

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF FURMAN UNIVERSITY]

## Water Effects upon the Photochemical Bromination of Acetophenone

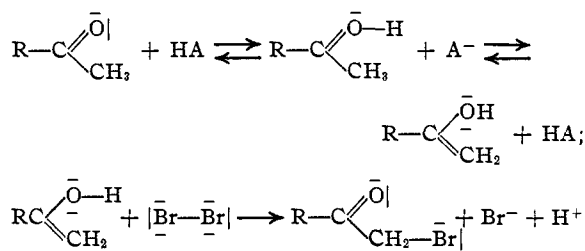
BY ELIJAH M. HICKS, MYERS H. HICKS AND JOHN R. SAMPEY

Although the effect of water upon the bromination of phenyl-alkyl ketones has been considered in several investigations,<sup>1</sup> little quantitative study of the effect, particularly in non-aqueous solvents, has been made. Paul and Hammett<sup>2</sup> give measurements of the rate of bromination of *m*-nitroacetophenone in a "mixed water-acetic acid solvent." Evans, Morgan, and Watson<sup>1d</sup> and Nathan and Watson<sup>1c</sup> have also given quantitative values for the reaction of ketones in solutions of fifty and seventy-five per cent. acetic acid in water. Hughes and Watson<sup>1b</sup> observed a decrease in the rate of bromination of acetone in moist chloroform as compared with the dry solvent. More particularly, the nature of the photochemical interaction has received little attention. It has been found, however, that artificial illumination increases the velocity of the interaction in carbon tetrachloride sufficiently to make studies of the course of the reaction comparatively simple.<sup>3</sup>

The present investigation deals with the nature of the photochemical bromination of acetophenone in a non-aqueous solvent, carbon tetrachloride, as indicated by the formation and decomposition of the bromine-acetophenone intermediate.<sup>1a,3</sup> In a continuation of the previous study,<sup>3</sup> certain aspects of the effect of water upon the bromination led to investigation of various conditions known to alter the course of the reaction, namely, drying agents, catalysts, and agitation.

## Nature of the Reaction

Extensive study of the halogenation of carbonyl compounds has clearly established the reaction to be a prototropic change. The non-photochemical interaction in which radiation is no factor, is represented by Hammett<sup>4</sup> and indicated by previous workers<sup>1a,b,c,d,5</sup> as an acid catalyzed interaction proceeding as follows



Evidently any condition tending to decrease the concentration of acid would result in a corresponding decrease in the rate of prototropic keto-enol shift. Since the bromination of the enol form is instantaneous, the former step determines the reaction velocity. Addition of acid would, of course, increase the rate.

In the non-aqueous solvent carbon tetrachloride, water, even in minute amounts, results in a definite decrease in the rate of bromination. This observation is easily explained by the fact that any water present has a greater affinity for hydrogen bromide than does the solvent. Therefore the acid concentration in the carbon tetrachloride is maintained inappreciable until the distribution coefficient of hydrogen bromide between water and carbon tetrachloride is exceeded. Then the reaction goes to completion very rapidly due to the autocatalytic effect of the hydrogen bromide liberated.

To follow closely the decomposition of the intermediate, a method of withdrawal of samples for a series run was designed. Quantities of 0.05 molar acetophenone were measured rapidly with a 5-ml. pipet into a 300-ml. Pyrex Erlenmeyer flask; 100.0 ml. of c. p. carbon tetrachloride was added, and the flask equipped with a siphon and atomizer bulb for quick withdrawal of samples. The flask was placed in the thermostat at 30° under the irradiation of a 200-watt clear glass Mazda bulb supported exactly six inches above the reaction mixture; 8.0 g. of bromine (0.05 *m*) in 50.0 ml. of c. p. carbon tetrachloride was added; at the end of one minute a sample was withdrawn into a weighed flask containing 20 ml. of 20% potassium iodide solution and 0.8 g. of sodium acetate buffer,<sup>6</sup> this sample serving as a standard

(1) (a) Hahn, *Ber.*, **44**, 1552-1553 (1911); (b) Hughes and Watson, *J. Chem. Soc.*, 1945-1954 (1929); (c) Nathan and Watson, *ibid.*, 217-220 (1933); (d) Evans, Morgan, and Watson, *ibid.*, 1167-1173 (1935); (e) Kröhnke, *Ber.*, **69B**, 921-935 (1936); (f) Cowper and Davidson, *Org. Syn.*, **19**, 24-26 (1939).

(2) Paul and Hammett, *THIS JOURNAL*, **58**, 2182-2187 (1936).

(3) Sampey and Hicks, *ibid.*, **63**, 1098-1101 (1941).

