# The Mechanism of Bromination by Hypobromous Acid

By ALICIA GASTAMINZA, H. M. GILOW, and J. H. RIDD*
(*Chemistry Department, University College, 20 Gordon Street, London* WC1H OAJ)

*Summary* A purely kinetic argument is used to show that acid-catalysed bromination by hypobromous acid does not always involve attack by a pre-formed positive brominating agent.

THE mechanism of the acid-catalysed halogenation of aromatic compounds by hypohalous acids has been a matter of dispute for many years.[1] At a given acidity, the kinetic form of the bromination reaction follows equation (1)† but the rate coefficient ($k_2$) is a function of the acidity. The original[2] and still the most common interpretation[3] of this kinetic form assumes the formation of a small concentration of "positive bromine"‡ in equilibrium with hypobromous acid [equation (2)]; the rate-determining stage is then considered to be the attack of this "positive bromine" on the aromatic system [*cf.* equation (3)]. Against this, it would seem on thermodynamic grounds that the concentration of "positive bromine" (as either $\overset{+}{\mathrm{Br}}$ or $\mathrm{H_2O\overset{+}{B}r}$) is too low to serve as a reaction intermediate.[4,5] The thermodynamic argument is here supported by kinetic studies.

$$\text{Rate} = k_2[\mathrm{ArH}][\text{hypobromous acid}] \qquad (1)$$

$$\mathrm{HOBr} + \mathrm{H^+} \rightleftharpoons \overset{+}{\mathrm{Br}} + \mathrm{H_2O} \qquad (2)$$

$$\text{Rate} = k_2'[\mathrm{ArH}][\overset{+}{\mathrm{Br}}] \qquad (3)$$

The new kinetic evidence comes from an extension of our previous study[6] of these bromination reactions to cover a wider range of acidity. A logarithmic plot of $k_2$ (eqn. 1) against $\mathrm{H_0}$ for a number of substrates covering the full range of acidity is shown§ in the Figure. The parallelism

---

† Hypobromous acid is written out in full in this equation to show that the stoicheiometric concentration is implied.

‡ For the purpose of this note it is unnecessary to distinguish between the bromine cation ($\mathrm{Br^+}$) and related hydrated forms (*e.g.*, $\mathrm{H_2O\overset{+}{B}r}$).

§ The use of $H_0$ as abscissa is merely to facilitate the step-wise comparison of reactivities. As before,[6] $H_0$ values at acidities below and $0{\cdot}1\,\mathrm{M}$-$\mathrm{HClO_4}$ are equated with $-\log_{10}C(\mathrm{H^+})$ and are otherwise taken from the review by Paul and Long.[7]

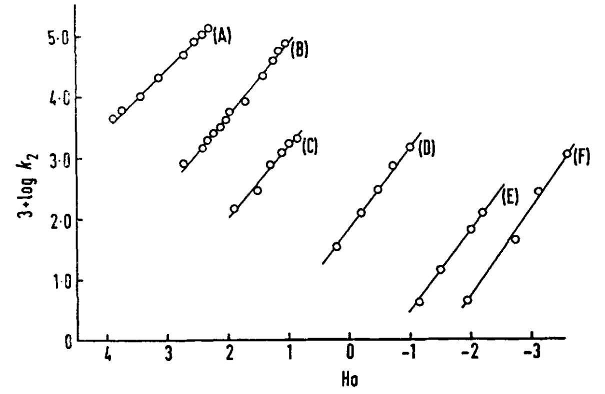


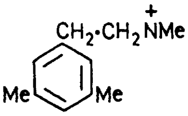
FIGURE. *Plot of log* $k_2$ *against* $H_0$ *for the reaction of benzene derivatives with hypobromous acid in aqueous sulphuric acid and aqueous perchloric acid at 25°. The measurements in perchloric acid are limited to acidities below* $H_0$ 1·0. (A) $3,5\text{-}Me_2C_6H_3(CH_2)_2\overset{+}{N}Me_3$; (B) $3\text{-}MeC_6H_4(CH_2)_2\overset{+}{N}Me_3$; (C) $Ph(CH_2)_2\overset{+}{N}Me_3$; (D) $PhCH_2\overset{+}{N}Me_3$; (E) $Ph\overset{+}{N}Me_3$; (F) $4\text{-}ClC_6H_4\overset{+}{N}Me_3$. *The results for substrates* (D) *and* (E) *have been reported previously.*[6]

of the plots at a given acidity permits the calculation of relative reactivities of the aromatic compounds and relative rates of bromination at widely differing acidities. In this way, we have calculated that the rate coefficients of equation (1) for a given substrate should increase by a factor of $1{\cdot}9 \times 10^9$ in going from $H_0$ 3·85 ($1{\cdot}42 \times 10^{-4}$M-$HClO_4$) to $H_0 - 3{\cdot}6$ (7·5M-$H_2SO_4$).

