252. *Sterically Hindered S_N2 Hydroxide Attack of the Bromomolybdenum*(II) *Group.*

By J. C. Sheldon.

The alkaline hydrolysis of the hexahydroxobromomolybdate(II) ion, $[(Mo_6Br_8)(OH)_6]^{2-}$ (unlike that of the hexahydroxochloromolybdate(II) ion [1]) is autocatalysed, though the rate of hydroxide substitution can be studied in the presence of hydrogen peroxide which inhibits the autocatalysis. It is then possible to derive approximate overall second-order rate constants, the rate being dependent on both bromomolybdate(II) and hydroxide-ion concentrations. A bimolecular rate determining step is suggested and steric factors are discussed that may account for the unusual observation that the rate of hydrolysis of the bromo-compound is much slower than the chloro-compound.

The rate of hydroxide substitution of the hexahydroxochloromolybdate(II) ion, $[\{Mo_6Cl_8)(OH\}_6]^{2-}$, has been found to be a second-order function involving chloromolybdate(II) and hydroxide-ion concentrations. A similar study has now been attempted of the hexahydroxo-octa-μ_3-bromohexamolybdate(II) ion, $[(Mo_6Br_8)(OH)_6]^{2-}$ [referred to in short as the bromomolybdate(II) ion].

The Autocatalytic Alkaline Hydrolysis of Bromomolybdate(II).—The alkaline hydrolysis of bromomolybdate(II) differs from that of the chloromolybdate(II) in that the former is autocatalysed. Little is known of the products of either system but the reasonable assumption may be made that hydrolysis yields a sequence of μ_3-hydroxo-derivatives, $[\{Mo_6X_{8-n}(OH)_n\}(OH)_6]^{2-}$ where n is 1, 2, 3, etc. The end product is a dark brown precipitate of unknown composition. The soluble and precipitated products are strong reducing agents and interfere with argentimetric assay of halide ions. The difficulties of following the hydrolysis of the bromomolybdate(II) ion and of formulating a rate law from the data, namely (i) autocatalysis, (ii) precipitation of unknown products, and (iii) unsuitability of argentimetric assay, have been overcome by the presence in the hydrolysing solution of hydrogen peroxide which destroys the catalyst, precipitate, and reducing agents. This action of the peroxide produces a further release of bromide ions, $12H_2O_2 + (18\text{-}n)OH^- + [\{Mo_6Br_{8-n}(OH)_n\}(OH)_6]^{2-} \longrightarrow 6MoO_4^{2-} + (8\text{-}n)Br^- + 24H_2O$, and thus the observed release of bromide ions under these conditions is no longer a function of hydrolysis alone. Nevertheless, useful data are obtained. For example the autocatalysis of the bromomolybdate(II) system can be quantitatively demonstrated.

The curves in Fig. 1 describe the reaction progress in 1M-hydroxide solution, expressed as the fraction of total bromide released and measured under different conditions. Curve 1 represents the released bromide measured after each portion for assay was treated with hydrogen peroxide; the sigmoidal shape is characteristic of autocatalysis. Curve 2 was

---

[1] Sheldon, *J.*, **1963**, 4183.

obtained by the same procedure but differs in that the reaction solution was " seeded " at zero time with a drop of bromomolybdate(II) hydrolysis product from another experiment. The curve shows an enhanced initial rate which must be due to catalysis by the bromomolybdate(II) hydrolysate. The final experiment demonstrated that the action of hydrogen peroxide itself could not account for either of the previous curves. The hydrolysis was carried out in the presence of the peroxide and curve 3 obtained. A much lower rate is observed, presumably due to the absence of catalysis. Moreover it is then found that the effective rate of bromide release, although resulting from several unknown hydrolytic and oxidative steps is approximately of first order with respect to bromomolybdate(II), and it is therefore feasible to study the kinetics of the hydroxide–bromomolybdate(II) reaction.