(4) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, Chapter 8.

(5) Lapworth, *J. Chem. Soc.*, 30-42 (1904).

(6) Dawson and Ark, *ibid.*, 1740-1745 (1911); Nathan and Watson, *ibid.*, 217-220 (1933).

for the remainder of the run. Upon the appearance of the intermediate, samples were withdrawn at fifteen second intervals into weighed flasks containing potassium iodide; the liberated iodine was removed with excess standard thiosulfate, the excess being determined by titration with standard iodine using starch iodide indicator. Disappearance of the bromine color was used to indicate completion of the reaction.

It was observed that although the time of formation of the intermediate compound varied greatly, the time required for its decomposition was approximately constant. Therefore plotting time against per cent. bromination resulted in similar curves for all reactions. This fact is strikingly shown in Fig. 1, which was obtained by moving all curves along the time axis until they coincided. Because of this behavior, it is necessary to give the per cent. bromination at only one time in order to express the complete course of a specific reaction. Table I contains the results of all runs made under the conditions listed.

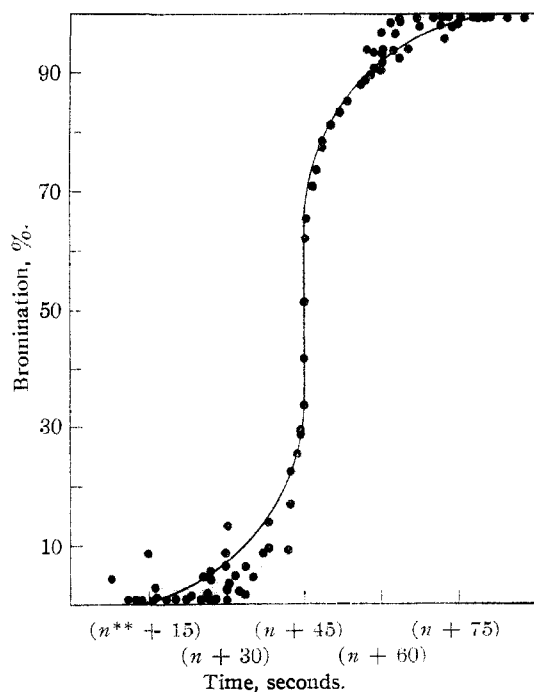


Fig. 1.—Nature of the decomposition of the bromine-acetophenone intermediate. \* Curve taken from three runs with pure acetophenone (no catalysts present). The value nearest 50% in each individual run (Table I) placed on the curve and the other points plotted in relation to that one. \*\*  $n$  chosen for each run as described in note (\*).

The lack of correlation between the amount of water added and the time of intermediate forma-

Experimental conditions	Water added	Time in seconds of appearance of intermediate	Time in seconds of per cent. bromination $\frac{x}{t}$	
No stirring	None	216	266	47.1
	None	270	305	3.7
	None	275	315	18.0
	None	220	255	9.3
	None	149	180	83.0
	None	169	210	65.7
	None	157	195	78.2
	None	150	210	70.5
	0.1 ml.	312	360	4.2
	0.1 ml.	480	570	81.0
	0.1 ml.	332	360	83.1
	0.2 ml.	492	555	61.7
	0.2 ml.	498	630	7.8
	0.3 ml.	568	723	100.0
	0.3 ml.	770	900	73.5
0.4 ml.	1120	1230	21.2	
0.5 ml.	890	975	41.5	
1.0 ml.	440	540	9.4	
Stirring	None	243	270	89.0
	0.2 ml.	1333	1395	33.5
Concd. hydrochloric acid	0.3 ml.	63	90	25.6
Dry hydrogen chloride in CCl <sub>4</sub>		12	30	29.3
Phosphorus pentoxide added	0.1 g.	45	90	51.3
	0.5 g.	28	60	77.2
Sulfur added	0.1 g.	270	360	30.9

tion is probably due to the condition of water in carbon tetrachloride. Whereas 0.1 ml. of water dissolves and 0.2 ml. and 0.3 ml. produce turbidity, larger amounts of water form two clear layers; therefore the larger amounts do not present proportionately larger surfaces.

However, each run indicates that once the water becomes sufficiently saturated with hydrogen bromide, the decomposition is independent of other conditions, due to the strong autocatalytic effect of the acid. That the phenomenon involves the degree of dispersion is definitely indicated by the effect of agitation upon the reaction when only 0.2 ml. of water is present.

Hydrogen chloride, as was predicted, greatly increased the prototropy, and even 0.3 ml. of concentrated hydrochloric acid increased the rate twice over. The latter observation indicates the small amount of acid necessary to catalyze the shift, whether it be added or appear as a product of the reaction.

