

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 69.23; H, 7.69; neut. equiv., 208. Found: C, 69.43; H, 7.53; neut. equiv., 212.

The quantitative determinations were performed microanalytically according to Pregl.¹⁶

Acknowledgment is made here to Mr. Franz K. Silbert of this Laboratory for performing the analyses, and to Mr. Louis Krautmann for his assistance in preparing some of the above mentioned compounds.

Summary

Saturated alkyl phenyl ethers (isopropylphenyl and cresyl ethers) were rearranged to the corresponding substituted phenols by means of a mixture of concentrated sulfuric and glacial acetic acid. Proofs for the probable structure of the products obtained were advanced and a general rule as to the way of migration of the alkyl groups was given.

As the possibility of rearranging even short chain, saturated phenyl ethers has now been demonstrated, a series of related problems such as the rearrangement of some of the more important phenyl ethers of mono and poly functional alkanes are now being investigated.

The physiological properties of the substituted phenols mentioned before are being studied.

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EFFECT OF NEUTRAL SALTS ON THE RATE OF HYDROLYSIS OF CELLULOSE ACETATE IN ACETIC ACID SOLUTIONS¹

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Introduction

The effect of the presence of neutral salts of the alkali metals on the rate of chemical reactions has been the subject of the investigation of several workers in recent years. The published results appear to have been concerned mostly with crystalloids. L. E. Bowe² has investigated the effect of sodium chloride and sodium bromide on the rate of saponification of ethyl acetate by hydrochloric acid. Grube and Schmid³ studied the hydrolysis of cyanamide to urea by nitric acid in the presence of nitrates, and the saponification of ethyl acetate by hydrochloric acid in the presence of alkali and alkaline earth chlorides. Hawkins⁴ worked on the

¹⁶ Pregl, "Quantitative Organic Micro Analysis," Blakiston's Sons, Philadelphia, 1930.

¹ Study carried out under the direction of H. LeB. Gray, Superintendent of the Organic Research Laboratory.

² Bowe, *J. Phys. Chem.*, **31**, 298 (1927).

³ H. Grube and G. Schmid, *Z. physik. Chem.*, **119**, 19 (1926).

⁴ J. E. Hawkins, University of Pennsylvania, "Thesis," 1927.

hydrolysis of ethyl acetate in dilute aqueous solutions; Kautz and Robinson⁵ gave results of an investigation of the hydrolysis of sucrose by hydrochloric acid in the presence of alkali and alkaline earth chlorides. Sherman, Caldwell and Cleaveland⁶ ascertained the effect of neutral salts on the rate of inversion of starch by amylase, and Roberts and Terry⁷ investigated the velocity of saponification of ethyl formate by ammonium hydroxide in the presence of ammonium salts. In general, it has been observed that neutral salts increase the reaction velocity in rather widely different types of reactions.

As far as has been learned, however, no publication has been made of the effect of neutral salts on the rate of hydrolysis of cellulose esters. Since these compounds present a different aspect of the general problem in that their dispersions are colloidal in character, an investigation of the results obtained by the addition of neutral salts appeared of interest.

Experimental

Cellulose acetate was prepared by the esterification of cellulose in the form of cotton linters, through the action of a mixture consisting of acetic anhydride, acetic acid and a catalyst. A calculated amount of water more than sufficient to convert the excess acetic anhydride to acetic acid was added. In this way the difficulty of redissolving cellulose triacetate in acetic acid with possible lack of uniformity of the solution was overcome. The concentration of the various components of the solutions used in the hydrolysis experiments was as follows: cellulose triacetate, 89 g., acetyl content 43.5 to 44.2% (theoretical 44.8%); acetic acid, 563.5 g.; water, 22.9 g.; sulfuric acid, 0.9 g.; phosphoric acid, 2.7 g., and sodium bisulfate, 2.0 g.

Four groups of experiments were carried out. In each series fresh preparations of cellulose triacetate were made in sufficient quantity for all of the experiments in that group. The procedure employed in acetylation was the same in all cases.

