Tetrahedron. Vol. 34, pp. 205 to 208. Pergamon Press 1978. Printed in Great Britain

THE HALOGENATING AGENT IN HYPOHALOUS ACID SOLUTIONS CONTAINING H^+_{aq}, IN AROMATIC SUBSTITUTIONS

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(Received in the UK 23 May 1977; Accepted for publication 2 August 1977)

Abstract—H_2OX^+ is one of the prominent but doubtful species suggested in recent years to explain the electrophilic substitution in halogenations of organic substrates. The present studies are aimed at revealing the role of this hypothetical species in such reactions on the basis of related kinetic and conductance data and also on the basis of equilibria affecting the formation of H_2OX^+ in aqueous solutions.

The nature of the halogenating agents in aromatic substitutions has been the subject of much interest over the past few decades.[1-3] In view of the generally accepted mechanism of these reactions[4,5] wherein the halogenating agent is positively charged, the electrophile has been variously described as the halonium cation (X^+), the solvated halonium cation (X^+_{aq}), etc. Although in course of time all these suggestions have been found to be unacceptable,[6-8] the protonated hypohalous acid, H_2OX^+, is still regarded by many, as such a species.[9,10] However, H_2OX^+ too has invoked criticism.

In the present study, the existence of H_2OX^+ has been investigated from three different angles.

(1) The kinetics of halogenation of an aromatic substrate has been carried out under such conditions that could favour the formation of H_2OX^+. For this purpose, *a typical halogenation*, viz the bromination of *o*-acetotoluidide (OAT) by hypobromous acid (HOBr) containing known proportions of hydrochloric/perchloric acid, is carried out in aqueous solution. It is already known that the bromination of aromatic substrates by HOBr is slow but becomes rapid on addition of H^+_{aq}. Recently,[11,12] Gilow and Ridd have carried out kinetic studies on the bromination of a range of aromatic compounds of varying reactivity by acidified aqueous solutions of hypobromous acid. From a stepwise comparison of the reactivities of these compounds at various acidities, they have shown that 2,6-dimethylpyridinium ion is less reactive than 2-(3,5 dimethylphenyl) ethyltrimethyl-ammonium ion by a factor of 5.6×10^{11} at the same acidity. From these results, they have estimated the maximum limit for the equilibrium constant for the formation of the "positive brominating species" and also the specific reactions rates for the bromination by this species. These specific rates are impracticably high, thereby casting serious doubt on the prior formation of the "positive bromine" in such systems.

In contrast to the above studies, we have carried out kinetic investigations on a single, typical aromatic substrate (OAT) in such a way as to elucidate quantitatively, the specific rate dependence on the $[H^+_{aq}]$ and these studies have enabled us to comment about the existence of the positive species.

Since the reaction with HOBr alone is very slow, its kinetics can be studied by a conventional method. But this cannot be adopted when H^+_{aq} is added to HOBr because the reaction becomes too rapid. Hence the rapid kinetics has been studied by employing the rotating platinum electrode (RPE) technique.[13] This is possible because only HOBr is electroreducible at the RPE among the reactants and products and diffusion currents linearly proportional to HOBr concentrations can be obtained.

(2) Since the contemplated H_2OBr^+ species is expected to have a distinctly different conductance from that of either HOBr or H^+_{aq}, conductance studies of HOBr solutions containing different H^+_{aq} concentrations are likely to reveal the existence of H_2OBr^+. Hence, equivalent conductance measurements of HOBr and HCl mixtures, in various proportions, have been carried out and compared with those of pure HCl solutions of the same concentrations as in the mixtures.

(3) Besides the above studies, the various equilibria existing in these aqueous solutions have been examined in the light of the Lowry–Bronsted theory of acids and bases. These equilibria are likely to affect vitally the formation of H_2OBr^+.

The bromination of OAT by HOBr is slow, the specific rate being 2.36×10^{-2} M^{-1} s^{-1} at 25.0°. On addition of H^+_{aq} the specific rate increases monotonously with $[H^+_{aq}]$† *and even at a hundred fold relative* $[H^+_{aq}]$, *the specific rate does not tend to level off to a limiting value* (Ref. Fig. 1).

This effect of H^+_{aq} is confirmed by observing almost identical results when HOBr is mixed with perchloric acid instead of hydrochloric acid.

