[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

A Lower Limit for the Velocities of Formation of the Tri-halide Ions in Aqueous Solution

BY R. S. HALFORD

The fact that interchange occurs rapidly between a halogen and its corresponding halide ion was demonstrated experimentally[1,2,3] several years ago. The experiments cited employed radioactive halide ions for the purpose of detecting the reactions which may be represented by the equation

$$XX + \overset{*}{X}^- = X\overset{*}{X} + X^-$$

Two different methods of investigation were employed and it will now be shown that it is possible to extend the conclusions reached by one of these methods so as to provide a definite lower limit for the velocity of the chlorine–chloride ion interchange. This experimental lower limit when compared with upper limits calculated for several plausible mechanisms permits the elimination of all but one of these, namely, interchange through the formation and decomposition of trichloride ion. In addition, arguments will be presented to justify the inference that the same lower limit is also applicable to the velocities of the bromine–bromide ion and iodine–iodide ion interchange reactions.

It is of interest to compare briefly the two methods of investigation and the conclusions which they afford. The first method was employed for investigation of the bromine–bromide ion interchange[1a,b,c] and also for investigation of the iodine–iodide ion reaction.[2] It consists simply of mixing ordinary halogen with radioactive halide ions, of known specific radioactivity, in solution. After an interval the halogen is separated from the solution and the amount of interchange which has occurred can be determined from the decrease in specific radioactivity of the halide ion. It was found in this way, for both of the reactions referred to above, that considerable interchange takes place during the course of several minutes but the reaction velocity could not be more definitely specified.[1c] However, the nature of the experiments (particularly with respect to the time required to ensure good mixing and to effect the subsequent separation of the reactants) would make it difficult to extend, by this method, the upper limit below a value of the order of one minute for the time required for complete interchange. These reactions are so much faster that this limit does not provide a satisfactory indication of their real speed.

The second method was applied by Long and Olson, who investigated the chlorine–chloride ion interchange. They required to know, in connection with another investigation,[4] whether the velocity of interchange was fast or slow compared with the velocity of chlorination of acetanilide in aqueous solution. They therefore determined the velocity of the former reaction relative to that of the latter by a competitive method. Chlorine was introduced into a solution containing both radioactive chloride ion and acetanilide, resulting in the formation of chloroacetanilide. Radioactivity in the chloroacetanilide would indicate that interchange had occurred prior to chlorination and the amount of radioactivity so found would provide a measure of the velocity of interchange relative to the velocity of chlorination. Long and Olson found by this method that, within an experimental error of the order of 1%, complete interchange occurs prior to chlorination. This requires that the velocity of interchange be at least one hundred times as great as the velocity of chlorination of acetanilide under their experimental conditions. Since this result was satisfactory for their purpose Long and Olson concluded that the interchange must be an extremely rapid reaction, for chloroacetanilide appeared to be formed instantly. It is apparent that this method could be made to yield a quantitative value for the velocity of interchange by a suitable choice of systems of competitive reactions. Experimental conditions could be varied and, if necessary, other rapidly chlorinated substances could be employed in place of acetanilide until a system was found in which the velocity of interchange was comparable with the velocity of

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[1] (a) A. V. Grosse and M. S. Agruss, THIS JOURNAL, **57**, 591 (1935); (b) S. Roginskiĭ and N. Gopshtein, *Physik. Z. Sowjetunion*, **7**, 672 (1935); R. W. Dodson and R. D. Fowler, THIS JOURNAL, **61**, 1215 (1939).

[2] D. E. Hull, C. H. Shiflett and S. C. Lind, *ibid.*, **58**, 535 (1936).

[3] F. A. Long and A. R. Olson, *ibid.*, **58**, 2214 (1936).

[4] A. R. Olson, C. W. Porter, F. A. Long and R. S. Halford, *ibid.*, **58**, 2467 (1936).

chlorination. The rate of chlorination could be determined in a series of separate competitions, referred to a substance which chlorinates at a measurable velocity.

In the absence of the results of such experiments it is still possible, however, to restate the conclusion of Long and Olson in a more quantitative way by placing a definite lower limit on the velocity of the interchange reaction. This can be done in view of the fact that the velocity of chlorination of acetanilide under the conditions used by Long and Olson can be estimated from other experiments. King and Orton[5] found that the chlorination of acetanilide was a bimolecular reaction in glacial acetic acid and gave the value of k as 40 liters mole^{-1} min.$^{-1}$ at about 17°. In a later investigation Orton, Soper and Williams[6] obtained a value of k equal to 11,000 liters mole^{-1} min.$^{-1}$ again at about 17° but in 40% aqueous acetic acid. In this investigation it was clearly demonstrated that the reaction is bimolecular. It is evident from the trend in these two values for k that a further increase is to be expected on going to a solvent still richer in water. In the experiment of Long and Olson the solvent was aqueous alcohol containing 95% water and in this solvent the value of k for the chlorination of acetanilide is therefore certainly greater than 10^4 liters mole^{-1} min.$^{-1}$. However, in order to be conservative this value will be adopted as a lower limit. The corresponding lower limit to be assigned to k_i, the velocity constant for the interchange, will depend upon the mechanism assumed for this latter reaction.