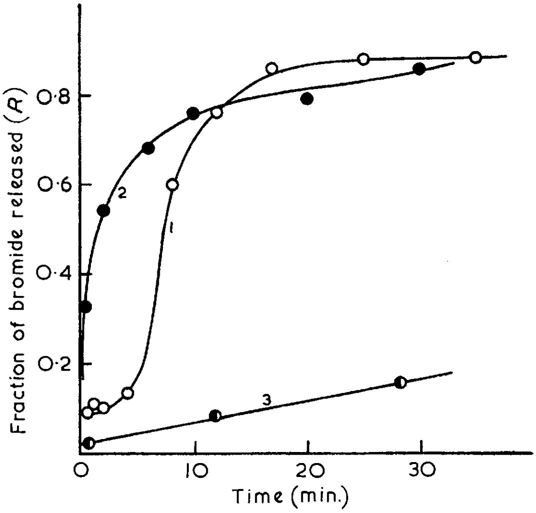

FIG. 1.

The Effect of Hydrogen Peroxide on the Rate of Hydroxide Substitution of the Chloromolybdate(II) *Ion*.—The bromomolybdate(II) ion is not a reducing agent, but it is desirable to know to what extent hydrogen peroxide interacts with this ion and its μ_3-hydroxo-derivatives under the conditions of rate measurement by a study of the rate of bromide-ion release with variation of hydrogen peroxide concentration. However the somewhat variable autocatalysis observed at low concentrations of peroxide has rendered this separate study impossible. On the other hand, the chloromolybdate(II) ion is hydrolysed by 1M-hydroxide at a convenient and reproducible rate at 30°, and therefore the behaviour of hydrogen peroxide in the hydrolysis of the chloromolybdate(II) has been investigated instead and the results tentatively assumed to be true of the bromomolybdate(II) system also. This is a fair assumption since the reported chemistries of the chloro- and bromo-molybdenum(II) compounds are so similar.[2] The large difference in rate of uncatalysed alkaline hydrolysis of the chloro- and bromo-molybdate(II) ions (*see below*) represents one of the few significant differences of properties. Even the hydrolysis of chloromolybdate(II) is autocatalysed at elevated temperatures (70—90°), though not at temperatures employed in the reported studies.[1]

The rate of chloride release of $\sim10^{-3}$M-chloromolybdate(II) in 1M-hydroxide at 30° and in the presence of hydrogen peroxide obeys the equation $-\ln(1 - R) = kt$, where R is the fraction of the initially combined chloride that is released by time t. A typical rate curve

---

[2] Sheldon, *J.*, **1962**, 410.

is shown in Fig. 2, curve 1 (actually a run conducted at 70° for comparison with curve 2). k is an apparent and pseudo-first order rate constant (since the rate is hydroxide dependent [1]) for a particular peroxide concentration and here serves only as a comparative measure of the rate of chloride release. The plot of k against peroxide concentration, given in Fig. 3, has two parts, (i) a rapid initial rise at low concentration of peroxide, followed by (ii) a modest increase in k over a large range of peroxide concentration.

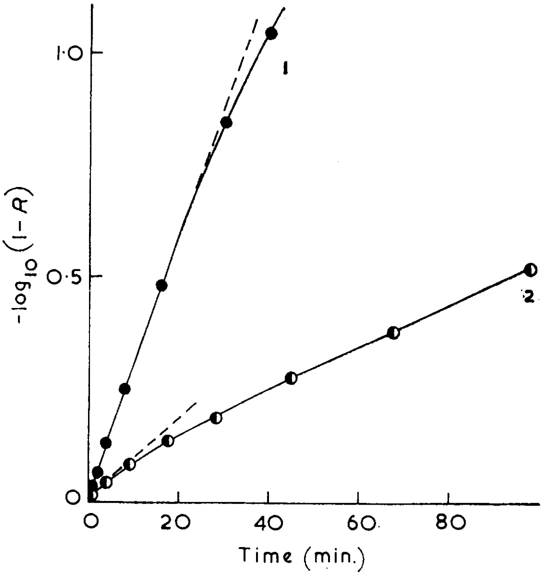

FIG. 2.

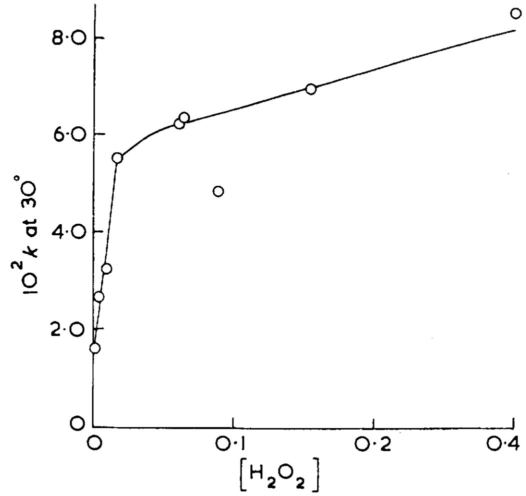

FIG. 3.