If H_2OBr^+ is indeed the species responsible for the faster bromination, it would be formed according to the equation

$$HOBr + H^+_{aq} \rightleftharpoons H_2OBr^+. \quad (1)$$

The expression for the equilibrium constant K for (1) is

$$K = \frac{[H_2OBr^+]}{[HOBr][H^+]}.$$

Hence for a given initial concentration of HOBr, the $[H_2OBr^+]$ would be proportional to $(K^{-1}[H^+_{aq}]^{-1} + 1)^{-1}$. Obviously, the $[H_2OBr^+]$ tends to a limiting value at higher relative concentrations of H^+_{aq}. Higher the K, lower is the $[H^+_{aq}]$ at which the limiting concentration of H_2OBr^+ is approached. Conversely, lower the K, higher would be the relative $[H^+_{aq}]$ at which the $[H_2OBr^+]$ would reach a limiting value. In the extreme case of a very low

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†The square brackets denote concentration.

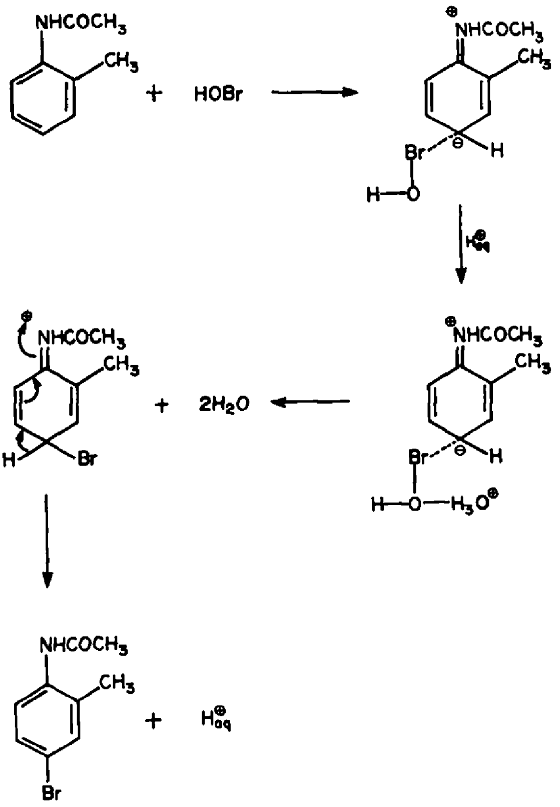
K, (or virtually no equilibrium) the relative $[H^+_{aq}]$ would have to be very high for the limiting $[H_2OBr^+]$ to be reached. If the increase in the specific reaction rate is attributed to H_2OBr^+, the variation of the specific rate with the relative $[H^+_{aq}]$ should, in turn, reflect the variation of the $[H_2OBr^+]$. Since the specific rate does not level off to a limiting value, the $[H_2OBr^+]$ too does not reach a limiting value even at high relative $[H^+_{aq}]$. This clearly indicates that equilibrium (1) does not exist *or if it does, the K is too small to account for a significant* $[H_2OBr^+]$ required to explain the rapid bromination.

The conductance measurements show that the equivalent conductance of HCl_{aq} vs concentration curve is a straight line, as expected. A similar plot in the case of mixtures of HCl_{aq} and HOBr is a curve identical to the previous one. If H_2OBr^+ were to form, the second curve ought to have shown a distinct break at $c = 3.0 \times 10^{-3}$ M, i.e. $\sqrt{(c)} = 5.45 \times 10^{-2}\ M^{0.5}$. These results indicate that H_2OBr^+ is virtually not formed in the solution as a distinct species.

HOBr in aqueous solution is known to be a weak acid[14] whose dissociation constant is 2×10^{-9} at 25°. Comparatively, water is a much weaker acid[15] (and consequently a much stronger base) than HOBr since the self-ionization constant of water† is 1.8×10^{-16}. Further, the concentration of water is about a million times that of HOBr in these kinetic studies. On these two accounts, protonation in such a solution would so overwhelmingly be of water than of HOBr that the $[H_2OBr^+]$ would be inconceivably small.

Considering that very dilute, colourless aqueous solutions of HOBr containing H^+_{aq} are used in these studies and also that H_2OBr^+, if at all existed, would be present in an extremely low concentration, the use of spectroscopy to study the existence of H_2OBr is not feasible.