Three 550-g. portions of cellulose triacetate solutions of the composition given above were taken for the first series of experiments. One contained in addition 17 g. of sodium nitrate, the second 20 g. of potassium nitrate, while the third contained no neutral salt, this portion serving as a control. The hydrolyses were carried out in glass-stoppered bottles, maintained at $53 \pm 1^\circ$ in a constant-temperature air-bath. After various intervals throughout the saponification approximately 100-g. samples were removed and these, after dilution with an equal volume of acetone to assist in obtaining fluffy precipitates which could be easily washed, were precipitated by pouring slowly into warm water (approximately 60°) with vigorous stirring. The precipitated cellulose acetates were then washed with water until the residual acid had been removed, as indicated by testing the precipitates with brom thymol blue. They were then air-dried.

The acetyl content of each sample was determined using a modification of the Knoevenagel method as given below.

Approximately one-half gram of the material after air-drying is placed in a small glass weighing bottle and further dried at 105° for sixteen to eighteen hours. After cooling in a desiccator over anhydrous calcium chloride, the bottle and contents are weighed. The cellulose acetate is transferred to a 250-cc. Erlenmeyer flask, the bottle again weighed and the weight of sample obtained by difference.

⁵ C. F. Kautz and A. L. Robinson, *THIS JOURNAL*, 50, 1022 (1928).

⁶ H. C. Sherman, M. L. Caldwell and M. Cleaveland, *ibid.*, 52, 2436 (1930).

⁷ E. N. Roberts and E. M. Terry, *ibid.*, 52, 2604 (1930).

Twenty cubic centimeters of 75% ethyl alcohol (by weight) are added and, after covering the flask, maintained at 56° in an air-bath for thirty minutes. At the end of this time 20 cc. of 0.5 *N* sodium hydroxide is pipetted into the flask. The flask is then stoppered and after heating at 56° for fifteen minutes it is permitted to stand at room temperature for approximately twenty-four hours. The excess alkali is back-titrated using 0.5 *N* hydrochloric acid. The acetyl content is calculated using the formula

$$\% \text{CH}_3\text{CO} = \frac{(\text{Cc. of NaOH taken} \times N - \text{cc. HCl used} \times N) \times 0.043}{\text{Weight of sample}} \times 100$$

The results obtained in the first series are given in Table I and graphically in Fig. 1.

TABLE I
EXPERIMENTAL RESULTS

| Time of hydrolysis, hours | Acetyl content | | |
|---------------------------|---------------------------------------|--------------------------------------|------------------------|
| | 17 Grams of NaNO ₃ present | 20 Grams of KNO ₃ present | Check, no salt present |
| 0 | 44.7-44.7 | 44.7-44.7 | 44.7-44.7 |
| 16 | 44.2-44.0 | 44.1-43.8 | 42.7-42.9 |
| 20 | 44.3-44.4 | 44.5-44.1 | 42.3-42.3 |
| 24 | 44.1-43.5 | 44.0-43.5 | 41.2-41.0 |
| 40 | 43.5-43.5 | 39.4-39.6 | 40.2-39.6 |
| 42 | 44.3-43.7 | 43.7-43.4 | 39.7-39.3 |

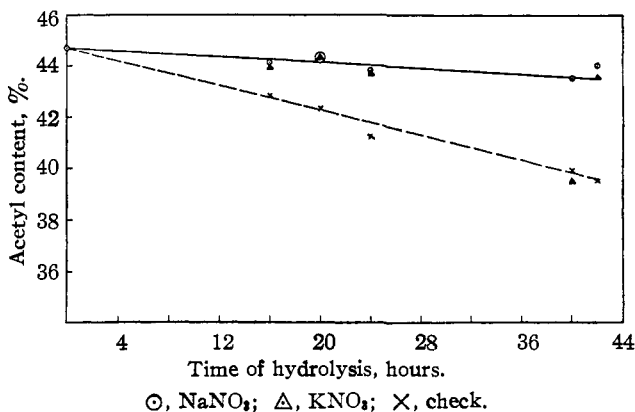


Fig. 1.

The sample from the hydrolysis in the presence of potassium nitrate after forty hours appears to have met with an accident during analysis.

A second series of experiments was carried out using solutions of the same composition as employed in the first group of experiments, but adding 10 g. of sodium nitrate to one of three samples, maintaining two as controls. This was done to confirm the results previously obtained. The hydrolysis procedure and method of determination of acetyl content were the same as those previously described. The results are given in Table II and graphically in Fig. 2.

