

THE BROMINATION OF PARA-CRESOL IN THE PRESENCE
OF
STRONG ACIDS

THESIS

BY

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INTRODUCTION

The purpose of this work has been to determine whether or not the formation of an oxonium compound of a cresol would change the directing influence of the hydroxyl group.

On the theory of electron displacement¹ in derivatives of benzene, Hart² has studied the bromination of para cresol in the presence of strong acids; Under the conditions employed by Hart, Kendall and Carpenter³ have shown that two addition products between para cresol and 100% H₂SO₄ could be isolated. These two compounds have the formulae (C₇H₇OH)₂H₂SO_{3.4} m.p. 11.0 C. and C₇H₇OH(H₂SO₄)₂ m.p. 93.5 C. The sharpness of the maximum of the freezing point curve in addition to its high melting point indicates that the latter compound is quite stable. On the basis of the electron displacement theory it would be predicted that the formation of an addition product between para cresol and 100% H₂SO₄ would change the ortho and para directing hydroxyl (OH) group to a meta directing oxonium (OH(H₂SO₄)₂) group. Due to unexpected sulphonation Hart was unable to draw any conclusion from his results as to whether or not the presence of the strong acid had any influence on the directing power of the hydroxyl group.

1. H.J. Lucas, J. Am. Chem. Soc. 48, 1827 (1926)

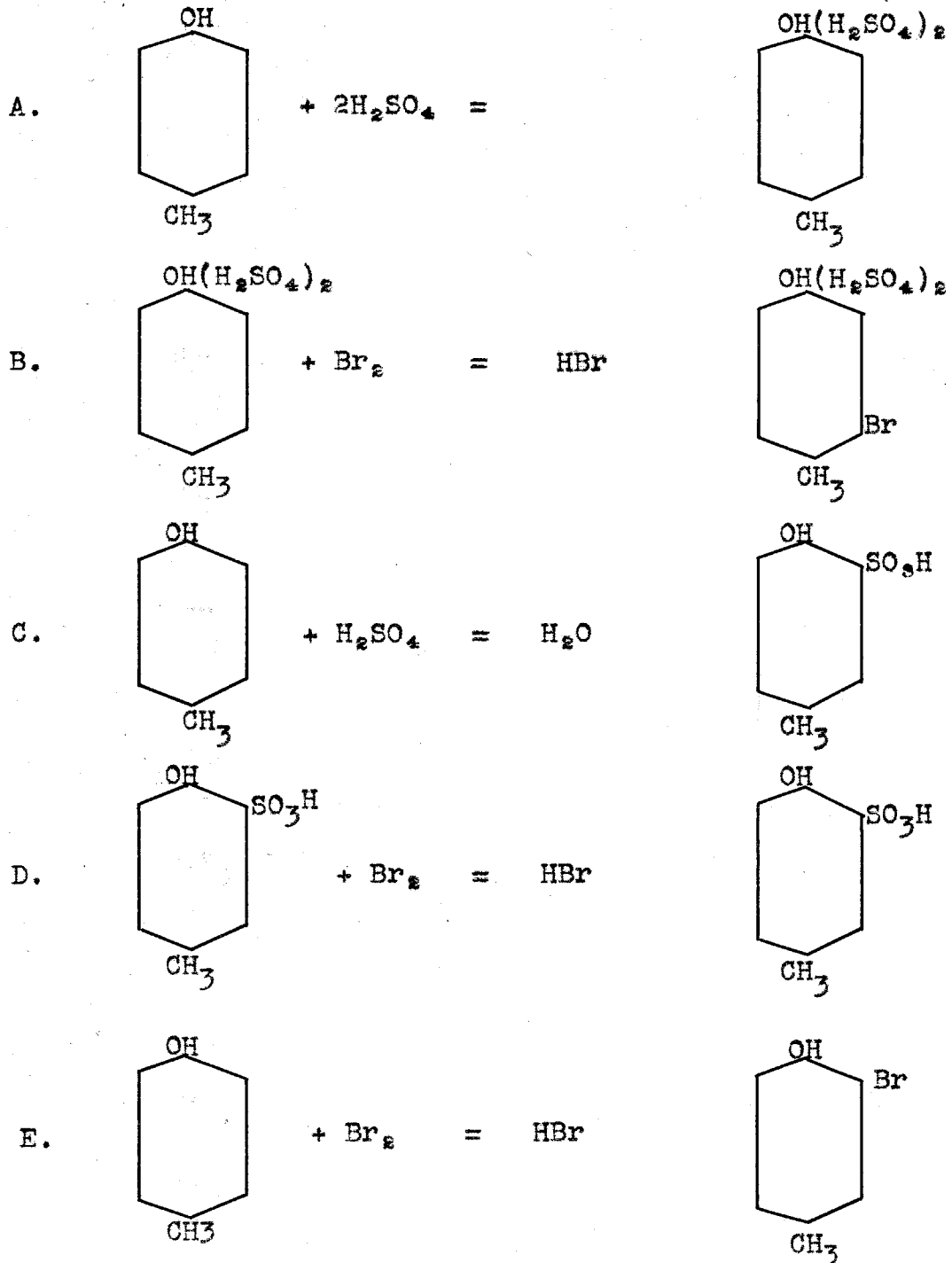
2. E.V. Hart, C.I.T. Thesis (1924)

