[CONTRIBUTION FROM THE WALKER CHEMICAL LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

THE BROMINATION OF ACETONE IN ORGANIC SOLVENTS[1]

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Introduction

The halogenation of ketones has offered a fertile field to investigators. Lapworth,[2] Dawson[3] and Rice[4] have made the most specialized contributions to this topic. Since these workers confined their studies mainly to reactions in aqueous solutions catalyzed by acids, an investigation of the natural autocatalytic reaction between acetone and bromine was carried out.

Purification of Materials

Acetone was purified by the sodium iodide addition-compound process of Shipsey and Werner.[5] A few minor changes were necessary to insure an anhydrous product. The acetone resulting from the iodide process was allowed to stand over phosphoric oxide for twenty-four hours. A deep red coloration appeared. On fractionation, discarding the first few cc., a material boiling at 56.38 ± 0.01° was obtained; density at 0°, 0.8035; at 25°, 0.7886.

Bromine was extracted three times with 10% sodium hydroxide solution and then distilled in an all-glass apparatus, once alone, and twice over phosphoric oxide.

Carbon tetrachloride was fractionated nine or ten times over phosphoric oxide until three liters distilled at 76.70–76.83°.

Carbon bisulfide was allowed to stand over bright, clean mercury for two weeks. It was then fractionated over phosphoric oxide; b. p. 46.10 ± 0.01°.

Chloroform was purified immediately before use. Technical chloroform was washed with water to free it from alcohol. It was then dried over calcium chloride and fractionated over phosphoric oxide; b. p. 61.30 ± 0.02° at 769 mm.

Apparatus

In the first part of this investigation the reaction was followed by titration of the bromine. Two hundred and fifty-cc. volumetric flasks were immersed in ice shavings. One hundred cc. of solvent at the bath temperature was pipetted into the flask. A small vial containing a weighed amount of bromine was dropped into the solvent, the ground glass stopper being removed as it fell. The flask was then well shaken and the reaction started by adding a known amount of acetone, usually 10 cc. Samples were withdrawn after suitable intervals, run into potassium iodide solution and titrated immediately with 0.05 N sodium thiosulfate.

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[1] This article is based on a thesis submitted by Irving Cohen to the Faculty of the Rensselaer Polytechnic Institute in partial fulfilment of the requirements for the degree of Master of Science.

[2] Lapworth, *J. Chem. Soc.*, **85**, 30 (1904); **93**, 2163 (1906); **95**, 2187 (1908).

[3] Dawson, *ibid.*, **96**, 1860 (1909); **98**, 2048 (1910); **101**, 1503 (1912); **105**, 1093 (1914).

[4] Rice, THIS JOURNAL, **47**, 379 (1925).

[5] Shipsey and Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

In the second part of the investigation the reaction was determined by following the change in conductivity of the reaction solution. Assuming that hydrobromic acid is the only substance formed which can affect the conductivity, the conductance of these solutions affords a measure of the concentration of the acid at any time. Since the specific conductance of these solutions approaches the order of 10^{-9} mhos per centimeter, special equipment was necessary.

Conductance Cell.—Dipping electrodes of polished platinum, 6.5 by 3 cm., mounted approximately 4 mm. apart, and fastened together firmly by glass rivets, were used. This combination was sealed on a glass tube having leads for connections through the tube. Since these electrodes were not platinized and exerted a large condenser action in water, it was difficult to obtain an accurate cell constant using the potassium chloride solutions of Washburn. The mean of a number of determinations gave 0.0218 ± 0.009. Because of the large uncertainty in the cell constant, all readings are given as the observed cell conductance, these values being easily reproduced to within 0.5%. The electrodes were not platinized for two reasons: (1) platinization might catalyze the reaction, (2) gaseous hydrobromic acid might be adsorbed due to the increased surface.

Resistance Box.—It was necessary to use resistances as non-inductive as possible. Three boxes, type 102J, serial No. 868 made by the General Radio Company of Cambridge, Massachusetts, were available, giving a possible variable resistance from 0 to 33,000 ohms.

Variable Air Condenser.—In order to balance the bridge satisfactorily, the capacitance of the conductance cell must be tuned out by a variable condenser. The instrument used had a capacity of 0 to 1500 m.m.f. and was made by the General Radio Company, being type 246L and serial No. 335.

