum yields of 19 have been obtained, activated molecules alone will not suffice to explain the reaction mechanism. The absorption in this region is continuous and dissociation as a primary act might be expected to occur, but, as in the case of crotonaldehyde, the volatile decomposition

products indicate an over-all decomposition of very low efficiency. In a previous publication³ it has been suggested that the failure of a substance to give decomposition products under these circumstances might be due either to the fact that in the case of a complex molecule absorption which appears continuous may not actually be so, or to the fact that a predominating reverse reaction may occur following decomposition. Recently, in a very helpful survey of the photochemistry of the aldehydes, Rollefson⁶ has shown that the former of these postulations is the more probable and that absorption spectra alone are not sufficient evidence of the formation of free radicals by light.

By assuming the formation of free radicals, however, as at least one of the results of light absorption, it is possible to present an interpretation of most of the known experimental facts concerning the photochemistry of acrolein. That very little dissociation occurs by the reaction



is indicated by the fact that the total volume of permanent gas produced is small and that the ratio of ethylene to carbon monoxide in this gas is

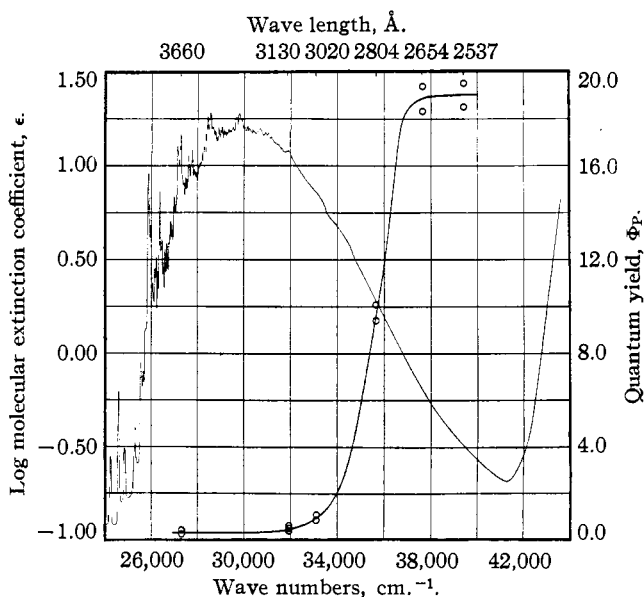
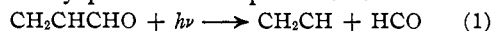


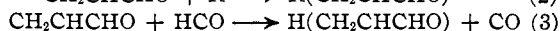
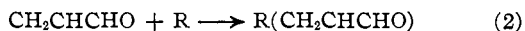
Fig. 2.—Showing the relationship between the character of absorption (irregular curve) and quantum yields of polymerization (smooth curve).

far from unity. In addition to absorption followed by collisional deactivation, it may be reasoned by analogy to the other aldehydes,^{2,6} that the following primary process takes place to some extent

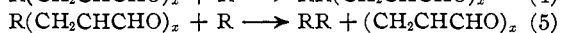
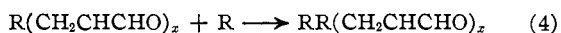


(6) Rollefson, *J. Phys. Chem.*, **41**, 259 (1937).

By postulating that the free radicals thus formed may react with acrolein molecules, perhaps at the C=C bond, a mechanism of polymerization may be set up involving a number of chemical processes which are illustrated by the following equations. In these R is used to designate either CH₂CH, HCO, H (from HCO → H + CO) or a resultant of the interaction of one of these radicals with a neutral molecule. *x* is a number which may vary from unity to a moderately large number.



The radical R(CH₂CHCHO) may act as a nucleus to condense other aldehyde molecules until R(CH₂CHCHO)_{*x*} has been synthesized.



In view of the definitions of R and *x*, it must be recognized that most of these reactions are of a very general nature. However, in addition to emphasizing the very complex process which probably occurs they serve to explain the experimental facts which have been obtained. A chain involving reaction 2 and



could account for the high quantum yields which have been observed, but the facts that the solid produced does not have the properties to be expected of the simple dimer and that the gaseous residue is largely carbon monoxide indicate that other reactions take place.

The high ratio of carbon monoxide to the other gaseous products is accounted for by reaction 3 followed by one or more steps, the net result of which is the addition of CH₂CH and H (from HCO) to the larger molecules. After making a microanalysis (for C, H and O) of the solid produced by irradiation, Thompson and Linnett⁴ concluded that the adsorption of a small amount of ethylene by a polymer of acrolein would best account for their results. Obviously, the mechanism which has been proposed above is also in accord with their analysis.

One of the products of reaction 5, RR, can be (by definition of R) either a molecule of high molecular weight or a gaseous substance such as butadiene, ethylene or hydrogen. The atoms or groups of atoms in RR may not necessarily be the same as those in the R groups of the reactants. It is to be expected that reaction 4 would predominate over reaction 5. However, the evi-

dence in regard to this point is inconclusive since for the most part RR may consist of non-volatile substances. The reactions which have been postulated² to explain the photodecomposition of the saturated aldehydes have not been included in this discussion since if reaction 2 occurs readily there would be little probability of reactions occurring between the products of reaction 1.