3. Kendall and Carpenter, J. Am. Chem. Soc. 36, 2498 (1914)

Hart carried out the bromination in the absence of a carrier. Prof. Lucas suggested on the basis of considerations taken up in the next section that the presence of a carrier would speed up the bromination and perhaps avoid sulphonation. This work has to do in particular with the carrying out of this suggestion.

SURVEY OF REACTIONS AND
NECESSARY CONDITIONS

The following equations represent the most probable reactions that may occur in the bromination of para-cresol in the presence of 100% H_2SO_4 .



Equations A and B represent the desired reaction. It is evident that if the concentration of the free cresol be made small compared to the concentration of the addition product, the desired reaction (B) will be favored, while the undesired reactions (C and E) will be retarded.

The ratio of the concentration of the addition product to the concentration of the para cresol may be made large by employing an excess of 100% H_2SO_4 in order to shift the equilibrium of the reaction to the right.

Sulphonation(C) may be retarded by keeping the reacting materials cool(below 10C)(see also Kendall and Carpenter) However, due to the the large free energy decrease attending this reaction, if it once starts it is very liable to go to completion. Therefore as a further aid to retarding this reaction it is desirable to have a slight excess of free SO_3 (2%) to combine with any water formed;

From the above considerations it is apparent that if the reaction (B) may be speeded up by a catalyst such as anhydrous aluminum bromide, and reactions (C) and (E) retarded, by reducing the concentration of the paracresol and by cooling the reacting materials, the desired end may be attained;

It is to be pointed out here that the conditions favoring the desired reaction are not as clear cut as might be supposed from the above considerations, for

although sulphonation may be retarded by low temperatures, the desired reaction (B) is also retarded, and further the presence of bromine is thought to catalyze the sulphonation.

OUTLINE OF WORK

The results and conclusions derived from a series of qualitative and quantitative experiments will be given in this section, while the details of the quantitative experiments will be reserved for a later section.

The addition product may be prepared by adding cold 100% H_2SO_4 to p-cresol. There is a slight heat of solution. A light yellow liquid results which upon standing solidifies to a white mass. This white solid is not soluble in most organic solvents as is to be expected, however, the above mentioned liquid is completely soluble in water. The expected hydrolysis of the addition product to form the insoluble p-cresol apparently requires some time, for upon standing several hours a white flocculent precipitate comes down. However, this point was not carefully investigated for it was assumed that the precipitate was the expected p-cresol derived from hydrolysis of the addition product which as a matter of fact probably would come down as a liquid due to lowering of the melting point of the cresol by absorbed water.

P-cresol was brominated in the cold (the reaction flask was constantly in an ice water bath) dissolved in just enough 100% H_2SO_4 to form the addition product, that is a mol. ratio of 1 to 2. in the absence, and in the presence of anhydrous aluminum bromide. It was found that the bromination

proceeded as rapidly as the bromine was added in ether case, although it did appear to go more smoothly in the presence of the carrier. Before the theoretical amount of bromine had been added (80%) the reacting materials solidified. After the excess bromine had vaporized, the material was thrown upon crushed ice, yielding an oil which solidified upon standing. This water insoluble material when crystallized from petroleum ether was found to have a melting point of 48-9 C which corresponds to 3,5 di brom p cresol. Apparently due to the relatively low concentration of free cresol and the high excess of bromine, the di brom is the main product. This would seem to confirm the conclusions drawn in the previous section.