Vacuum Tube Oscillator.—This was the Western Electric 4-B oscillator delivering frequencies of 100 to 5000 cycles per second. The output was capable of fine adjustment, so that during an experiment in which the conductance varied between wide limits, it could be varied to suit the need.

Slide Wire Bridge.—A Leeds and Northrup Slide Wire Bridge having a high resistance per unit length of wire was used. This sacrifices some precision but has the advantage of having the balance occur at exactly one point on the bridge wire. This condition is imperative when the conductance is changing rapidly with time.

Telephones.—These phones were made by S. G. Brown, Ltd., of London. They are equipped with a mechanical tuning device and were especially designed for conductivity work.

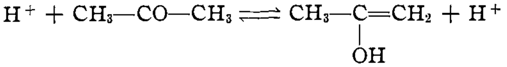
The procedure for determining a typical reaction velocity by the conductance method was as follows. Twenty cc. of acetone was pipetted into a glass cylinder. A vial containing a weighed amount of water was introduced and the acetone whirled in the cylinder. One hundred and twenty-five cc. of carbon tetrachloride was added and the liquids mixed thoroughly. A cork carrying the mounted electrodes was inserted into the cylinder and the latter immersed in a thermostat kept at 25.00 ± 0.01°. After a half hour had elapsed, a second vial containing a weighed amount of bromine was dropped into the solution by means of a glass tube leading through the cork. The time of adding the bromine was taken as the zero time of the reaction. The solution was always shaken for thirty seconds to allow the bromine to distribute itself equally throughout the solution. At suitable intervals, time and bridge wire readings were taken.

To obtain a reading, the following steps were required. The switch to the oscillator was closed. The bridge was then balanced to a minimum of sound, next the air condenser, and so alternately until a final balance on the bridge was obtained. The time was taken to the nearest five seconds and the switch to the oscillator opened. The entire procedure took at most ten seconds.

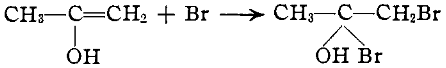
In assembling the above apparatus, the principles of design advocated by Washburn,[6] Morgan and Lammert[7] and Taylor and Acree[8] were used.

Theory and Results of Experiments

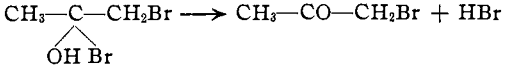
Lapworth[9] has explained the reaction of acetone with the halogens by means of the equations:



$$H^+ + CH_3\text{—}CO\text{—}CH_3 \rightleftharpoons CH_3\text{—}\underset{\underset{OH}{|}}{C}\text{=}CH_2 + H^+ \qquad (1)$$



$$CH_3\text{—}\underset{\underset{OH}{|}}{C}\text{=}CH_2 + Br \longrightarrow CH_3\text{—}\underset{OH\;Br}{\overset{}{C}}\text{—}CH_2Br \qquad (2)$$



$$CH_3\text{—}\underset{OH\;Br}{\overset{}{C}}\text{—}CH_2Br \longrightarrow CH_3\text{—}CO\text{—}CH_2Br + HBr \qquad (3)$$

Reactions 2 and 3 were assumed to be practically instantaneous, while the rate of attaining the keto–enol tautomeric equilibrium expressed by Reaction 1 was assumed to be comparatively slow. This mechanism explained why the velocity of this reaction was independent of the concentration of the bromine. It was also observed that the reaction was enormously catalyzed by hydrogen ions.

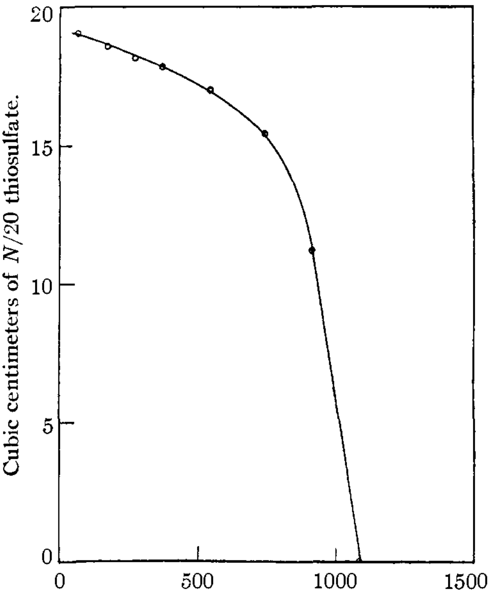


Fig. 1.—Temp., 0°; 110 cc. of acetone; 0.840 g. of bromine.