It is of interest to consider this mechanism in the light of the known facts regarding the absorption of acrolein. The fact that Φ_P is the same at λ 2654 and λ 2537 indicates that the absorption is of the same character at these two wave lengths, *i. e.*, the progressive change in the absorption spectrum toward shorter wave lengths is complete before λ 2654 is reached. On the basis of the volume of carbon monoxide produced, it might be reasoned that very little dissociation occurs in the primary act. However, reactions 4 and 5 effectively combine the molecular fragments produced in reaction 1, and hence it is possible in the case of acrolein at least that the volume of carbon monoxide produced during irradiation is not a reliable measure of the amount of dissociation which actually occurs in the primary process. If reaction 1 takes place much more often than the decomposition quantum yield indicates, it would follow that HCO is rather stable at room temperature. Instead of dissociating spontaneously, or following collisional activation as illustrated by reaction 3, into carbon monoxide and a hydrogen atom, it may behave as R in the above reactions. This is in accordance with other research involving the formyl group.⁷

The Induction Period.—From Table I and Fig. 2 it is evident that there is a relationship between the quanta absorbed in the induction period and the absorption spectrum. In general, the quanta required to get the reaction well under way become less as the discontinuous absorption decreases, there being a reduction of approximately one hundred fold in the induction quanta between λ 3660 and λ 2654. Contrary to the quantum yields, but in agreement with the molecular spectrum, a comparison of numerical values would indicate that λ 2804 is in very much the same region of absorption as λ 2654 and λ 2537.

The evidence is not sufficient to warrant drawing a conclusion regarding the cause of the induction. A possible cause would be the intro-

(7) Kistiakowsky, *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 44 (1935).

duction of a small amount of impurity, such as water vapor, with each new sample of acrolein. If the impurity would act as a remover of radicals, the polymerization process as outlined above would be retarded until such time as the inhibitor was eliminated.

Summary

1. A definite correlation between photochemical polymerization and the absorption spectrum of acrolein has been found. In the region of sharp-banded absorption, λ 3660 to λ 3130, the quantum yield, Φ_P , is less than 0.5; at λ 3020, where the absorption is very diffuse, Φ_P is 1.0; at λ 2804, which lies on the border line between

banded and the continuous region of absorption, Φ_P is 10; and at both λ 2654 and λ 2537, which presumably are definitely in the continuum, Φ_P is 19.

2. A mechanism involving free radicals has been proposed to account for the large quantum yields. The experimental results found by the authors and others are in good agreement with this mechanism.

3. An induction period has been found in the polymerization experiments. A possible cause of this induction has been suggested but further experiments will have to be done before the cause of induction can be established.

LOS ANGELES, CALIF.

RECEIVED AUGUST 23, 1937

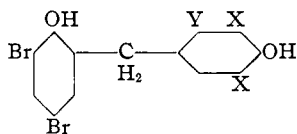
[CONTRIBUTION FROM THE CHEMICAL AND BACTERIOLOGICAL RESEARCH LABORATORIES OF HYNSON, WESTCOTT & DUNNING, INC.]

Condensation Products of 2-Hydroxy-3,5-dibromobenzyl Bromide with Phenols and their Germicidal Power

BY WILTON C. HARDEN AND JOHN H. BREWER

Auwers and Rietz,¹ Kohn and Jawetz² and others have described the condensation of various pseudo phenols with phenols. The purpose of the present paper is to report the preparation and some of the properties of a new series of benzyl phenols prepared by such condensations.

The dibromohydroxybenzyl bromide (2-hydroxy-3,5-dibromobenzyl bromide) used was prepared from *o*-cresol by the method of Auwers and Schröter.³ This compound was condensed with the following phenols: phenol, resorcin, *o*-cresol and *m*-cresol, to give products having the general formula



where Y represents H, OH, or CH₃ and X represents H, CH₃, Br, or I.

The dibromo and in one case the diiodo derivatives of these substituted benzyl phenols were prepared. The properties of these compounds are summarized in Table I.

Similar condensations with *p*-cresol, naphthol, thymol and guaiacol have been made. Tri-

(1) Auwers and Rietz, *Ber.*, **38**, 3302 (1905).

(2) Kohn and Jawetz, (a) *Monatsh.*, **44**, 198 (1923); (b) *ibid.*, **45**, 251 (1924).

(3) Auwers and Schröter, *Ann.*, **344**, 142 (1906).

bromo, tetrabromo, and diiodo-*o*-hydroxybenzyl bromides also have been prepared and condensed with various phenols. The resulting compounds will be described subsequently.

Experimental Part

The condensations were carried out by several different methods: (1) in boiling toluene in the presence of a piece of zinc; (2) in boiling toluene in the presence of anhydrous sodium carbonate; and (3) using aqueous alkali as described by Kohn and Jawetz.^{2a} In general, the latter method gave the best yields, although in some cases even by this method the yields were poor. The following will serve as typical examples.

Preparation of 2-Hydroxy-3,5-dibromobenzyl-*o*-cresol.—34.5 grams of 2-hydroxy-3,5-dibromobenzyl bromide, 60 g. of *o*-cresol, 10 g. of sodium hydroxide and 10 g. of water were mixed and boiled gently with stirring under a reflux condenser for two hours. The mixture was then allowed to stand overnight, made acid, and steam distilled to remove unreacted *o*-cresol. The residue was dissolved in ether, dried with anhydrous sodium sulfate and crystallized twice from toluene; m. p. 154–155°. *Anal.* Calcd. for C₁₄H₁₂O₂Br₂: Br, 42.89. Found: Br, 43.04.

Preparation of 2-Hydroxy-3,5-dibromobenzyl-mono-bromo-*o*-cresol.—7.4 grams of dibromohydroxybenzyl-*o*-cresol was suspended in 50 cc. of glacial acetic acid and 7.0 g. of bromine in 25 cc. of glacial acetic acid was added drop by drop to the warm solution. The solution was warmed on the water-bath and stirred mechanically for one-half hour. It was then cooled, the crystals filtered, washed with cold water and recrystallized from dilute alcohol;