An attempt was made to brominate p cresol in the cold when dissolved in an excess of 100% H_2SO_4 both in the presence and in the absence of a carrier. The ratio of the cresol to the acid was 1 to 5. In the absence of a carrier no reaction was observed, i.e. no evolution of HBr. After the reacting materials had stood 72 hours the solution had gradually darkened to a deep green, there was a pronounced odor of SO_2 indicating oxidation. What the actual reactions were, was not investigated, however bromination was not one of them. In the presence of the anhydrous aluminum bromide, the bromination appeared to proceed, but very slowly. After standing 24 hours the material

yielded a small amount of a water insoluble product which was later identified as tetra-brom-*p*-cresol.

The preceding experiments have been of a qualitative nature, a quantitative experiment was now carried out. *p*-cresol was dissolved with constant stirring in the cold in 102% H_2SO_4 . The mol. ratios being 1 to 5 as before. When the cresol had completely dissolved bromine which contained 1% by weight of aluminum bromide was slowly added. It required three hours to add the theoretical amount of bromine, during this time the reaction was observed to proceed slowly, however the concentration of the bromine was slowly building up as evident from the dark red color of the solution. The reacting material was allowed to stand 2⁺ hours at the end of this time crystals were observed in the solution. Stirring was continued for another three hours at the end of this time the material was thrown upon crushed ice. A small quantity of water insoluble material was obtained, which when crystalized from alcohol melted at 196-197 C. This compound was later found to be tetra brom *p* cresol. The aqueous solution was not worked up. A second quantitative experiment was carried out as the preceding experiment with the difference that it was carried out in one day. The ^{same} product resulted, but a much poorer yield was obtained in this case. The aqueous phase of this experiment was partially worked up but nothing definite was learned.

It was not considered worth while to pay a great deal of attention to the material that was completely soluble in water, for the reason that sulphonation has occurred forming the soluble sulphonic acid, which for the object in view Hart has shown leads to indeterminate results.

From the above described experiments no definite conclusion can be drawn as to whether or not the presence of the strong acid has any influence upon the directing power of the hydroxyl group. However, it would appear from these results that the addition product is a meta directing group because of the slowness of the bromination. Due to the large excess bromine present at any time any free cresol was completely brominated to the tetra brom cresol. It has been suggested by Prof. Lucas that nitration might be employed instead of bromination with better success. This suggestion was partially carried out. P cresol was easily nitrated in the cold when dissolved in an excess of 102% H_2SO_4 a mol ratio of 1 to 5 being used. One half hour was required for the nitration, at the end of this time the material was thrown upon crushed ice yielding a water soluble material. The nitro cresols are fairly soluble in water, so that after partial neutralization of the acid the solution was extracted with ether. No ether soluble material was obtained, which should have been the case if any nitro or free cresol had been present. The aqueous phase yield a precipitate upon heating to 100 C and standing for several hours. What this solid was, was not determined, but the phase smelled strongly of the

characteristic nitro compound odor.

During the course of the preceeding experiments it became desirable to run a quantitative bromine analysis upon brom cresol and tetra brom cresol. The method of Robertson⁴ which has been modified by Buxton⁵ was employed. The exact details of the modification employed by Buxton were n t given in his thesis, they have been worked out and will be given in a later section.

4. Robertson, J. Chem Soc. 107, 902 (1915)

5. BUXTON, C. I. T. Thesis (1936)

DETAILS OF EXPERIMENTS

The apparatus employed to carry out the reactions in was similiar to that used by Hart. That is, the reaction was carried out in a one liter three necked flask. A mercury seal stirrer was introduced in the central opening, while the acid was introduced by means of separatory funnel through one side opening, the HBr vapor was conducted out of the reaction flask through the other side opening. The bromine was introduced in the same way as the sulphuric acid.

The 102% H_2SO_4 was prepared by adding the calculated quantities of 95% acid and fuming sulphuric. (100 g. 95% acid to 99.2 g of 24% fuming acid.) The final acid concentration was checked by titration with a standard bases.