Phosphorus pentoxide with its drying properties removed from the carbon tetrachloride sufficient water to greatly increase the rate of enolization. The resultant acid possibly had a minor effect in the catalysis.

The addition of sulfur was made to see if a mere surface in molecular dispersion had any effect detectable. The negative result seems logical in view of the reaction mechanism.

**Acknowledgment.**—The authors take this opportunity to express to Dr. E. Emmet Reid their appreciation for his advice and interest in this study, and to Dr. H. S. Taylor and Dr.

Gregg Dougherty for suggestions concerning its presentation.

### Summary

1. Rates of photochemical bromination of acetophenone in the presence of varying concentrations of water, hydrogen chloride, phosphorus pentoxide, and sulfur are given.

2. The results obtained in the bromination of acetophenone in the presence of the above agents indicate that the theory of prototropic reaction of carbonyl compounds is applicable even in non-aqueous solvents, *e. g.*, carbon tetrachloride.

PRINCETON, NEW JERSEY RECEIVED JANUARY 8, 1942

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

## The Photolysis of the Aliphatic Aldehydes. X. Acetaldehyde and Iodine Mixtures

BY F. E. BLACET AND JULIUS D. HELDMAN

In the photolysis of the aliphatic aldehydes the nature of the primary process has been an uncertain factor which has caused a great deal of speculation in recent years. By using iodine vapor to remove free radicals, Gorin<sup>1</sup> has presented evidence which appeared to settle the matter for acetaldehyde at wave lengths 3130 and 2600 Å. His work indicated that at both of these wave lengths primary decomposition both into the radicals CH<sub>3</sub> and HCO and into CH<sub>4</sub> and CO occurred. The CH<sub>3</sub> radicals reacted with iodine to give CH<sub>3</sub>I and the sums of the quantum yields of CH<sub>3</sub>I and CH<sub>4</sub> were equal to unity at each wave length. In the spectral region employed iodine vapor does not absorb.

Gorin's work appeared to warrant repetition and extension to other experimental conditions. In this article are reported results obtained at λ3130. Since others may wish to ascertain why our results differ from those reported by Gorin, experimental methods are described in considerable detail.

### Experimental Procedures

Monochromatic light was obtained from an atmospheric pressure mercury arc and a crystal quartz monochromator. The radiant energy was measured by means of a thermopile-galvanometer system which was standardized against two calibrated lamps obtained from the Bureau of Standards. Since the thermopile could not be used at the elevated temperatures employed in this work, the energy

entering the empty cell was measured at room temperature before a run, and the amount absorbed calculated with the aid of previously obtained curves of per cent. absorption *vs.* molecular concentration. The work of Leermakers<sup>2</sup> and Grahame and Rollefson<sup>3</sup> has shown that no serious error is introduced by assuming a constant absorption coefficient over the temperature range used in this study. The light intensity was kept constant during a run by controlling the amperage of the arc.<sup>4</sup>

The reaction system is shown diagrammatically in Fig. 1. That part within the dotted lines can be thermostated at whatever temperature is desired. The fused quartz reaction cell, A, is 3 cm. in diameter and 20 cm. in length. CDE is a magnetic circulating pump.<sup>5</sup> FGH is a magnetic valve through which acetaldehyde vapor can be introduced into the reaction system from S, and non-condensable reaction products can be collected by means of a Toepler pump placed beyond the mercury trap, J.

After thoroughly drying the reaction system by repeatedly flushing it with dry nitrogen, a weighed amount of iodine in an open capsule was dropped in the trap, B. B was then sealed in such a way that no moisture from the flame entered it. Next, after freezing the iodine with an alcohol-carbon dioxide refrigerant, the nitrogen was removed completely, the thermostat brought to the desired temperature, and the iodine allowed to vaporize into the reaction system. Then with the cut-off trap, I, open, F was raised and acetaldehyde vapor forced through a capillary tube into the reaction system where it was mixed with the iodine vapor by means of the magnetic pump.

After irradiation, all condensable substances were frozen in B by using liquid air, and the non-condensable gases collected for analysis with the aid of the Toepler pump.

(1) (a) Gorin, *Acta Physicochim. U. S. S. R.*, **9**, 681 (1938); (b) *J. Chem. Phys.*, **7**, 256 (1939).

(2) Leermakers, *THIS JOURNAL*, **56**, 1537 (1934).

(3) Grahame and Rollefson, *J. Chem. Phys.*, **8**, 98 (1940).

(4) Blacet and Lu Valle, *THIS JOURNAL*, **61**, 273 (1939).

(5) Blacet and Volman, *ibid.*, **61**, 582 (1939).