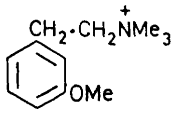
On the conventional interpretation based on equation (2), the variation of $k_2$ with acidity comes from the variation of the ratio $[\overset{+}{Br}]$/[hypobromous acid]. From the constancy of the slope of log $k_2$ *vs.* $-H_0$ at the highest acidities in the Figure, the value of this ratio would appear to be much less than unity. If, as an upper limit we put $[\overset{+}{Br}]$/[hypobromous acid] = 0·5 in 7·5M-sulphuric accid then the upper limit for this ratio at $H_0$ 3·85 would appear to be $0{\cdot}5/1{\cdot}9 \times 10^9 = 2{\cdot}6 \times 10^{-10}$.

A difficulty then arises in the calculation of the true rate constants for the reaction of positive bromine with the aromatic compound at the lower acidities. Using the above upper limit for the ratio $[\overset{+}{Br}]$/[hypobromous acid] at $H_0$ 3·85, the values of $k_2'$ [equation (3)] for the bromination of the ion (I) at this acidity comes to be $> 1{\cdot}7 \times 10^{10}$ mol$^{-1}$ s$^{-1}$. The corresponding rate coefficient for the ion (II) is at least $10^2$ faster. These values greatly exceed that for reaction on encounter and are therefore physically impossible.

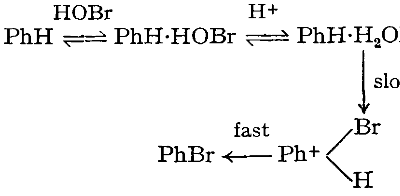
This difficulty could be removed by assuming that we are dealing with two or more effective brominating agents over this region of acidity but the linearity of the logarithmic plot of relative rates for bromination against relative rates of nitration for a series of substrates brominated over the range $4{\cdot}76 \times 10^{-3}$—4·74M-sulphuric acid[6] does not suggest any change in the selectivity of the brominating agent. A related interpretation would be to assume that the acidity dependence of the rate of bromination derives in part from medium effects on the value of $k_2$ in equation (3) but it seems unlikely that such medium effects are sufficiently great. We are led therefore to assume that, at least at the lower acidities, the transition state is reached by the protonation of a preformed complex of the aromatic compound with hypobromous acid. If so, the protonation would appear to involve a pre-equilibrium, for the solvent deuterium isotope effect on the bromination of benzene in perchloric acid (0·16M) gives $k(D_2O)/k(H_2O) = 2{\cdot}2$. The rate-determining stage appears therefore to involve a subsequent step [equation (4)]. There is no primary hydrogen isotope effect in the bromination of benzene[8] and so the final stage of this equation is not rate-determining.



(I)



(II)



$$PhH \overset{HOBr}{\rightleftharpoons} PhH{\cdot}HOBr \overset{H^+}{\rightleftharpoons} PhH{\cdot}H_2OBr^+ \xrightarrow{\text{slow}} Ph^+\!\!\left\langle{}^{Br}_{H}\right. \xrightarrow{\text{fast}} PhBr \qquad (4)$$

This interpretation is similar, although not identical, to that previously put forward on thermodynamic grounds.[5] It avoids the paradox concerning encounter rates but one difficulty remains, for it is not clear why this reaction path should be available for bromination but not nitration. Our own studies on the nitration of the above compounds accord with those of Coombes, Moodie, and Schofield[9] on other reactive substrates in that the nitration of the ions (I) and (II) above is limited by the rate of encounter with nitronium ions.[10]

We thank Professor P. B. D. De la Mare for helpful discussions. One of us (A.G.) thanks C.I.C. (Pcia. Buenos Aires) and the Universidad del Sur, Argentina, for financial support.

(*Received, November 22nd,* 1971; *Com.* 2000.)

---

[1] J. Arotsky and M. C. R. Symons, *Quart. Rev.*, 1962, **16**, 282.

[2] E. A. Shilov and N. P. Kanyaev, *Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **25**, 890; D. H. Derbyshire and W. A. Waters, *J. Chem. Soc.*, 1950, 564.

[3] P. B. D. De la Mare and J. H. Ridd, "Aromatic Substitution, Nitration and Halogenation", Butterworths, London, 1959, p. 119; R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds", Elsevier, Amsterdam, 1965, p. 122.

[4] R. P. Bell and E. Gelles, *J. Chem. Soc.*, 1951, 2734.

[5] E. A. Shilov, F. M. Vainshtein, and A. A. Yasnikov, *Kinetika i Kataliz*, 1961, **2**, 214.

[6] A. Gastaminza, J. H. Ridd, and F. Roy, *J. Chem. Soc.* (*B*), 1969, 684.

[7] M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1.

[8] P. B. D. De la Mare, T. M. Dunn, and J. T. Harvey, *J. Chem. Soc.*, 1957, 923.

[9] R. G. Coombes, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1968, 800.

[10] H. M. Gilow and J. H. Ridd, unpublished work.