In order to ascertain the natural rate of reaction between acetone and bromine without using any solvent, 110 cc. of acetone and 0.840 g. of bromine were allowed to react. Figure 1 represents the concentration of bromine in 10 cc. of the mixture as a function of the time. The solution remains deep red until near the end of the reaction, when the liquid becomes lighter in color and then decolorizes practically instantaneously. From Fig. 1 it may be calculated that approximately 50% of the original bromine is converted into monobromo-acetone and hydrobromic acid during the last few seconds of

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[6] Washburn, This Journal, **38**, 2431 (1916); **39**, 238 (1917).

[7] Morgan and Lammert, *ibid.*, **45**, 1692 (1923).

[8] Taylor and Acree, *ibid.*, **38**, 2396, 2403, 2415 (1916).

[9] Lapworth, *J. Chem. Soc.*, **85**, 30 (1904).

the reaction, thus indicating the high speed of the reaction at that time. Since hydrogen bromide is continually formed during the reaction, we should expect autocatalytic effects, *viz.*, the amount of bromine decomposed per unit time should be greater as the concentration of hydrogen bromide increases in the solution. Figure 1 shows that such is the case (see Table I).

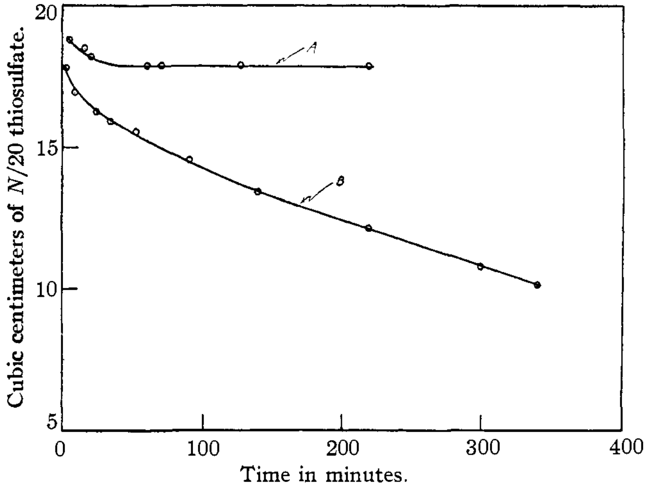

Fig. 2.—Temp., 0°; 110 cc. of acetone; 0.840 g. of bromine. Curve A, 0.50 g. of pyridine; Curve B, 0.70 g. of quinoline.

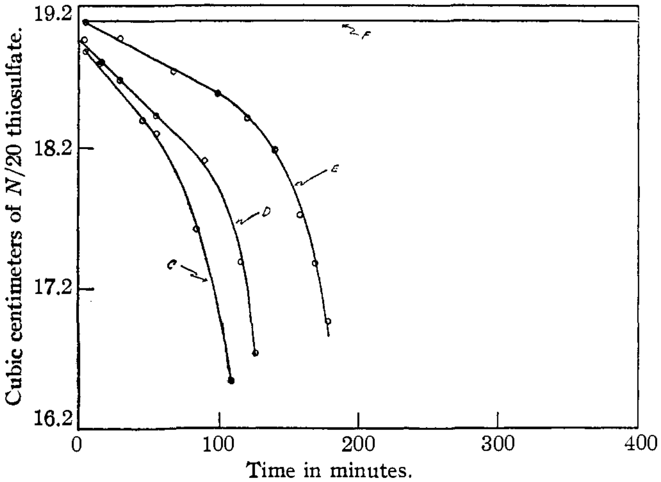

Fig. 3.—100 cc. of solvent; 10 cc. of acetone; 0.810 g. of bromine; temp., 0°. Solvents: Curve C, CS_2; D, $CHCl_3$; E, CCl_4; F, H_2O.