Part (i) of the curve suggests that only the μ_3-hydroxo-products are affected by the peroxide since the rapid change in k with concentration of peroxide indicates oxidation of some chloromolybdate(II) species, analogous to that described in the equation, and yet the limited extent of part (i) excludes the oxidation of the initial $[(Mo_6Cl_8)(OH)_6]^{2-}$ ion. Part (ii) of the curve probably results from the slow oxidation of some weakly reducing chloromolybdate(II) species, but since this effect is small compared with that at low concentration of peroxide it may be concluded that the rate of chloride release is relatively insensitive to the hydrogen peroxide concentration when present in sufficient amounts, say 0·1M.

The Kinetics of Hydroxide Substitution of the Bromomolybdate(II) *Ion in the Presence of Hydrogen Peroxide.*—The rate of bromide release of $\sim 10^{3}$M-bromomolybdate(II) in 0·1—2M-hydroxide solution, with an initial concentration of about 0·1M-hydrogen peroxide, proceeds with a convenient rate at 70°. The data were treated on the assumptions that the rate was (i) of first order dependence on bromomolybdate(II) concentration, (ii) pseudo-independent of the concentration of hydroxide, (iii) independent of concentration of hydrogen peroxide, and that (iv) effectively all the bromo-groups are kinetically equivalent. These assumptions proved to be largely valid since the plot of $-\ln(1 - R)$, where R is the fraction of the initially combined bromide that is released by time t, against t is approximately linear. A typical plot is given in Fig. 2, curve 2, and the small curvature observed is attributed to the small dependence of the rate on peroxide concentration which changes somewhat through the run by thermal decomposition. Curves of this form were obtained up to 80% total bromide released, and at greater reaction times the peroxide concentration had usually diminished to a level that did not prevent autocatalysis. Approximate first-order rate constants, k, can be obtained from the slope of the relatively linear positions of such curves at from moderate to large values of t, *vide* curve 2, Fig. 2. These constants show a first-order dependence on concentration of hydroxide ion and are converted into second-order constants k'. The latter are given in the Table along with the

Temp.	$[OH^-]$	[Elect.]*	$10^3k'$
70°	2·0	2·0	5·5
	2·0	2·0	6·3
	1·0	1·0	4·6
	1·0	1·0	4·1
	1·0	1·0	4·6 †
	1·0	1·0	5·1 †
	0·5	1·0	5·3
70°	0·2	1·0	5·1
	0·1	1·0	5·3
	0·1	1·0	6·6
	0·2	0·2	4·4
	0·2	0·2	3·7
	0·1	0·1	3·2
	0·1	0·1	4·1
50°	1·6	1·6	0·51
	1·0	1·0	0·69
	0·5	0·5	0·60
	0·5	0·5	0·57
90°	1·0	1·0	46
	1·0	1·0	44
	0·1	0·1	39

* Uni-univalent electrolyte. † Rate determined spectrophotometrically. The units of k' and l. mole^{-1} min.$^{-1}$.

concentrations of hydroxide ion and uni-univalent electrolyte employed. The second-order constants found at 70° and ionic strength of 1·0 fall, with one exception, within ±20% of the mean value ($5·1 \times 10^{-3}$ l. mole^{-1} min.$^{-1}$) over a ten-fold range of hydroxide-ion range. Moreover, since the constants show only a small change with ionic strength, there is in effect only a similar variation of constants over the twenty-fold (0·1—2·0M) range of hydroxide concentration. This spread of values is almost certainly due to the small dependence of rate on peroxide concentration. The rate data can therefore best be interpreted as second-order kinetics dependent on both hydroxide-ion and bromomolybdate(II)-ion concentrations.

