

## The Bromination of Acetone in Non-Aqueous Solutions

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The autocatalytic reaction of acetone with bromine and iodine in non-aqueous solutions has been studied by Dawson<sup>1</sup>, by Watson<sup>2</sup>, and by Cohen<sup>3</sup>. Preparatory to studies of the catalytic effects of different acids in non-aqueous media, it was decided to repeat some of the previous work which has been done on this reaction and to extend it to include other solvents and mixtures of solvents.

### Materials

**Acetone.** The best obtainable grade of acetone was purified by the method of Shipsey and Werner<sup>4</sup>. Freshly prepared acetone, boiling at 56.15°C. (760 mm.), was used in all determinations. The density,  $D_{4}^{25^{\circ}}$  was 0.7865.

**Ethyl Alcohol.** Absolute alcohol was prepared by several refluxings with very active quick-lime and subsequent fractional distillations. Freshly prepared alcohol was used in making all solutions. The boiling point was 78.36°C. (760 mm.) and the density,  $D_{4}^{25^{\circ}}$ , was 0.7852.

**Benzene.** Thiophene-pure benzene was purified by the method of Peterson and Rodebush<sup>5</sup>. The boiling point of the purified solvent was 80.07°C. (760 mm.).

**Carbon Disulphide.** After filtering through dry paper, the disulphide was refluxed for three hours over calcined lime. It was then distilled, and the distillate was treated with dry, powdered potassium permanganate (5 g. per liter). After distillation, the product was treated with purified mercury and fractionated twice from phosphorus pentoxide. The boiling point of the purified solvent was 46.10°C. (760 mm.), and the density,  $D_{4}^{25^{\circ}}$ , was 1.2899. It was stored in the dark until ready for use.

**Carbon Tetrachloride.** The method of purification was the same as that employed by Mills and MacRae<sup>6</sup>. The boiling point of the product was 76.74°C. (760 mm.) and the density,  $D_{4}^{25^{\circ}}$ , was 1.5936 and  $D_{4}^{0^{\circ}}$ , was 1.63266.

<sup>1</sup> (a) Dawson and Leslie, *Journ. Chem. Soc.*, 95, 1860 (1909); (b) Dawson, *ibid.*, 99, 1 (1911); (c) Dawson and Powis, *ibid.*, 101, 1503 (1912).

<sup>2</sup> Watson, *ibid.*, 3065 (1927); (b) Hughes and Watson, *ibid.*, 1945 (1929).

<sup>3</sup> Cohen, *Journ. Am. Chem. Soc.*, 52, 2627 (1930).

<sup>4</sup> Shipsey and Werner, *Journ. Chem. Soc.*, 103, 1255 (1913).

<sup>5</sup> Peterson and Rodebush, *Journ. Phy. Chem.*, 32, 714 (1928).

<sup>6</sup> Mills and MacRae, *Journ. Phy. Chem.*, 15, 54 (1911).

**Chloroform.** The method of Cohen<sup>7</sup> was employed to purify chloroform. The boiling point of the product was 61.15°C. (760 mm.) and the density,  $D_{4^{\circ}}$ , was 1.5247.

**Ethyl Acetate.** The method of purification was that described by Wade and Merriam<sup>8</sup>. The boiling point of the purified solvent was 77.20°C. (760 mm.) and the density,  $D_{4^{\circ}}$ , was 0.8945.

**Ethylene Dichloride.** This solvent was dried over phosphorus pentoxide for 24 hours and fractionated twice. The middle portion, boiling at 82.95°C. (760 mm.) was used.

**Dichloroethyl Ether.** The product of the Eastman Kodak Company was first dried with anhydrous calcium chloride, followed by metallic sodium. The dry ether was then distilled, and the middle portion was used. The boiling point was 172.5°C. (739 mm.).

**Bromine.** Three extractions were made with 10% sodium hydroxide solution. The bromine was then distilled in an all-glass apparatus, once alone, and twice from phosphorus pentoxide. It was stored in an all-glass container from which the bromine was forced into a calibrated tube.

### Method

The reaction mixture consisted of 100 ml. of the solvent, 10 ml. of acetone, and 1.0817 g. of bromine, unless otherwise specified. The mixture was placed in a 250 ml. closed volumetric flask which was immersed in an ice bath. Samples (2 ml.) were withdrawn at intervals. These were immediately diluted with an aqueous potassium iodide solution and titrated with 0.05 N sodium thiosulphate solution.