Thus, the existence of H_2OBr^+ as a distinct species in aqueous solution is highly doubtful. If existed, the H_2OBr^+ would be formed in an extremely low concentration that is unable to provide the adequate number of collisions to explain the very high specific rates of bromination observed in the presence of H^+_{aq}. This is especially significant in view of the appreciable (e.g. 35.6 kJ mole^{-1} at 5-fold relative $[H^+_{aq}]$) energy of activation for the reaction.



Considering the foregoing discussion, a catalytic effect of H^+_{aq} on the reaction can explain the faster bromination with acidified solutions of HOBr. The following mechanism which is similar to the one suggested by Shilov *et al.*[9] is *proposed.*

OAT first forms a complex with HOBr, then gets converted into protonated complex and ultimately into a σ complex. If either the protonation or the subsequent step were rate determining, then the observed kinetics could be accounted for.

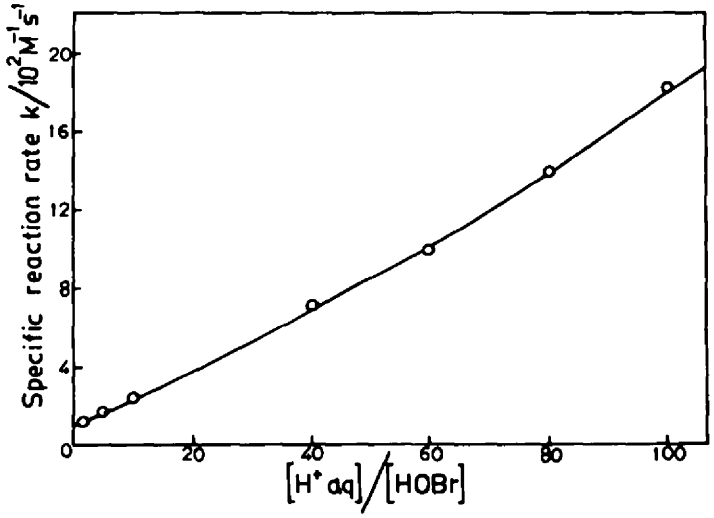


Fig. 1.

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† $\frac{[H^+][OH^-]}{[H_2O]}$.

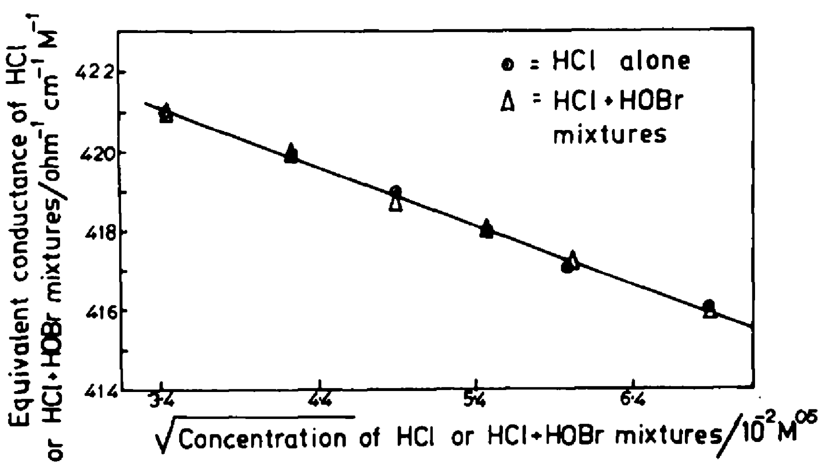

Fig. 2.

Table 1. Kinetics of bromination of OAT by HOBr at 25.0°C (conventional method) Concentration of OAT = 0.03 M; Concentration of HOBr = 0.03 M

Time (s)	Concentration of HOBr remaining [HOBr]/10^{-2} M	(1/[HOBr])/10 M^{-1}
0	3.00	3.33
180	2.83	3.54
300	2.68	3.73
570	2.40	4.17
800	2.17	4.60
1080	1.91	5.26

Slope of the curve 1/[HOBr] vs time.
= specific reaction rate.
= 2.36 × 10^{-2} M^{-1} s^{-1}.