Three mechanisms suggest themselves immediately as being the most plausible. When chlorine is introduced into an aqueous solution containing chloride ion it enters into two reactions which ordinarily come rapidly into equilibrium. These reactions are: (1) the hydrolysis of chlorine which can be formulated kinetically in two ways[7]

$$\text{(a)}\quad \mathrm{Cl_2 + OH^- \underset{k_i}{\overset{k'}{\rightleftarrows}} Cl^- + ClOH} \qquad K_a = 4 \times 10^{10}$$

or

$$\text{(b)}\quad \mathrm{Cl_2 + H_2O \underset{k_i}{\overset{k'}{\rightleftarrows}} Cl^- + H^+ + ClOH} \qquad K_b = 4 \times 10^{-4}$$

and (2) the formation of trichloride ion[8]

$$\mathrm{Cl_2 + Cl^- \underset{k_i}{\overset{k'}{\rightleftarrows}} Cl_3^-} \qquad K_2 = 0.01$$

In the presence of acetanilide these reactions are, of course, unable to establish equilibrium but if any or all of them are to be responsible for the interchange they may be considered to be practically at equilibrium with the concentration of chlorine existing at any instant. This must be true since the velocity of interchange is known to be at least one hundred times as great as the velocity of chlorination.

The equations written above contain three substances: chlorine, hypochlorous acid and trichloride ion, which might be regarded as chlorinating agents capable of acting on acetanilide. However, Orton, Soper and Williams[6] state that the velocity of chlorination by hypochlorous acid is very slow compared to that by chlorine; and it can be inferred from their observations, wherein the addition of chloride ion at high concentrations retards chlorination, that trichloride ion is not an effective chlorinating agent. The interchange observed by Long and Olson must come about, therefore, through the introduction of a radioactive chlorine atom into the chlorine molecule prior to the reaction of the latter with acetanilide. This can occur through the reverse reaction for each of the first two equilibria written above, and through a decomposition of a trichloride ion formed in the third equilibrium above. Consequently, ignoring the initial period preceding the establishment of equilibrium, we can write for the velocity of interchange[9]

$$\text{(1a)}\quad v_i = k_i(\overset{*}{\mathrm{Cl}}{}^-)(\mathrm{ClOH}) = k_iK_a(\mathrm{Cl_2})(\mathrm{OH^-})$$

$$\text{(1b)}\quad v_i = k_i(\overset{*}{\mathrm{Cl}}{}^-)(\mathrm{ClOH})(\mathrm{H^+}) = k_iK_b(\mathrm{Cl_2})$$

or

$$\text{(2)}\quad v_i = k_i(\overset{*}{\mathrm{Cl}}{}_3^-) = k_iK_2(\mathrm{Cl_2})(\overset{*}{\mathrm{Cl}}{}^-)$$

corresponding to mechanisms 1a, 1b and 2, respectively, as indicated in the parentheses at the left. The right-hand member has been obtained from the middle member in each case by substitution from the appropriate mass law expression.

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[5] H. King and K. J. P. Orton, *J. Chem. Soc.*, **99**, 1369 (1911).

[6] K. J. P. Orton, F. G. Soper and Gwynn Williams, *ibid.*, 998 (1928).

[7] The value of K_a is derived from that of K_b. The latter has been taken from "International Critical Tables," Vol. VII, p. 234.

[8] M. S. Sherrill and E. F. Izard, THIS JOURNAL, **53**, 1667 (1931).

[9] The velocity, expressed as a product of rate constant and concentrations, has a value fixed by experiment. During the initial period preceding equilibrium the product of concentrations is less than the equilibrium value; hence the true rate constant must be greater than the one calculated using equilibrium concentrations. Thus, ignoring the initial period merely gives too low a value for the lower limit to be assigned to k_i. In the problem under consideration the error introduced in this way is trivial since, in order to distribute the radioactivity randomly between $\mathrm{Cl_2}$ and $\mathrm{Cl^-}$, the quantity of ClOH or $\mathrm{Cl_3^-}$ which must react is of the order of 1000 times the equilibrium quantities of these substances.