TABLE II
EXPERIMENTAL RESULTS

| Time of hydrolysis, hours | Acetyl content | | |
|---------------------------|---------------------------------------|--------------------------|---------------------------|
| | 10 Grams of NaNO ₃ present | Check I, no salt present | Check II, no salt present |
| 0 | 44.2-43.9 | 44.2-43.9 | 44.2-43.9 |
| 16.5 | 44.1-44.2 | 41.4-41.3 | 41.7-41.7 |
| 18 | 43.4-43.6 | 41.0-41.3 | 41.1-41.2 |
| 21 | 43.1-43.3 | 41.0-40.9 | 40.6-40.8 |
| 24 | 43.4-43.0 | 40.6-40.2 | 40.5-40.4 |
| 40 | 42.8-43.1 | 38.6-38.7 | 39.6-39.6 |
| 43 | 43.1-42.8 | 38.6-38.7 | 39.0-39.2 |

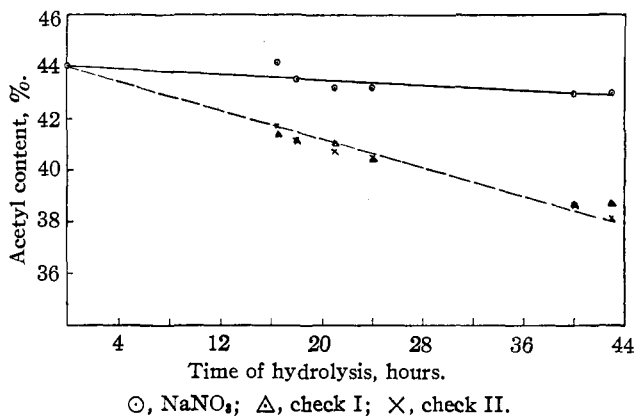


Fig. 2.

Since Hawkins found that the alkali sulfates exerted an effect on the saponification of ethyl acetate of approximate numerical equality but opposite in sign from that of the nitrates, it appeared of interest to ascertain the results of sodium and potassium sulfates in place of the corresponding nitrates in the hydrolysis of cellulose acetate.

The procedures employed were the same as those previously described. The amounts of sodium and potassium sulfates added were approximately molecular equivalents of the corresponding nitrates used in the first series of experiments, that is, 15 g. of potassium sulfate and 14 g. of sodium sulfate, both being in the anhydrous form.

The results of the third series of experiments are given in Table III and graphically in Fig. 3.

In the fourth series of experiments, the run was made using sodium chloride for comparison with the results obtained using sodium nitrate and sodium sulfate. Two experiments were made to determine whether the addition of the neutral salts after partial hydrolysis would exhibit the same effect as when added at the start of the reaction.

Five portions of cellulose triacetate solution were taken; to one was

TABLE III
 EXPERIMENTAL RESULTS

| Time of hydrolysis, hours | Acetyl content | | Check, no salt present |
|---------------------------|--|---|------------------------|
| | 14 Grams of Na_2SO_4 present | 15 Grams of K_2SO_4 present | |
| 0 | (43.5) | (43.5) | (43.5) |
| 16 | 42.6-42.7 | 43.2-43.1 | 41.6-41.7 |
| 18 | 43.1-43.2 | 43.3-42.9 | 41.6-41.2 |
| 20 | 42.9-43.2 | 42.6-42.8 | 41.0-40.9 |
| 22 | 43.0-42.5 | 42.9-43.2 | 40.2-40.9 |
| 24 | 43.4-42.8 | 42.8-43.6 | 40.4-40.2 |
| 40 | 42.7-42.5 | 42.5-42.6 | 39.2-39.2 |

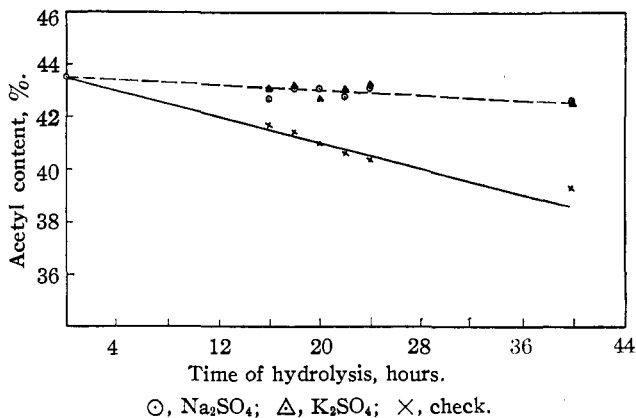


Fig. 3.