Table 3. Variation of specific reaction rate at 5-fold relative [H^+_{aq}], with temperature

Temperature (T/K)	Specific reaction rate, (M^{-1} s^{-1})
283	84.1
288	107
293	138
298	170
303	221

Slope of the curve, log k vs T^{-1} = −1.848 × 10^{3} K.
Energy of activation = −2.303 × 8.32 × (−1.848 × 10^{3}) J mole^{-1}; = 35.6 kJ mole^{-1}.

Table 2. Kinetics of bromination of OAT by HOBr containing 5-fold relative [H^+_{aq}] at 25.0°C (RPE method). Concentration of OAT in the reaction mixture = 1.0 × 10^{-4} M; Concentration of HOBr in the reaction mixture = 1.0 × 10^{-4} M; Concentration of HCl in the reaction mixture = 5.0 × 10^{-4} M; Potential applied at RPE vs SCE = +0.2 V; Diffusion current in terms of galvanometer deflection for 1.0 × 10^{-4} M solution of HOBr containing 5.0 × 10^{-4} M HCl = 50.0 cm

Time (s)	Diffusion current in terms of galvanometer deflection (cm) 1	2	3	Mean	Concentration of HOBr remaining, ([HOBr]/10^{-4} M)	(1/[HOBr])/10^{4} M^{-1}
20	37.5	37.6	37.4	37.5	0.75	1.34
30	33.0	33.1	32.9	33.0	0.66	1.50
40	29.4	29.4	29.6	29.5	0.59	1.70
50	26.5	26.7	26.4	26.5	0.53	1.90
60	25.1	24.8	25.2	25.0	0.50	2.00
70	23.1	23.1	22.8	23.0	0.46	2.20
80	21.0	21.0	21.0	21.0	0.42	2.38
90	19.4	19.5	19.5	19.5	0.39	2.56

Slope of the curve 1/[HOBr] vs time.
= specific reaction rate.
= 170 M^{-1} s^{-1}.

EXPERIMENTAL

Preparation of solutions Hypobromous acid. (HOBr) was prepared by stirring Br-water with excess of Ag_2O and filtering the soln. Its strength was determined by iodometric titration. Stock solns of 0.03 M KCl, 0.03 M OAT, 0.02 M HCl and 0.02 M $HClO_4$ were also prepared. All the solns were maintained at 25.0 ± 0.05°.

(i) The bromination of OAT by HOBr alone was followed by mixing the two reactants (0.03 M each) and carrying out iodometric titrations with aliquots of the mixture at intervals of time to estimate the concentration of unreacted HOBr. The slope of the curve, 1/[HOBr] vs time gave the specific rate of the reaction.

(ii) The bromination of OAT by HOBr in the presence of H^+_{aq} was studied by using the RPE which was rotated at 600 revolutions per minute with +0.2 V applied at it vs saturated calomel electrode (SCE). The RPE and SCE were introduced into a beaker. 100 ml of 2×10^{-4} M HOBr containing a known concentration of the HCl and 0.02 M KCl (the supporting electrolyte) were rapidly mixed with 100 ml of 2×10^{-4} M OAT containing 0.02 M KCl, in the reaction beaker. The diffusion current due to the unreacted HOBr was noted at 10 s intervals, using a moving coil mirror galvanometer (0.01 μA sensitivity). The deflections of the galvanometer were separately calibrated over a range of HOBr concentrations containing the stipulated concentration of the strong acid. From these, the concentrations of HOBr at intervals of time and hence the specific rate of the reaction was determined.

The specific reaction rates are reproducible to within ±2% considering the various errors in the measurements.

(iii) A series of such experiments was carried out with increasing proportions of HCl, the concentration of the latter relative to that of HOBr being varied over a wide range, viz 1–100.

(iv) A further series of experiments was carried out using perchloric acid instead of HCl.

(v) At 5-fold concentration of H^+_{aq} relative to that of HOBr, the reaction was studied at different temps. to evaluate the energy of activation of the reaction under these conditions.

(vi) In another series of experiments, the conductances of HClaq in the concentration range 1×10^{-3}–5×10^{-3} M, were measured. Similarly, measurements were also carried out with mixtures of HCl and HOBr wherein the concentrations of HCl were the same as those in the above series, but those of HOBr were complementrary, i.e. the total concentration in all the cases was 6×10^{-3} M.

The results are presented in Tables 1–3 and Figs. 1 and 2.

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