Writing for the velocity of chlorination of acetanilide

$$v = k(\mathrm{Cl_2})(\mathrm{Ac})$$

in which (Ac) denotes the concentration of acetanilide, and requiring the ratio of the velocity of interchange to the velocity of chlorination to be greater than 100 we can solve for the value of k_i appropriate to each mechanism. In this way we obtain as lower limits

$$\text{(1a)}\quad k_i > 100\,\frac{k(\mathrm{Ac})}{K_a(\mathrm{OH^-})}$$
$$\text{(1b)}\quad k_i > 100\,\frac{k(\mathrm{Ac})}{K_b}$$
$$\text{(2)}\quad k_i > 100\,\frac{k(\mathrm{Ac})}{K_2(\overset{*}{\mathrm{C}}\mathrm{l^-})}$$

In the experiment performed by Long and Olson the concentrations of the several substances were: $(\mathrm{OH^-}) = 10^{-14}\ M$, $(\mathrm{Ac}) = 0.06\ M$, and $(\mathrm{Cl^{*-}}) = 0.15\ M$. Introducing these values along with those for K_a, K_b and K_2 and the lower limit which has been previously established for k we obtain as lower limits for the specific rate constant of the interchange reaction according to the several mechanisms

$$\text{(1a)}\quad k_i > 10^8 \text{ liters mole}^{-1}\text{ min.}^{-1}$$
$$\text{(1b)}\quad k_i > 10^8 \text{ liters}^2\text{ mole}^{-2}\text{ min.}^{-2}$$
$$\text{(2)}\quad k_i > 4 \times 10^7 \text{ min.}^{-1}$$

Upper limits can also be established for k_i, according to each mechanism, with the assistance of the statistical theory of reaction velocity.[10] In this theory the velocity constant for a reaction can be calculated from the equation

$$k = \frac{\mathrm{k}T}{h} e^{\Delta S^*/R}\, e^{-\Delta H^*/RT} = 3.6 \times 10^{14}\, e^{\Delta S^*/R}\, e^{-\Delta H^*/RT} \text{ min.}^{-1} \text{ at } 17^\circ \quad (1)$$

where ΔS^* and ΔH^* are, respectively, the molal entropy and molal heat of formation of the critical complex and the other symbols have their usual significance. From thermal data given by Bichowsky and Rossini[11] it can be calculated that the reactions 1a and 1b, when occurring in the reverse direction, are endothermic by 19.8 and 6.1 kcal., respectively. These figures are minimum values for the heat of formation of the critical complex in each reaction and may therefore be used with equation (1) to calculate upper limits for k_i. The critical complexes for both of these reactions are formed by coalescence of several molecules into one and a decrease of entropy should therefore accompany the process. Hence, neglecting this entropy change in the calculation will lead to a value of k_i which is too high but nevertheless still a valid upper limit. The upper limits obtained in this way are

$$\text{(1a)}\quad k_i < 0.36 \text{ liter mole}^{-1}\text{ min.}^{-1}$$
$$\text{(1b)}\quad k_i < 10^{11} \text{ liters}^2\text{ mole}^{-2}\text{ min.}^{-1}$$

It is evident that mechanism 1a must be discarded since the calculated upper limit lies below the previously deduced lower limit for this mechanism. Furthermore, while mechanism 1b cannot be unequivocally eliminated it must be regarded as highly improbable since every error and omission which has been made in setting the upper and lower limits tends to make the domain separating them too large. One power of ten correction to each limit would suffice to eliminate this mechanism. It is not at all improbable that the actual corrections should be larger than these.

Thermal data are not available for reaction 2 but it can be estimated from the heats of formation of tribromide ion and triiodide ion that the decomposition of trichloride ion is exothermic to the extent of about 2 kcal. The heat of formation of the critical complex can therefore be quite small.

The entropy of formation of the critical complex should also be small and the upper limit appropriate for k_i for this mechanism would appear to be of the order of 10^{14} min.$^{-1}$. Both this and the lower limit can be corrected by several powers of ten without excluding the mechanism. It therefore appears highly probable that the interchange between chlorine and chloride ion occurs through the formation and decomposition of trichloride ion.

In order that the equilibrium relation be satisfied it is necessary that the rate constant for the formation of trichloride ion lie between the limits

$$4 \times 10^5 \text{ liters mole}^{-1}\text{ min.}^{-1} < k' < 10^{12} \text{ liters mole}^{-1}\text{ min.}^{-1}.$$

The specific velocities of formation of tribromide ion and of triiodide ion are probably greater than that for trichloride ion in the order named. This conclusion can be deduced from comparisons among reactions of the type

$$\mathrm{A + BC \longrightarrow AB + C}$$

Variation of A acting on a given BC gives specific velocity constants in the order[12] $\mathrm{I^-} > \mathrm{Br^-} > \mathrm{Cl^-}$.