added 10 g. of sodium nitrate and to the second 7 g. of sodium chloride, an approximately molecular equivalent of the sodium nitrate. The remaining three portions were hydrolyzed without the addition of salts. All five samples were maintained at $53 \pm 1^\circ$. After forty-two hours' hydrolysis, two of the samples to which no salt had been added were removed from the air-bath for sufficient time to permit the addition of 10 g. of sodium nitrate to one and 7 g. of sodium chloride to the other, each of the salts being dis-

 TABLE IV
 EXPERIMENTAL RESULTS

| Time of hydrolysis, hours | Acetyl Content | | | | |
|---------------------------|-------------------------------------|----------------------------------|------------------------|--------------------------|--------------------------|
| | 10 Grams of NaNO_3 present | 7 Grams of NaCl present | Check, no salt present | No salt present at start | No salt present at start |
| 0 | 43.3 | 43.3 | 43.3 | 43.3 | 43.3 |
| 24 | 42.4-42.7 | 42.1-42.6 | 41.6-41.2 | 41.2-41.2 | 41.1-40.8 |
| 42 | 43.2-42.9 | 40.9-41.0 | 40.4-40.2 | 40.0-40.4 | 40.5-40.7 |
| 66 | 42.1-42.2 | 39.1-39.5 | 38.6-38.9 | 39.6-39.5 | 37.9-37.9 |
| 74 | 42.2-42.3 | 37.5-37.9 | 36.9-37.0 | 38.9-38.7 | 37.6-37.8 |
| 90 | 41.2-41.5 | 37.2-36.9 | 35.7-35.8 | 39.2-39.5 | 37.4-37.7 |

solved in 50 cc. of glacial acetic acid before addition. This required from three to five minutes, after which they were replaced in the air-bath at 53°.

The procedure from this point was as previously described. The results are given in Table IV and graphically in Fig. 4 for the experiments in which

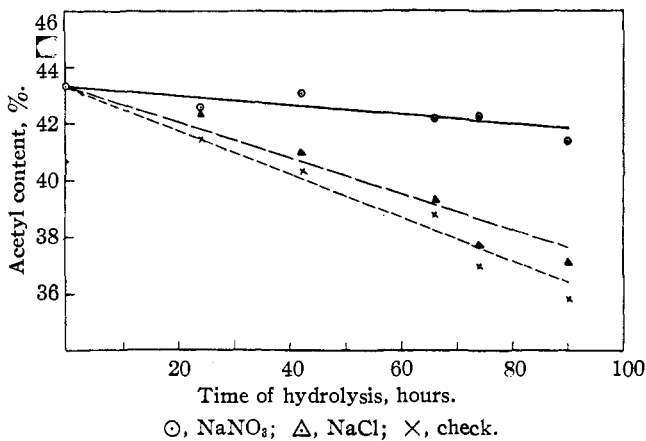


Fig. 4.

the salts were added at the start of the hydrolysis, and in Fig. 5 where the salts were added after partial saponification.

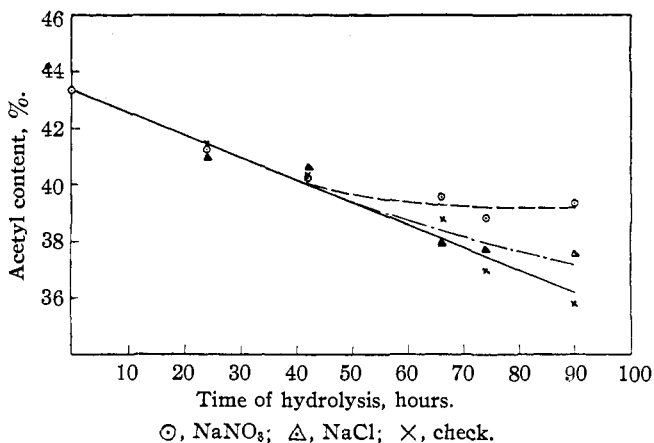


Fig. 5.

Discussion

From an examination of the data there appear several points of interest to be considered. It is seen that in all cases the presence of the neutral salts of the alkali metals tried, resulted in a retardation of the rate of saponification. The factors influencing this saponification in colloidal

solution and in media in which activity coefficients do not appear to have been accurately determined, make this reaction too complex and the data too meager to permit of calculation of the reaction constants. It is thought, however, that the qualitative results of this problem are of sufficient interest to warrant brief discussion.