### Results and Discussions

The rate of the reaction was found to be independent of the concentration of bromine but to depend upon the concentration of acetone. This is in keeping with the results obtained with aqueous solutions and lends support to the contention that the reaction whose rate is increased is one involving acetone alone. This reaction probably involves the keto-enol transformation, which would then be the reaction that is catalysed by hydrogen bromide. The bromination of the enol modification is assumed to be instantaneous.

The natural rate of the reaction was studied by adding 1.0817 g. of bromine to 110 ml. of acetone. Cohen, using 0.840 g. of bromine and the same quantity of acetone, found that the reaction was complete in approximately 18 minutes. We found it to be complete, i. e., all the bromine was consumed, in 12 minutes and to show a much more pronounced latent period (Table I) than Cohen observed.

In aqueous solution (Table II) the bromine was completely consumed in 67 hours. Here the reaction showed an initially rapid rate

<sup>7</sup> Cohen, *loc. cit.*

<sup>8</sup> Wade and Merriam, *J. Chem. Soc.*, 101:2429 (1912).

TABLE I.—Rate of the Reaction in Organic Solvents  
 N/20 Sodium Thiosulfate (ml. used to titrate 2 ml. sample)

Time (Min.)	Pure Acetone	Carbon Disulfide	Ethylene Dichloride	Carbon Tetrachloride	Chloroform	Dichlorodiethyl ether	Ethyl Acetate	Ethyl Acetate +HCl
0	5.30	5.30	5.35	5.30	5.30	5.30	5.05	5.30
1	4.85	4.80	4.90	4.90	4.80			4.90
2	4.80						4.80	4.60
3						5.30		
4	4.80	4.60	4.90	4.90	4.80			1.65
5								1.25
6	4.80							0.20
7		4.50					4.70	0.00
8	4.50			4.90	4.80	5.25		
9		4.40						
10	3.80							
11							4.70	
12	0.00	4.30			4.75			
13			4.85					
14				4.90				
15		1.50	4.70		4.70			
16		0.00					4.70	
17						4.00		
18				4.85	4.60			
20					4.50		4.60	
22			2.70		4.30			
24						1.15	4.50	
25				2.70				
26			0.00		3.00	0.40		
29				0.00				
30					0.20			
31					0.00	0.00		
33							0.40	
35							0.00	

TABLE II.—Reaction in Water

Time		N/20 Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (in ml.)
Hours	Minutes	
	0	5.30
	0	4.70
	0	4.60
	0	4.31
	0	4.30
	1	4.30
	1	4.30
	1	4.26
	4	4.20
	7	4.20
	18	3.02
	22	2.60
	26	2.18
	29	1.75
	42	0.80
	49	0.50
	55	0.30
	67	0.00

during the first hours. Suddenly, it practically ceased for a period of approximately six hours; it then became much faster, the rate at which hydrobromic acid was formed increasing with the time. The reaction became slower again after some 40 hours.

Blanks were run for all the organic solvents used in the experiments. Their purpose was to determine whether or not bromine reacts with the solvent to an appreciable extent at 0°C. After six hours, no decrease in the quantity of sodium thiosulphate solution required in the titration could be detected except for alcohol, where a decrease in titre of 0.6 ml. occurred.

TABLE III.—Reaction in Ethyl Alcohol

A.		B.	
Alcohol dried in usual manner (Wt. of Br <sub>2</sub> = 0.9196 g.)		Intensively dried alcohol (Wt. of Br <sub>2</sub> = 0.8107 g.)	
Time in Minutes	(ml.) N/20 Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Time in Minutes	* (ml.) N/20 Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>
0	3.8 ml.	0	3.35 ml.
12	3.00	12	2.35
26	2.65	22	2.10
41	2.30	38	1.70
51	2.10	43	1.30
62	2.00	48	.95
71	1.80	56	.30
91	1.35	61	0.00
103	1.20		
114.5	.70		
117	.60		
121	.60		
126	0.00		