First Experiment

Wt of p-cresol C_7H_7OH	25 grams	= .231 mols	ratio 1
Wt of 102% H_2SO_4	113 grams	= 1.160 mols	5
Wt of bromine	40 grams	= .250 mols	1
Wt of aluminum	.37 grams		

The acid was run through a separatory funnel into the flask containing the cresol with constant stirring. The reaction flask was immersed in an ice and water bath, the acid had just previously been kept in an ice water bath. To the theoretical amount of bromine required to produce the mono brom cresol 1% by weight of aluminum plus the amount of bromine required to combine with the aluminum was added. The bromine plus aluminum bromide

was slowly added with constant stirring to the contents of the flask. The addition of the bromine required about three hours, during this time a slow evolution of HBr was observed. During the addition of the bromine the color of the solution gradually changed from a light amber to a deep cherry red indicating a building up of the concentration of bromine. The contents of the flask was allowed to stand over night at the end of this time crystals had separated out, however the solution was still a deep red color. Stirring was started again and continued for three hours, at the end of this time, the still deep red solution, was poured upon crushed ice. The final volume of the solution being 250 cc. The above mentioned crystals were insoluble along with a white precipitate obtained on dilution with water

The solid was washed with water and dried (weight 6.2g) when crystalized from alcohol it melted at 195-6. The fact that this compound was tetra brom cresol was not recognized at first, because it was found to be insoluble in 6 n NaOH which would indicate that the OH group had been absent. However, it was later found to be soluble in dilute NaOH.

No attempt was made to work up the solution for the reason already given.

Second Experiment

Wt. of p-cresol C_7H_7OH	25 grams	= .231 mols
Wt of 102% H_2SO_4	113 grams	= 1.16 mols
Wt of bromine	40 grams	= .231 mols
Wt of aluminum	.37 grams	

The acid was prepared and run into the reaction flask as before. Before the bromine was added what appeared to be the addition product began to precipitate, however, the bromine was slowly added requiring about two hours. During the course of the experiment the solid that first separated out dissolved. When approximately 90% of the bromine had been added (aluminum had been previously added to this bromine and had reacted to form aluminum bromide as in the preceding experiment) a solid began to separate out. The solution gradually became a cherry red as before. The contents of the reaction flask was poured on 240 grams of ice, a white precipitate resulted. This precipitate when washed and dried weighed (3.6gr) This solid when crystallized from alcohol melted at 195-6 corresponding as before to tetra brom cresol. An attempt was made to work up the above filtrate but nothing of interest was learned.

The very low yields, based upon the cresol (6.3% in the first experiment and 3.7% in the second case) of the water insoluble tetra brom cresol would indicate that despite precautions a great deal of sulphonation had

occured. As mentioned before, bromination of the addition product appears to take place very slowly if at all, and due to the high excess of bromine present as indicated by the cherry red solution any free cresol is completely brominated to the tetra brom compound. As the bromination of the cresol occurs the equilibrium of the reaction (A) evidently shifts to the left since the amount of the tetra brom product is proportional to the duration of the experiment. The above mentioned fact in connection with the previously mentioned slow rate of hydrolysis of the addition product would seem to indicate that the equilibrium of reaction (A) may be shifted only very slowly.

DETAILS OF HALOGEN ANALYSIS

PROCEDURE

The method of halogen analysis proposed by Robertson⁴ consists in brief of decomposing the halogen by means of concentrated sulphuric acid and chromic anhydride. The liberated halogen and halogen acid are absorbed in sodium hydroxide and hydrogen peroxide. The amount of halogen absorbed is determined by the Volhard method. Robertson mentions in his work the fact that due to the presence of the H_2O_2 the red color of the $Fe(SCN)_4$ of the end point disappears rather rapidly. At the suggestion of Prof. Lucas, Buxton⁵ found that by boiling the absorption solution with ferric hydroxide which catalysis the decomposition of H_2O_2 a much better end point in the Volhard determination could be obtained. Buxton did not give the complete details of his modification. Since this halogen analysis procedure is more or less routine work the complete details are here give.

The apparatus is that employed by Buxton, in assembling the apparatus it is advisable to connect the parts by thick walled rubber tubing, both the ground glass stoppers and the tubing should be lubricated with syrupy phosphoric acid in order facilitate removal and to prevent the halogen from reacting with the rubber.

