

16. *An Acid-catalysed Chlorination by means of Hypochlorous Acid.*

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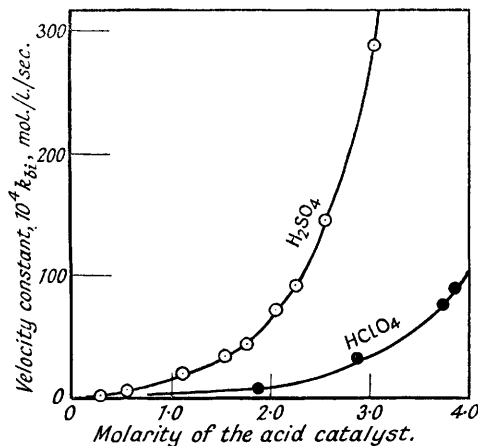
The chlorination of sodium toluene- ω -sulphonate by hypochlorous acid has been studied, both sulphuric and perchloric acids being used as catalysts. It is a second-order reaction involving chlorine cations, Cl^+ or $(\text{H}_2\text{OCl})^+$. The formation of these active cations from hypochlorous acid becomes significant only at much higher acidities than those needed for the production of the corresponding cations from hypobromous acid (*J.*, 1950, 564). Sulphuric acid proves to be a much more effective catalyst than perchloric acid in the concentration range 0.3—4 molar.

WE have now extended our kinetic study of the acid catalysis of the bromination of sodium toluene- ω -sulphonate by means of hypobromous acid (*J.*, 1950, 564) to the analogous case of its chlorination by means of hypochlorous acid. The two substitution processes are similar in that (a) they are both bimolecular and (b) they do not proceed in the absence of a mineral acid catalyst. However, whilst the production of a bromine cation $[\text{H}^+ + \text{HOBr} \rightleftharpoons (\text{H}_2\text{OBr})^+]$ occurs so easily that a second-order velocity constant of 10^{-2} mole/l./sec. can be attained by the use of perchloric acid of only 6.3×10^{-4} molar concentration, a similar chlorination velocity requires the presence of 3.9M-perchloric acid, or 2.3M-sulphuric acid at the same temperature (21.5°). Consequently our measurement of an aromatic-substitution reaction involving chlorine cations has needed acid catalysts which are so concentrated that the activities of the reacting entities do not correspond closely to their molar concentrations.

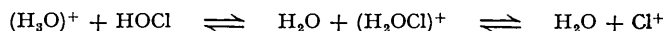
The figure, which illustrates our results, shows that the chlorination of sodium toluene- ω -

sulphonate is inappreciable at hydrogen-ion concentrations of less than 0.1 mol./l. and that, as would be expected, it rises sharply in the acid-concentration range 0.5—4 molar. Consequently, either the chlorine cations involved, Cl^+ or $(\text{H}_2\text{OCl})^+$, are much less active substituting agents than are the corresponding bromine cations, Br^+ or $(\text{H}_2\text{OBr})^+$, or, more probably, the basic dissociation constant of hypochlorous acid, $K_b = [\text{H}_2\text{OCl}^+]/[\text{H}^+][\text{HOCl}]$, is of the order of 10^{-4} or less than that of hypobromous acid (cf. Gonda-Hunwald, Gráf, and Körösy, *Nature*, 1950, 166, 68; *Magyar Kémiai Folyóirat*, 1950, 56, 204).

Acid catalysis of the chlorination of sodium toluene- ω -sulphonate by hypochlorous acid.



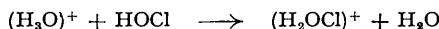
Whilst our observations with hypobromous acid showed that, in the concentration range of 0.1—1 molar, perchloric acid was, mole for mole, a slightly more effective catalyst than sulphuric acid, our present results show that, with respect to hypochlorous acid, sulphuric acid is the much more effective catalyst. This five- to ten-fold difference in the catalytic powers of sulphuric and perchloric acids indicates that the production of an active chlorinating agent from hypochlorous acid cannot simply be related to the molar concentrations of the ions and molecules involved in the equilibria:



over the concentration range which we have found it necessary to choose.

De La Mare, Hughes, and Vernon (*Research*, 1950, 3, 192, 242) have stated that with very reactive organic substrates, such as anisole or phenol, the rate of this acid-catalysed chlorination becomes of first order with respect to the hypochlorous acid, and of zeroth order with respect to the aromatic substrate. Consequently in their experiments the speed of formation of the cationic chlorinating agent, which they take to be the free ion Cl^+ , is rate-determining. With sodium toluene- ω -sulphonate as the substrate the velocity of chlorination is unmeasurably slow in the catalyst concentrations that De La Mare, Hughes, and Vernon have used; it attains a comparable speed only in mineral acid of about twenty times those concentrations. Since this slower chlorination of sodium toluene- ω -sulphonate by hypochlorous acid is a reaction of first order with respect to the aromatic compound, our results are self-consistent with those for its catalysed bromination by hypobromous acid, and indicate that the active cationic halogenating agent has attained its equilibrium concentration with respect to the acid catalyst by way of reversible reactions which are decidedly more rapid than the aromatic substitution process. Consequently our work, by itself, does not indicate whether the active product formed from hypochlorous acid is the free, physically solvated chlorine cation, Cl^+ , or the conjugate acid $(\text{H}_2\text{OCl})^+$, or even an acyl hypochlorite, *e.g.* $\text{Cl}\cdot\text{SO}_4\text{H}$, but since we have worked at much higher acidities than have De La Mare, Hughes, and Vernon it is inconceivable that our reactant can have been less active than theirs.