TABLE IV.—Reaction in Benzene

A.		B.	
Benzene dried in usual manner (Wt. of Br <sub>2</sub> = 1.2342 g.)		Intensively dried benzene (Wt. of Br <sub>2</sub> = 1.089 g.)	
Time (Minutes)	N/20 Sodium Thiosulfate (ml.)	Time (Minutes)	N/20 Sodium Thiosulfate (ml.)
0	5.10 ml.	0	4.50 ml.
1	4.60	10	2.70
24	4.60	15	2.70
59	4.60	20	2.55
71	4.50	25	2.50
81	2.20	33	0.00
86	0.00		

The results obtained when the course of the reaction was studied in carbon disulfide, ethylene dichloride, carbon tetrachloride, chloroform, ethyl acetate, and dichloroethyl ether are shown in Table I. The ethyl alcohol used as a solvent in the experiments reported in Table IIIA was dried in the manner previously described. The results obtained with this solvent could be reproduced to within 5-6 minutes for the period required for complete consumption of the bromine (about 120 minutes in all). Results for other solvents in which the time for complete reaction was shorter could be reproduced to within one minute. Table IIIB shows the results obtained with ethyl alcohol which had been subjected to prolonged and repeated treatments to remove the water originally present. Tables IVA and IVB show the results obtained by using benzene which had been treated, for widely different periods of time, with phosphoric anhydride.

The results obtained with these solvents differ from those reported by others in the following respects:

(1) Dawson and Leslie report that acetone and iodine react more rapidly in methyl alcohol than in benzene or carbon tetrachloride. This result was unexpected. One should expect the course of the reactions in alcohol to resemble that in water more closely than it does the reaction in carbon disulphide or benzene. According to our results in the reaction between bromine and acetone, ethyl alcohol in the role as solvent shows a greater similarity to water than do carbon tetrachloride and benzene. However, the reaction in alcohol is much faster than in water and becomes still more rapid as the alcohol is more completely dried.

(2) The time required for the utilization of all the bromine in the reaction is much less than the time reported by Cohen. We found, for example, that the reaction was complete in 16 minutes when carbon disulphide was used as solvent, in 29 minutes for carbon tetrachloride, and in 31 minutes for chloroform. Cohen's results for the same solvent, although he used less bromine, are approximately 110, 180, and 130 minutes. We believe that Cohen's results are too high and that they are caused by using acetone or solvents which contained appreciable amounts of water. When we added 0.0258 g. of water to 100 ml. of carbon tetrachloride and the usual quantities of bromine and acetone, we found that the reaction was complete in the same period of time as Cohen reports for anhydrous carbon tetrachloride, 180 minutes. This reaction had a very long latent period (over two hours) and then proceeded rapidly to completion.

The effect of small amounts of water in the solutions is also demonstrated by the results obtained in benzene and alcohol. There can be no doubt concerning the powerfully retarding effect of water upon the reaction. This fact supports the belief that molecular hydrogen bromide and not oxonium ion is the catalyst of the reaction.

(3) Cohen overlooked the latent period in all the reactions which he studied. This has been pointed out by Watson, although the latter does not offer any specific information on the point. It was first observed by Dawson and Leslie, whose results, however, like Cohen's,



indicate that the solvents or the acetone used by them contained water, which always increases the time required for the reaction. Our results show a latent period for the reaction in all organic solvents. In ethyl acetate this period is removed completely by the addition of dry hydrogen chloride.

(4) Except in the instance of benzene as solvent, there is no pronounced initial period of activity for non-aqueous solutions as has been shown to be true for the reaction in water. The initial decrease in the titre corresponds almost exactly in every case to the decrease in the concentration of bromine due to dilution when 10 ml. of acetone is added.

(5) The bromination reaction has a high initial velocity in the intensively dried benzene, which is entirely absent in benzene dried in an ordinary way. This cannot be caused by a catalyst originally present in the benzene since the period of activity at the beginning of the reaction was followed by a period of inactivity. One may venture the suggestion that a considerable quantity of enol acetone is present in intensively dried benzene and that this enolic form is brominated instantaneously.

(6) The addition of 2 ml. of pyridine to the reacting mixture in carbon tetrachloride completely stopped the action of bromine upon acetone (for three hours).

(7) The addition of sodium acetate to the reacting mixture in ethyl alcohol retarded the reaction rate. During the first sixty minutes there was scarcely any reaction, whereas in the absence of the salt more than half of the bromine was consumed in the same length of time. Lithium chloride increased the rate of the reaction in ethyl alcohol.