Effect on the Reaction of the Possible Removal of HBr.—In order to study the reaction without the catalytic influence of hydrogen bromide, substances were added which were supposed not to be affected by bromine and yet combine with hydrogen bromide as fast as it was formed. Curve A, Fig. 2, represents the result of this experiment. There seems to be no reaction after an initial disturbance. While these experiments were in progress, an article by Watson[10] appeared, in which it was stated that quinoline retarded the rate of halogenation of ketones but did not actually stop the reaction. Since pyridine and quinoline are closely related compounds this difference in behavior seemed odd. Curve **B**, Fig. 2, gives the results of a run using quinoline in place of pyridine. The difference in behavior can be explained by assuming different degrees of stability of the bromo addition compounds of pyridine and quinoline.

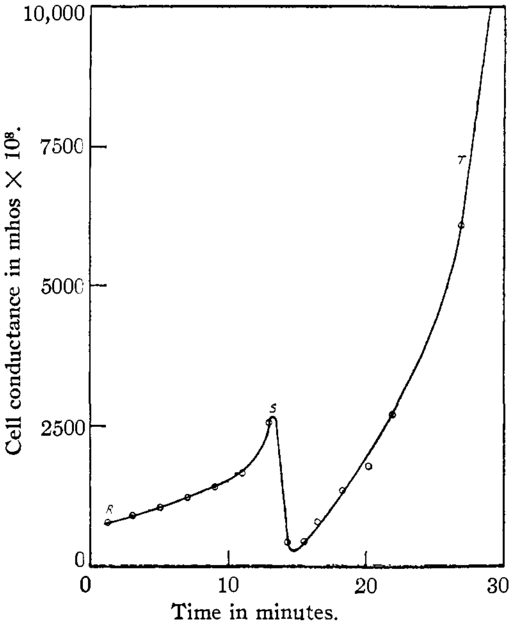

Fig. 4.

Effect of Various Solvents.—The reaction rate is affected by the solvent used, an extremely slow rate being observed for water, while maximum speed occurred with carbon disulfide as a solvent. Although the two other organic solvents (see Fig. 3) are chemically similar to carbon disulfide, they have a substantial influence on the reaction rate. We see also that the presence of a solvent does not change the general characteristics of the reaction (compare Figs. 1 and 3).

Effect of Varying Concentrations of Acetone and Bromine in Carbon Tetrachloride.—By suitably varying the concentrations of acetone and bromine, using carbon tetrachloride as solvent, it was found that the reaction rate was independent of the concentration of the bromine, while proportional to the concentration of the acetone.

The foregoing reactions were followed by titration. In the course of these experiments, some erratic results were obtained. The trouble was traced to water condensing on cold pipets and thus being introduced into the organic solvent. These small amounts of water were sufficient to practically stop the reaction. The effect of the addition of water to carbon tetrachloride on the rate of reaction of acetone and bromine was,

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[10] Watson, *J. Chem. Soc.*, 3065 (1927).

accordingly, investigated by a more accurate method, *viz.*, electrical conductance.

The conductance experiments were run at 25° since the conductances at 0° were of too low an order. Figure 4 represents a typical run on one of the carbon tetrachloride solutions. A few general observations apply to all of the solutions studied. (1) As soon as the solution decolorizes, it becomes turbid and fumes appear in the air space between the cork and the surface of the liquid in the cylinder. (2) Just after the point of decolorization, the resistance of the solution rises rapidly, usually exceeding the value of the initial resistance. Finally, the resistance decreases again to lower values. (3) The dielectric constant of the solution decreases considerably during the progress of the reaction.

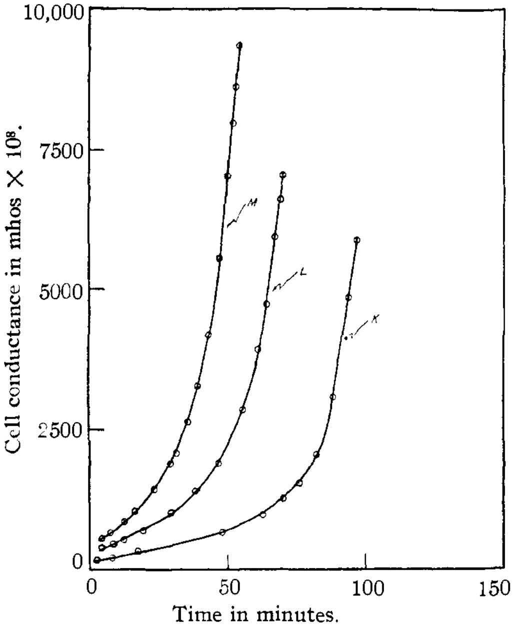

Fig. 5.—125 cc. of carbon tetrachloride; 20 cc. of acetone; 0.743 g. of bromine; varying amounts of water; temp., 25°. Curve K, 0.229 g. of water; L, 0.180 g. of water; M, 0.160 g. of water.

