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Abstract

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ON THE CHLORO-CATION AS A CHLORINATING AGENT IN AQUEOUS SOLUTION

To date there is no consensus on the question of the significance of the chloro-cation in the mechanism of chlorination in aqueous solutions. We have previously considered this problem (^{1,2}) and found that the chloro-cation, unlike the bromo- and iodo-cations, does not play a noticeable role in aqueous halogenation. This conclusion was suggested by the observation that additions of strong acids (with the exception of hydrochloric acid) only slightly accelerate the reactions of hypochlorous acid with organic compounds (^{3}), although the concentration of the chloro-cation should increase in proportion to the concentration of the hydrogen ion in accordance with the equation

$$\mathrm{HOCl} + (\mathrm{H_3O})^+ \rightleftharpoons (\mathrm{ClOH_2})^+ + \mathrm{H_2O}. \tag{1}$$

The work of Soper and his coworkers (^{4}) also gave no indication of the participation of the chloro-cation in the reactions of hypochlorous acid, although these authors admitted such an idea.*

However, several years ago Delamare, Hughes, Vernon, and Ketley (^{6,7}) proposed a theory according to which the chloro-cation is the principal active agent in the chlorination of organic compounds by dilute hypochlorous acid. The basis for such an assertion was the observation that the rate of chlorination of anisole, phenol, mesitylene, and methyl meta- and methyl para-tolyl ethers is almost independent of the concentration of the organic compound and can be expressed by the equation

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

From this arose an analogy with the nitration reaction, the rate of which under known conditions is limited by the stage of formation of the nitronium cation from nitric acid (^{8,9}). The English authors propose an analogous dissociation of HOCl as the rate-limiting stage of the chlorination reaction:

$$\mathrm{ClOH} \rightleftharpoons \mathrm{Cl^+} + \mathrm{OH^-} \quad \text{and} \quad \mathrm{ClOH} + \mathrm{H^+} \rightleftharpoons (\mathrm{ClOH_2})^+ \rightleftharpoons \mathrm{Cl^+} + \mathrm{H_2O}.$$

At the same time it was assumed that the possibility of formation of molecular chlorine was excluded by additions of silver salts.

In 1952 (^{10}) we noted that the decomposition of HOCl with formation of the chloro-cation is improbable and that the rate of the reactions investigated by the English authors is limited, apparently, not by the rate of formation of the chloro-cation, but by the rate of rehydrolysis of chlorine from HOCl at the expense of the traces of chloride ion present in the solution. Delamare and his coworkers did not agree with our arguments (^{7}), referring to the fact that our experiments concerned solutions of HOCl that were more concentrated and less acidic than theirs. In the present paper we present new evidence in favor of the fact that the chloro-cation is of no significance in the reactions of HOCl and that the kinetic relationships, established in the work of Delamar and his co-workers (^{6,7}), are associated with the formation of molecular chlorine.

Anisole was chosen as the chlorination substrate, since it is readily chlorinated in aqueous solution by chlorine, whereas HOCl acts on it much more weakly. We measured the rate of disappearance of active chlorine in mixtures containing, in addition to anisole, HOCl and nitric acid, also small amounts of chloride ion (in the form of KCl).

If it is assumed that the rate of chlorination of anisole v is determined by the rate of chlorine rehydrolysis, then

$$v = k[\mathrm{HOCl}] = k_R[\mathrm{H}^+][\mathrm{HOCl}][\mathrm{Cl}^-]$$

and, consequently,

$$k = k_R[\mathrm{H}^+][\mathrm{Cl}^-]. \tag{2}$$

The values of the rate constant of chlorine rehydrolysis, k_R, have been determined by various methods (^{11}). As a probable mean value we take

$$k_R = 6.5 \cdot 10^5\ \mathrm{l}^2 \cdot \mathrm{mol}^{-2} \cdot \mathrm{min}^{-1}$$

(at 0°).

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* Derbyshire and Waters (^{5}) found a catalytic action of strong acids on the reaction of hypochlorous acid with toluene-ω-sulfonic acid at very high catalyst concentrations (1-4 M), sulfuric acid proving much more active than perchloric acid. It is possible that under these conditions not the chloro-cation but acyl hypochlorites are formed.