Thermodynamic calculations (R. P. Bell and E. Gelles, forthcoming publication) show that the process



must be markedly endothermic, and so we hesitate, as yet, to believe that this proton transfer cannot, in some circumstances, be sufficiently slow to become rate-determining.

EXPERIMENTAL.

Hypochlorous Acid.—Aqueous solutions of hypochlorous acid were prepared by shaking *ca.* 0.04M-chlorine water with freshly prepared silver phosphate until the odour of free chlorine had disappeared (Shilov and Kaniaev, *J. Phys. Chem. U.S.S.R.*, 1934, 5, 655), and then distilling the product under reduced pressure from a water-bath at 40–50°, a blackened all-glass apparatus being used (compare *J.*, 1950, 571). The hypochlorous acid solutions thus obtained were about 0.02–0.03M. and had a faintly acid reaction (pH *ca.* 4.6; glass electrode). With this method of preparation the only likely impurity is that arising from the volatilization of free chlorine. Since the hydrolysis constant of chlorine at 25° is 4.48×10^{-4} (Jakowkin, *Z. phys. Chem.*, 1899, 29, 655) any trace of chlorine will be completely hydrolysed to give equivalent amounts of hydrogen and chloride ions. Consequently, since hypochlorous acid itself is an extremely weak acid, the chloride contents of our preparations could be estimated from their pHs. A typical sample gave on analysis: HOCl, 3.15×10^{-2} M.; H⁺, 2.6×10^{-3} M.; hence $[Cl^-]/[HOCl] = 0.07\%$. As shown below this trace of chloride would have a negligible effect upon the reaction velocity. Nevertheless the solutions of hypochlorous acid were further purified before use by shaking them with yellow mercuric oxide and then centrifuging them (compare Pryde and Soper, *J.*, 1931, 1513). As in our previous work (*loc. cit.*) the reactions were carried out with 50-ml. batches of mixtures contained in blackened glass-stoppered flasks immersed in a thermostat at $21.5^\circ \pm 0.05^\circ$. 5-Ml. samples were withdrawn at intervals for semi-microtitration, 0.01N-sodium thiosulphate being used. The comparative results of Table I show that the reaction is kinetically of second order, *i.e.*

$$d[HOCl]/dt = k_{bi}[HOCl][PhCH_2SO_3Na]$$

TABLE I.

Test of second-order reaction, sulphuric acid being used as catalyst.

PhCH ₂ SO ₃ Na = 3.342×10^{-2} M.			PhCH ₂ SO ₃ Na = 6.684×10^{-2} M.						
HOCl = 3.819×10^{-3} M.			HOCl = 3.716×10^{-3} M.						
H ₂ SO ₄ = 1.185M.			H ₂ SO ₄ = 1.185M.						
Time,		Titre, ml.	HOCl remaining, %.	10 ³ k _{bi} (obs.) (mol./l./sec.).	Time,		Titre, ml.	HOCl remaining, %.	10 ³ k _{bi} (obs.) (mol./l./sec.).
min.	sec.				min.	sec.			
0	0	3.74	100	—	0	0	3.64	100	—
29	58	3.35	89.6	1.85	15	4	3.25	89.6	1.88
60	0	3.00	80.2	1.86	30	2	2.90	79.9	1.89
94	54	2.68	71.7	1.78	59	57	2.34	64.5	1.92
150	0	2.21	59.1	1.80	90	0	1.88	48.5	1.89
210	0	1.79	52.1	1.81	120	0	1.50	41.4	1.83
270	0	1.45	38.8	1.83	155	0	1.15	31.7	1.89
330	0	1.17	31.3	1.84	224	0	0.67	18.5	1.94

Mean k_{bi} = $(1.82 \pm 0.04) \times 10^{-3}$ mole/l./sec. Mean k_{bi} = $(1.89 \pm 0.05) \times 10^{-3}$ mole/l./sec.

TABLE II.

Chlorination of sodium toluene- ω -sulphonate with hypochlorous acid in 2.254M-sulphuric acid: the effect of the addition of chloride.

PhCH ₂ SO ₃ Na, m. $\times 10^{-2}$.	HOCl, m. $\times 10^{-3}$.	KCl, m. $\times 10^{-4}$.	10 ³ k _{bi} (obs.) (mol./l./sec.).
3.342	3.806	nil	9.14 ± 0.34
1.114	4.016	nil	9.18 ± 0.27
3.342	4.132	0.96	12.1 ± 1.7
3.342	4.248	3.86	20.1 ± 2.8
1.114	4.196	5.78	26.1 ± 4.2
3.342	4.280	5.78	25.9 ± 4.8

Table I indicates that the reaction rate increases very slightly when most of the hypochlorous acid has been consumed, and this trend was noticed generally. It is possibly due to the presence of a trace of chloride ions in the initial reaction mixture. Table II shows the magnitude of the reaction-velocity changes which can be brought about by adding appreciable quantities of chloride anions, so as to replace some of the hypochlorous acid by free chlorine. Though this addition does lead to an increase in the reaction velocity, and to a more noticeable divergence with reaction time from a strictly second-order course, it will be seen that as much as 8 per cent. of chloride ions has to be added to hypochlorous acid in 2.254M-sulphuric acid in order to double the velocity of chlorination of the aromatic substrate.

The data of Table I are typical of the collected results shown graphically on the figure.

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