At the point of decolorization a large quantity of bromine is converted into hydrogen bromide. On this basis, we would expect a very rapid rise in conductance but we find the reverse to be true. However, the solubility of gaseous hydrogen bromide in carbon tetrachloride is very small. When this large amount of gas is released throughout the solution it must of necessity be in the form of minute bubbles of gas surrounded by liquid. This cuts down the conducting area between electrodes and therefore raises the resistance. On shaking, the bubbles unite and leave the solution, thus making the area larger and decreasing the resistance. Figure 4 was obtained under just such experimental conditions. From R to S is that part of the curve in which we are interested. The readings from S to T are unessential for measurement of velocity constant and have therefore been omitted from all further data.

Table I

110 Cc. of Acetone, 0.840 g. of Bromine. Temp., 0 °C.

Time, seconds	0	60	164	264	366	538	738	910	1086
0.05 N $Na_2S_2O_3$, cc.	...	19.05	18.56	18.20	17.83	17.05	15.50	11.25	0

Since the dimensions of the electrodes are fixed, any change in the adjustment of the condenser used for balancing must perforce come from a change in the dielectric constant of the solution whose conductance is being measured. All of the solutions exhibited a decrease in dielectric constant with time. This may be due to the gradual chemical combination of the water added initially, with some other compound.

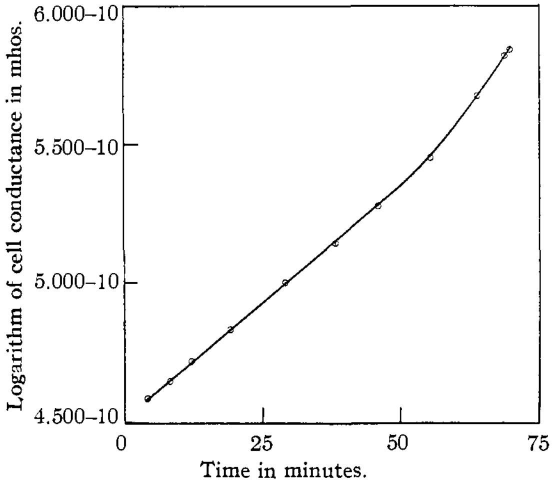

Fig. 6.—125 cc. of carbon tetrachloride; 20 cc. of acetone; 0.743 g. of bromine; 0.180 g. of water; temp., 25°.

On adding increasing amounts of water to a solution of 125 cc. of carbon tetrachloride and 20 cc. of acetone, the liquid becomes turbid at a certain point, due to the slight solubility of water in this mixture. The quantity

Table II

With Curve M of Fig. 5

125 cc. of carbon tetrachloride; 20 cc. of acetone; 0.743 g. of bromine; 0.160 g. of water; temp., 25°

Time, minutes	Cell conductance, mhos	Time, minutes	Cell conductance, mhos	Time, minutes	Cell conductance, mhos
3.00	0.00000501	21.17	0.00001305	41.00	0.00003699
4.25	556	23.00	1425	43.17	4185
5.25	577	25.00	1569	45.00	4781
7.00	652	27.00	1727	47.00	5554
8.33	692	29.00	1897	49.00	6681
9.00	716	31.00	2079	50.00	7036
10.00	758	33.17	2333	51.00	7455
12.17	850	35.33	2623	52.00	7990
14.00	937	37.00	2888	53.00	8624
16.00	1027	39.17	3271	54.17	9340
18.17	1127				

TABLE III

EXPERIMENTAL RESULTS FIG. 7

Velocity constant...	0.0136	0.0200	0.0264	0.0400	0.0434	0.0498
Mg. of water.......	229	180	160	98	90	61

of water necessary to cause the first appearance of turbidity was 100 mg. The turbidity seems to have no effect on the reaction, the water having an effect commensurate with what it would have in a clear, homogeneous solution. Figure 5 illustrates this fact. Curves K, L and M, represent solutions containing 229, 180 and 160 milligrams of water, respectively (see Table II). Experiments run on clear solutions containing 98, 90 and 61 mg. of water give the same form of curve, with the rates of reaction increasing with decreasing amounts of water. It was impossible to obtain the reaction velocity of the anhydrous substances, the entire reaction being complete within thirty seconds.