From the first series of experiments (Table I, Fig. 1) in which sodium nitrate and potassium nitrate were present at the beginning of the saponification in approximately molecular equivalents, it appears that the retarding effect is not influenced by the difference in atomic weight between sodium and potassium, but that the controlling influence is dependent upon the presence of the nitrate radical. When sodium or potassium nitrate is used, the decrease in acetyl content in forty-two hours is approximately 1%, whereas the saponification in the absence of salt had resulted in a reduction of the acetyl content of 5%. This corresponds to the removal of 2.2% of the available acetyl in the case of saponification in the presence of sodium and potassium nitrate and 11.2% in the absence of neutral salts. The data given in Table II and Fig. 2 confirm the results of the first group of experiments as regards the effect of sodium nitrate and indicate the degree of reproducibility of such saponification.

When sodium and potassium sulfates were employed in approximately molecular equivalents of the corresponding nitrates, retardation was again observed (Table III, Fig. 3). In this case the neutral salts permitted saponification of but 2.3% of the available acetyl as compared to 9.9% for the control. It therefore appears that the effect of the sulfate radical is approximately equal to that of the nitrates previously mentioned. The effect noted in these experiments is different from that observed by Hawkins in the saponification of ethyl acetate in which it was found that the sulfates and nitrates had opposite effects upon the saponification rate.

In the fourth series of experiments (Table IV, Fig. 4) a comparison of the first two experiments, in which sodium nitrate and sodium chloride were used, indicates that during forty-two hours of saponification the effect of the former is almost double that of the latter, the percentage of available acetyl removed in the case of sodium nitrate being 2.7% and for sodium chloride 5.3%. During the same period the control decreased 7.0%. All of the hydrolyses to which no salts were added during the first forty-two hours show the same acetyl content, within experimental error, being 40.3, 40.2 and 40.6%. A comparison of the results when sodium nitrate and sodium chloride were added after forty-two hours of saponification shows the following at the end of forty-eight hours' subsequent hydrolysis. The experiment in which sodium nitrate was used showed a decrease of 2.5% of the remaining available acetyl content, the sodium chloride experiment 7.4%, while the control to which no salt had been added decreased 8.7%. The curves indicate that the effect of the addition

of neutral salts after saponification has proceeded for some time is not instantaneous.

In general, it is noted that the effect of the presence of neutral salts of the alkali metals in a reaction involving the saponification of cellulose acetate in colloidal dispersion in acetic acid, is opposite to that recorded by investigators of similar reactions involving crystalloids.

The subject matter of this paper is covered by a pending patent application of Eastman Kodak Company and the publication of this paper is not to be taken in any way as suggesting or permitting the commercial use of this development.

Summary

The effect of the presence of the nitrates, sulfates and chlorides of sodium and potassium on the rate of saponification of cellulose acetate dispersed in acetic acid has been studied.

It has been found that all of these salts appear to exert a retarding influence on the reaction rate. A greater effect was observed when nitrates and sulfates were used than when chloride was employed.

Addition of neutral salts after the reaction had proceeded for forty-two hours showed an effect similar to that noted when they were present at the beginning of the saponification.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

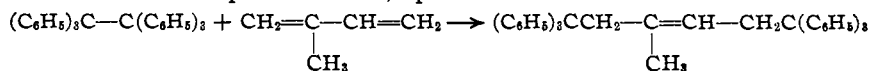
THE ADDITION OF FREE RADICALS TO UNSATURATED COMPOUNDS (PRELIMINARY PAPER)

By J. B. CONANT AND H. W. SCHERP

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Free radicals containing trivalent carbon such as triphenylmethyl are known to combine with quinones (forming a di-ether) and with free radicals containing divalent nitrogen. Aside from these reactions there seems to be no published account of the addition of a free radical to an unsaturated organic compound. We have now found that triphenylmethyl (hexaphenylethane) combines with isoprene and dimethylbutadiene; the addition takes place in the 1,4 position.



The structure of the product obtained from isoprene was established by ozonization. Triphenylpropionic acid and 1,1,1-triphenylbutanone-3 were obtained from the ozonide by decomposition and oxidation with silver oxide. The identity of these compounds was proved by mixed melting