The Chlorinium Ion as an Intermediate in Chlorination of Aromatic Compounds by Hypochlorous Acid

By C. Gardner Swain and Arthur D. Ketley

Chlorinations of phenol, anisole, methyl p- or m-tolyl ether or mesitylene by hypochlorous acid in aqueous or aqueous dioxane solution containing excess silver perchlorate at 25° have the kinetic form

$$- \frac{d[HOCl]}{dt} = k[HOCl] + k'[H^+][HOCl] + k''[H^+][HOCl][ArH]$$ [1]

The first two terms might represent slow steps forming H_2OCl^+ (from H_2O and $HOCl$ or H_3O^+ and $HOCl$)[2] and the third term, which is relatively more important with the most reactive aromatic compounds, might represent a termolecular reaction. Alternatively it has been suggested[1] that the first two terms represent slow steps forming Cl^+ (from $HOCl$ or H_2OCl^+) and that the third term represents direct chlorination by H_2OCl^+. There has been no experimental evidence to discriminate between these two alternative interpretations but the second interpretation requires a concentration of Cl^+ intermediate much too high to be consistent with the equilibrium constant $[Cl^-][Cl^+]/[Cl_2] = 10^{-60}$ calculated by Bell and Gelles.[3]

To decide experimentally between these two interpretations we compared rates in light and heavy water (protium and deuterium oxides). Methyl p-tolyl ether was used because the third term is negligibly small for this compound. The second term was made to predominate strongly over the first by using a high concentration (0.5 M) of perchloric acid. If the second term represents a rate-determining proton transfer to form H_2OCl^+ as an intermediate, the rate should be faster in light than in heavy water, because of the difference in zero-point energies of H_3O^+ and D_3O^+.[4] If it represents a rate-determining fission of H_2OCl^+ to form Cl^+ as an intermediate, the rate should be slower in light than in heavy water, because the acid dissociation constants of protium-protonated substrates (such as H_2OCl^+) are generally higher than those of deuterium-protonated substrates (such as D_2OCl^+), hence the hypochlorous acidium ion would be in lower concentration in the light solvent.[5]

We found that the rate in light water was only 52% of that in heavy water. Using 0.044 M methyl p-tolyl ether, 0.0008 M hypochlorous acid, 0.052 M silver perchlorate and 0.50 M perchloric acid in a solvent of 37.5% light or heavy water–62.5% dioxane at 25°, the rate constant was 4.9 $\times$

10^{-2} min.$^{-1}$ with light water and 9.46×10^{-2} min.$^{-1}$ with heavy water.

This experimental result requires the interpretation[1] involving chlorinium ion, Cl^+, as an intermediate.

Experimental

Procedures were those previously described[1] except as noted below. All standard solutions were prepared with either light or heavy water. Methyl p-tolyl ether (Eastman Kodak) was purified by fractional distillation, b.p. 174–175° at 762 mm. Total volume of reacting solutions was 100-ml. and 10-ml. portions were removed for titration.

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(1) P. B. D. de la Mare, C. A. Vernon and E. D. Hughes, *Research*, 3, 192 (1950); P. B. D. de la Mare, A. D. Ketley and C. A. Vernon, *J. Chem. Soc.*, 1290 (1954).

(2) D. H. Derbyshire and W. A. Waters, *ibid.*, 73 (1951).

(3) R. P. Bell and E. Gelles, *ibid.*, 2734 (1951).

(4) F. H. Westheimer and N. Nicolaides, This Journal, 71, 25 (1949); M. Cohen and F. H. Westheimer, *ibid.*, 74, 4387 (1952); J. D. Roberts, C. M. Regan and I. Allen, *ibid.*, 74, 3679 (1952); O. Reitz, *Z. physik. Chem.*, 183A, 371 (1939); O. Reitz, *Z. Elektrochem.*, 44, 693 (1938); C. G. Swain, R. Cardinaud and A. D. Ketley, This Journal, 77, 934 (1955).

(5) J. C. Hornel and J. A. V. Butler, *J. Chem. Soc.*, 1361 (1936); P. Gross, H. Steiner and F. Krauss, *Trans. Faraday Soc.*, 37, 877, 883 (1936); W. H. Hamill and V. R. La Mer, *J. Chem. Phys.*, 4, 294 (1936); F. R. Duke and R. C. Pinkerton, This Journal, 73, 2361 (1951).

Friedel–Crafts Condensations of Benzenesulfonyl Chloride with Thiophenes

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Although the Friedel–Crafts process represents one of the general methods for preparing aryl sulfones,[1] it has not been applied successfully to the condensation of sulfonyl chlorides with simple heterocyclic compounds. Accordingly, it seemed of interest to study such applications, particularly with thiophene and its derivatives, in view of the greater stability toward acids of the thiophene nucleus over furan and pyrrole nuclei.

It has been reported that tars only are obtained on treating thiophene with benzenesulfonyl chloride in the presence of aluminum chloride.[2] Therefore, the more favorably disposed compound,[3] 2,5-dichlorothiophene, was considered first. Benzenesulfonyl chloride reacts with this substituted thiophene in the presence of aluminum chloride to give phenyl 2,5-dichloro-3-thienyl sulfone as determined by comparison with an authentic sample. Attempts to extend this reaction to thiophene, 2,5-dimethylthiophene, 2,5-diiodothiophene and 2-chloro-5-iodothiophene resulted in the formation of intractable tars, even when ferric chloride, stannic chloride or iodine were substituted for aluminum chloride. Furthermore, benzenesulfonic anhydride, which is superior to benzenesulfonyl chloride in the Friedel–Crafts synthesis,[4] also gave intractable tars with thiophene in the presence of aluminum chloride or phosphoric acid.

The greater difficulty of effecting sulfonylation in contrast to acylation is presumably related to the well-known greater tendency of the acyl chloride group to undergo nucleophilic displacement[5] as compared with the sulfonyl chloride group. Furthermore, it appears that electronegative substituents (chlorine) may sufficiently deactivate the thiophene nucleus toward polymerization to permit some sulfonylation.

Experimental

To a mixture of 17.6 g. (0.10 mole) of benzenesulfonyl chloride, 13.4 g. (0.10 mole) of aluminum chloride and 50

(1) C. M. Suter, "Organic Chemistry of Sulfur," John Wiley & Sons, Inc., New York, N. Y., 1944, p. 673.

(2) H. Burton and W. A. Davy, *J. Chem. Soc.*, 525 (1948).

(3) H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, p. 322.

(4) L. Field, This Journal, 74, 394 (1952).

(5) J. M. Tedder, *Chem. and Ind.*, 630 (1954).