Fig. 1. 1 –line of the values of k, 2 –line $k_R[\mathrm{H}^+][\mathrm{Cl}^-]$

Figure 1: Fig. 1. 1 –line of the values of k, 2 –line $k_R[\mathrm{H}^+][\mathrm{Cl}^-]$

The experiments were carried out at 0° in darkened vessels. Hypochlorous acid was prepared by double distillation of a solution obtained from chlorine water and Ag_3PO_4. For the kinetic experiments, solutions with a specific electrical conductivity of $2 \cdot 10^{-6}$–$2.6 \cdot 10^{-6}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$ at 0° were used. Samples of about 5 ml were titrated with 0.01 N thiosulfate solution from a pneumatic microburette. The chlorination reaction is very sensitive to traces of hydrochloric acid; therefore the reproducibility of the experiments depends on the quality of the initial hypochlorous acid preparation. In each individual experiment the constants of the first-order equation with respect to active chlorine are generally constant, although in some cases, especially in experiments without addition of KCl, a tendency for them to increase during the course of the experiment is noticeable.

Fig. 1. 1 –line of the values of k, 2 –line $k_R[\mathrm{H}^+][\mathrm{Cl}^-]$

Table 1*

	1	2	3	4	5	6	7	8	9	10	11	12	13
$A \times 10^3$	2.5	5	10	2	10	2	10	10	10	10	2.5	10	10
$[\mathrm{HOCl}] \times 10^3$	1	1	1	1	1	1	1	1	1	1	1	1	1
$(\mathrm{HNO_3}) \times 10^3$	–	–	–	1	1	1	1	1	2	3			
$(\mathrm{NaOH}) \times 10^5$											2	2	30
$(\mathrm{KCl}) \times 10^5$	–	–	–	–	–	2	2	1	1	1	–	–	–
$k \times 10^2$	0.09	0.11	0.15	0.2	0.34	1.0	1.7	1.4	3.0	4.2	0.1	0.18	0.4

* A is the concentration of anisole; square brackets denote true concentrations, parentheses analytical concentrations of the reagents; temperature 0°.

From the data in Table 1 it may be established that the rate of chlorination depends somewhat on the concentration of anisole*, and, in the presence of chloride ion, is directly proportional to the concentration of hydrogen ion. In what follows we use the data of experiments in which the hydrogen-ion concentration is constant and the anisole concentration is as high as possible.

In Fig. 1 the experimental values of k are compared, for two experimental series at different chloride-ion concentrations, with the values

* According to Delamar (7), the concentration of anisole has almost no effect on the rate of its chlorination. It is possible that this discrepancy with our observations is explained by the fact that the English authors carried out their experiments at a different temperature (25°).

$k_R[H^+][Cl^-]$ at identical concentrations of the reactants. The initial concentrations in all experiments were: anisole 0.01 M, HNO_3 0.001 M, HOCl 0.001 M. The experiments of one series were carried out with one and the same HOCl solution over several hours of one day.

We see that the straight line for the dependence of the chlorination rate (1) on the chloride-ion concentration and the straight line (2) $k_R[H^+][Cl^-]$ pass very close to one another, differing by a small constant amount. It is further clear that even at very small chloride-ion concentrations (of the order of 10^{-5} M), chlorination of anisole proceeds mainly through molecular chlorine. Extrapolating the line for the chlorination rate to the zero value of KCl additions, we find on the ordinate axis the value k_0, equal to 0.003 min^{-1}. Approximately this number is also given by experiments carried out without KCl.

The value k_0 is made up of: (a) chlorination of anisole by hypochlorous acid without participation of the chloride ion and hydrogen ion, (b) chlorination by traces of chlorine contained in the original HOCl solution, (c) chlorination by the chloronium cation (insofar as it participates in the reaction).