The reagents employed should be free from halogen,

The KSCN solution should be standardized against the standard silver solution by carrying through a complete blank run. This will take care of any trace of halogen in the reagents.

Sufficient sample to give the equivalent of 9 cc of .1 N AgNO_3 is weighed into the reaction flask, 30 cc of cold concentrated acid is then added to the reaction flask by means of a funnel. It is advisable to immerse the reaction flask in an ice water bath in order to control the reaction, further it is important that the substance should be completely dissolved in the acid before the chromic anhydride is added, this prevents loss of sample by volatilization. After 40 cc of N NaOH and 20 cc of $3\text{H}_2\text{O}_2$ have been placed in the absorption flask, the apparatus is assembled. Ten grams of chromic anhydride may then be added to the cold solution of the sample dissolved in the acid. The contents of the flask should be very gently heated at first, taking care that the reaction does not proceed too rapidly. After $3/4$ hour of heating the reaction is usually complete and in order to completely remove any halogen vapor a slow stream of air should be passed through the apparatus. To do this it is advisable to employ a manometer on the air supply in order to estimate the required pressure and also to prevent the contents of the flask from backing up.

4. Robertson, J. Chem. Soc. 107, 902 (1915)
5. Buxton C.I.T. Thesis (1926)

It was found that the total quantity of H_2O_2 contained in the absorption apparatus may be decomposed by boiling the alkaline solution for ten minutes in the presence of $Fe(OH)_3$. One cc of N $Fe(NO_3)_3$ added to the absorption solution has been found to be sufficient, if more is used it is very difficult to change the colloidal $Fe(OH)_3$ to the nitrate upon acidification.

After boiling the absorption solution with the ferric hydroxide, the solution should be cooled in an ice water bath and then acidified with 20 cc of 6 N HNO_3 . The excess acid is employed to prevent the hydrolysis of the ferric nitrate. After acidification 9 cc more of N $Fe(NO_3)_3$ is added to the solution. It is important that exactly the same total quantity of ferric nitrate be added in each case, the above amount has been found to give a sharp end point.

The above solution may now be titrated by the regular Volhard method for determining halogen. It may be pointed out here that in the determination of bromine it is not necessary to filter out the precipitated silver bromide but it is advisable because the silver bromide having a slight yellow color makes it difficult to recognize the first trace of red $Fe(SCN)_3$. To give an idea of the reliability of the above procedure and the accuracy of the end point the following results are given.

Four different runs were made on a fairly pure sample of tetra brom para cresol obtained from experiments one and two with the following results.

Run No.	Percent bromine	
	Found	Calculated
I	73.9%	75.45%
II	73.2%	
III	73.2%	
IV	74.5%	

The following results were obtained using a very pure sample of brom cresol.

Run No	Percent bromine	
	Found	Calculated
I	42.2%	42.7%
II	42.1%	

SUMMARY

(1) A presentation of the most probable reactions that occur in the bromination of para cresol in the presence of strong acids (100% H_2SO_4) is given, in addition to a discussion of the most likely conditions to achieve the desired result.

(2) The bromination of para cresol has been shown to proceed quite easily with or without a carrier in the presence of just sufficient 100% H_2SO_4 to form the addition product. The chief product insoluble in water being 3,5 di brom cresol.

(3) In an attempt to brominate p cresol without the aid of a carrier in the presence of an excess of 100% H_2SO_4 sulphonation and oxidation occurred.

(4) In brominating p cresol in the presence of anhydrous aluminum bromide the chief water insoluble product has been shown to be tetra brom p cresol. The formation of the compound has been explained to be due to the apparently slow speed of the bromination of the addition product, with the result that any free cresol is completely brominated by the large excess of bromine present.

(5) Details of the procedure for halogen analysis of organic compounds have been given.

In conclusion, I wish to take this opportunity to thank Prof. H.J. Lucas for his kindly advice and

help extended to me throughout the past two years, both in the laboratory and in the classroom.

DATA

2 brom p cresol	m.p. 55-56°C
3 brom p cresol	m.p. 17-18°C
3,5 di brom p cresol	m.p. 48-49°C
2,6 di brom p cresol	m.p. 97°C
2,3,5 tri brom p cresol	m.p. 102°C
tetra brom p cresol	m.p. 196-197°C