Discussion of the Kinetics of Alkaline Hydrolysis of Halogenomolybdenum(II) *Groups.*—Since the rate of chloride release by the chloromolybdate(II) in alkaline peroxide obeys a pseudo-first-order law it is plausible that there is only one rate-determining step, namely the bimolecular reaction $[(Mo_6Cl_8)(OH)_6]^{2-} + OH^{+} \longrightarrow [(Mo_6Cl_7OH)(OH)_6]^{2+} + Cl^-$ previously suggested[1] for the base hydrolysis of chloromolybdate, and that oxidation of products by peroxide proceeds faster than this step. It is noteworthy that the overall rate of base hydrolysis in peroxide solution is found to be similar to the rate of formation of reducing products of chloromolybdate(II) hydrolysis for which the same rate-determining step has been suggested, *i.e.*, at 30°, k(apparent) is $\sim 6 \times 10^2$ l. mole^{-1} min.$^{-1}$ for peroxide hydrolysis, and $4{\cdot}8 \times 10^2$ l. mole^{-1} min.$^{-1}$ for oxidimetrically determined rates.[1] The Arrhenius activation energy derived [1] from the latter rates is about 21 kcals. mole^{-1}.

A similar mechanism is now suggested for the hydrolysis of the bromomolybdate(II) in hydrogen peroxide to that for the chloromolybdate(II) since both have the same kinetic form. The Arrhenius activation energy for the bromomolybdate(II) reaction is now found to be about 26 kcals. mole^{-1} and the increase of 5 kcals. mole^{-1} appears to explain the much faster rate (by a factor of from 10^3 to 10^2) of chloro- than bromo-molybdate(II) hydrolysis. This rate difference appears to be quite exceptional since the ratio $k_{\text{Cl}}/k_{\text{Br}}$ has not been reported [3] outside the range 2·0—0·15.

The stereochemistry of the octa-μ_3-halogenohexamolybdenum(II) groups is unique amongst those of complexes studied by reaction kinetics and it is likely that quite special factors will be found to account for the reaction rates and mechanisms of the (Mo_6X_8) complex. It has previously been pointed out [1] that this group may be stereochemically rigid and that S_N1 processes are unlikely since the reaction intermediate of reduced co-ordination number cannot be stabilised by rearrangement of ligands, and a very high activation energy would result for these processes. An S_N2 process may well prove possible if sufficient room for entry of the incoming group exists. The Mo_6X_8 group is arranged as a cube of X groups with an octahedron of molybdenum atoms placed within this cube with one molybdenum at each cube face-centre. The axial length of the Mo_6 group [4] is about 3·7 Å in (Mo_6Cl_8) and it is here assumed that this distance is characteristic also of (Mo_6Br_8) since the arrangement of these groups appears to result from strong molybdenum–molybdenum bonds. The anion-anion distances in the lithium halides, here assumed to possess anion-anion contacts, are: Cl–Cl, 3·6; Br–Br, 3·9 Å. These distances are taken to be the closest approach possible between these ions. The stereochemistry of the (Mo_6X_8) group indicates that the preferred X–X distance will correspond to the Mo–Mo distance of 3·7 Å. Thus the chloro-groups need not touch in (Mo_6Cl_8) but the bromo-groups probably do so in (Mo_6Br_8) and some steric strain is likely. Hence more room for S_N2 attack probably exists in the chloromolybdenum(II) than in the bromomolybdenum(II) group and the higher E_a and lower hydrolysis rates for the latter may thus be explained.

Experimental.—The octa-μ_4-chloro- and octa-μ_3-bromo-hexamolybdenum(II) tetrahydroxides were prepared as previously described.[1,2] The kinetic procedure was essentially identical to that for the hydrolysis of the chloromolybdate(II).[1] The supporting uni-univalent electrolyte was sodium perchlorate. In general the samples for the assay of reaction progress were discharged into ice-cold excess of acetic acid solution containing sufficient sulphurous acid to destroy the hydrogen peroxide, and then titrated with silver nitrate to the potentiometric endpoint. The two reactions followed spectrophotometrically relied on the assay of unchanged bromomolybdate by the determination of the optical densities of diluted portions at 330 mμ, at which wavelength the bromomolybdate(II) ion possesses a band maximum of ε 5 × 10^3.

DEPARTMENT OF PHYSICAL AND INORGANIC CHEMISTRY,
THE UNIVERSITY OF ADELAIDE, BOX 498D, G.P.O.,
ADELAIDE, SOUTH AUSTRALIA.

[*Received, September* 30*th*, 1963.]

---

[3] Stransk, "Modern Coordination Chemistry," Interscience Publishers, Inc., New York–London, 1960, p. 118.

[4] Brosset, *Arkiv Kemi, Min., Geol.*, 1946, **20**, *A*, No. 7, *ibid.*, 1947, **22**, *A*, No. 11.