We find the fraction of reaction (a) by measuring the rate of anisole chlorination with small additions of alkali, when the concentrations of chlorine and chloronium cation decrease to a negligible value. This method is complicated by the fact that the reaction rate upon addition of alkali does not decrease, but increases to a certain maximum located at 25-30% neutralization of HOCl.* Extrapolating the values of k to the zero value of alkali additions, we obtained k_a for reaction (a) equal to 0.0015 min^{-1}. The difference $(k_0 - k_a)$, equal to 0.0015 min^{-1}, pertains to the sum of the constants of reactions (b) and (c). If all 0.0015 min^{-1} is attributed to molecular chlorine, then with the aid of k_R one can calculate the chloride-ion content in our kinetic mixtures introduced with the initial hypochlorous acid. The value obtained is $2.2 \cdot 10^{-6}$ M. It is quite possible, and even probable, that such chloride-ion concentrations were present in our solutions. Delamar and his co-workers believed that they freed their solutions from the presence of chloride ion by additions of silver salts (6,7,12). Apparently, they did not take into account that very finely dispersed silver chloride can act as dissolved chloride.

To estimate the effect of the presence of very small concentrations of AgCl, we carried out the following experiments. By mixing equimolar solutions of $AgNO_3$ and KCl, a $4 \cdot 10^{-5}$ M solution of AgCl was prepared, and from it, by dilution—

Table 2

	Series I	Series I	Series I	Series I	Series II	Series II	Series II	Series II	Series II	Series II	Series II
$(\mathrm{AgCl})\times 10^5$	–	–	0.5	0.5	–	0.25	0.5	1	2	0.5	–
$(\mathrm{KCl})\times 10^5$	–	0.5	–	0.5	–	–	–	–	–	2	–
$k\times 10^2$	0.38	0.75	0.64	1.0	0.2	0.57	0.6	0.8	0.9	2.2	1.5
$(k-k_0)\times 10^2$	0	0.37	0.26	0.62	0	0.37	0.4	0.6	0.7	2.0	1.3
$k_R[\mathrm{H}^+][\mathrm{Cl}^-]\times 10^2$	0	0.32	0.32	0.65	0	0.16	0.32	0.65	1.3	1.6	1.3

solutions of AgCl from $2\cdot 10^{-5}$ to $0.5\cdot 10^{-5}$ M were obtained. Solutions with a concentration of $2\cdot 10^{-5}$ M were slightly turbid in a thick layer; the less concentrated ones were completely transparent. The AgCl solutions obtained were introduced into the usual mixtures of our kinetic experiments, sometimes with an addition of KCl. In control experiments without anisole, silver chloride does not cause any noticeable decomposition of hypochlorous acid.

* This phenomenon is explained by the fact that the active chlorinating agent in alkaline solutions is chlorine oxide. Its formation from HOCl, which is a slow stage of the reaction, is accelerated upon alkalinization, probably due to the reaction
$\mathrm{HOCl} + \mathrm{OCl}^- \rightleftharpoons \mathrm{HO}^- + \mathrm{Cl_2O}$ (3).

Table 2 gives the values of the constants k for experiments in the presence of AgCl, in comparison with the quantities $k_R[\mathrm{H}^+][\mathrm{Cl}^-]$. In all experiments the temperature was 0°; concentrations (mol/l): anisole 0.005, HOCl 0.001, $\mathrm{HNO_3}$ 0.001. In the course of the experiment the constants k show only a slight upward drift. The concentrations of Cl^- are given as the sum of the concentrations of AgCl and KCl.

The data of Table 2 show that AgCl has a considerable catalytic effect on the chlorination of anisole by hypochlorous acid, noticeable even upon addition of KCl up to $2\cdot 10^{-5}$ M. The close agreement of $(k-k_0)$ with the value $k_R[\mathrm{H}^+][\mathrm{Cl}^-]$ indicates that, at low chloride content, silver chloride gives approximately the same catalytic effect as soluble chlorides. Therefore additions of AgCl could not give the English authors the result on which they had counted.

In general, the data of our new study, together with earlier observations ([1,2]), demonstrate that the chloro-cation is not significant in the reactions of chlorination of organic compounds by hypochlorous acid in aqueous solutions, even in the absence of chloride ion. From the theoretical point of view, this conclusion is explained by the fact that the equilibrium in reaction (1) is extremely unfavorable for the formation of the chloro-cation, or, in other words, that the basic properties of HOCl are extremely weak (cf. [5]). Thermodynamic calculations of possible equilibria of the chloro-cation with hypochlorous acid ([13]) also agree with this conclusion.

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