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[10] W. F. K. Wynne-Jones and H. Eyring, *J. Chem. Phys.*, **3**, 492 (1935).

[11] "Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York, N. Y., 1936.

[12] For example, see E. D. Hughes and U. G. Shapiro, *J. Chem. Soc.*, 1177 (1937); A. R. Olson and F. A. Long, THIS JOURNAL, **56**, 1294 (1934), and numerous other papers relating to the Walden Inversion.

The same order is likewise observed for variation of C with a given A and B.[11] It seems reasonable that the order for variation of B can be deduced from a comparison of the velocity of oxidation of iodide ion by chloric, bromic and iodic acids since it is probable that the important step in these reactions is substitution of iodine for hydroxyl on the central halogen atom.[13] The order observed for the velocities of these reactions is the one given above. Hence the lower limit which has been established for the specific velocity of formation of trichloride ion is apparently also a valid lower limit for the specific velocities of formation of tribromide and triiodide ions. It should be pointed out, however, that this order does not necessarily prevail for the specific velocities of decomposition of the several trihalide ions.

An alternative explanation for the results of Long and Olson could be based on interchange between chloride ion and chloroacetanilide subsequent to chlorination. This mechanism is eliminated from further consideration in view of the fact that the reaction of bromide ion with chloroacetanilide occurs very slowly.

Summary

1. The chlorine–chloride ion interchange occurs through the mechanism of formation and decomposition of the trihalide ion. This is probably also the mechanism for bromine–bromide ion and iodine–iodide ion interchanges.

2. Lower limits have been established for the velocity constants of the two reactions: (a) formation of trichloride ion: $k > 4 \times 10^5$ liters mole^{-1} min.$^{-1}$ and (b) decomposition of trichloride ion: $k > 4 \times 10^7$ min.$^{-1}$ at 17°.

3. The lower limit given above probably holds also for the velocities of formation of tribromide and triiodide ions.

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(13) This opinion is also held by Professor W. C. Bray who has drawn this conclusion from the results of his own unpublished investigations.

[CONTRIBUTION FROM THE LABORATORIES OF CHEMISTRY AND PHYSICS OF THE UNIVERSITY OF MICHIGAN]

The Molecular Structures of Methyl Isocyanate and Cyanic Acid by the Electron Diffraction Method. The Structural Chemistry of Cyanic Acid and its Derivatives

BY EUGENE H. EYSTER,[1] R. H. GILLETTE AND L. O. BROCKWAY

The theoretical picture of molecules whose ground states are achieved by resonance among several valence bond structures is now so well developed that it is not only possible to predict with confidence the qualitative aspects of the structures of cyanic acid and its derivatives, but also to anticipate many quantitative details of these structures. Indeed, it has been pointed out[1a] that the covalent cyanate group should be expected to have a linear configuration of over-all length 2.36 Å., with the carbon atom located approximately at the center. While this prediction is entirely compatible with the rather indirect evidence furnished by the vibration spectrum of the methyl ester of cyanic acid,[1a] it can hardly be reconciled with the assertion, by Herzberg and Verleger,[2] that cyanic acid itself is an extremely asymmetric molecule in the dynamic sense, a statement which has as its basis the unusually complex rotational structure of the third N–H harmonic band of cyanic acid. This structure seems, at least on superficial examination, to bear little resemblance to that of the corresponding band of hydrazoic acid, though the structural theory predicts very similar configurations for these two compounds. Since the cyanic acid bands have not been actually analyzed, and since there have been, indeed, no direct physical determinations of the structure of the covalent cyanate group,[3] it has appeared desirable to study the structures of the free acid and its methyl ester by the electron diffraction method. The investigations described in the following pages provide a complete confirmation of both the qualitative and quantitative aspects of the structural theory as applied to the covalent cyanate group, and we have also taken this opportunity to discuss its further applications to the structural

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(1) National Research Fellow in Chemistry 1939–1940; present address, California Institute of Technology, Pasadena, California.

(1a) Eyster and Gillette, *J. Chem. Phys.*, **8**, 369 (1940).

(2) Herzberg and Verleger, *Physik. Z.*, **3** , 444 (1937).

(3) The structure of the ionic cyanate group in potassium cyanate has indeed been studied by X-ray methods by Hendricks and Pauling, THIS JOURNAL, **47**, 2904 (1925), but their distance determinations in the cyanate group are not of sufficient precision to lead to significant conclusions concerning the relative contributions of various resonating structures to the ground state of the ion.