Velocity constants were calculated by the method outlined below. Figure 7 represents the plot used for a typical calculation. The actual reaction deviates from the assumed law toward the end of the reaction.

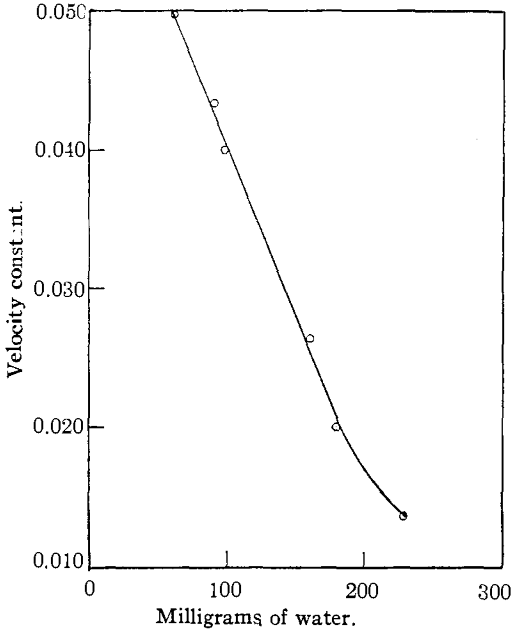

Fig. 7.

The numerical results of this investigation are given in Fig. 7. A very striking relationship is apparent. Water has an enormous retarding effect on this reaction and is no doubt intimately concerned in its mechanism.

Evaluation of Results

The sum total of all reactions occurring may be expressed as follows

$$CH_3COCH_3 + Br_2 \longrightarrow CH_3COCH_2Br + HBr$$

Let C_{HBr} = Concentration in moles per liter of hydrogen bromide at the time, t

C_A = Concentration in moles per liter of acetone. This may be considered constant for it is made large to insure the formation of monobromoacetone only

G = Conductance of the solution at the time, t

k = Velocity constant

K = Constant of proportionality between cell conductance and concentration of hydrogen bromide

G_0 = Constant of integration.

From our experiments we assume $d[C_{HBr}]/dt = kC_{HBr}\cdot C_A$. It is also necessary to assume $G = KC_{HBr}$. From these, $d[C_{HBr}]/dt = dG/Kdt = (kG/K)C_A$ or $dG/dt = kGC_A$. Integrating this equation and determining the value of the constant of integration by assuming a conductance due to a concentration of hydrogen bromide at the start of the reaction, we get $\ln G = kC_At + \ln G_0$, or passing to decimal logarithms and placing C_A = 1.874 moles per liter

$$\log G = \frac{1.874}{2.303}\,kt + \log G_0 = 0.8138\,kt + \log G_0$$

We can determine the numerical value of the velocity constant by plotting log G versus t, measuring the slope of the straight line obtained and dividing this value by 0.8138.

The author wishes to acknowledge his indebtedness to Dr. H. S. Van Klooster, Professor of Physical Chemistry at the Rensselaer Polytechnic Institute, under whose direction the investigation was carried out.

Summary

The kinetics of the bromination of acetone in organic solvents has been investigated.

Water has a powerful retarding influence on this reaction.

The extraordinary catalytic power of dry hydrogen bromide on the bromination of acetone is demonstrated.

The reaction is approximately first order with respect to hydrogen bromide.

A considerable change in the dielectric constant of the solutions used has been observed during the progress of this reaction.

TROY, NEW YORK

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE]

SULFONATION OF 2-NAPHTHOL IN PRESENCE OF BORIC ACID. 2-NAPHTHOL-1,6-DISULFONIC ACID

BY KARL H. ENGEL

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The use of boric acid as a catalyst in the sulfonation of 2-naphthol (one part of boric acid for two hundred parts of naphthol), for the purpose of improving yields and quality of the reaction products, has been patented by M. L. Crossley and G. S. Simpson.[1]

Two years before issue of the patent, the writer experimented in a similar direction, and observed that appreciable amounts of boric acid caused a striking change in the expected reaction course. A difference became outwardly noticeable—sulfonation masses, instead of remaining fluid, solidi-

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[1] Crossley and Simpson, U. S. Patent 1,570,046 (1926).