

791. S_N2 Hydroxide Attack on the Chloromolybdate(II) Group.

By J. C. SHELDON.

Replacement of chlorine by hydroxyl in the hexahydroxo-octachlorohexamolybdate(II) ion, $[\text{Mo}_6\text{Cl}_8(\text{OH})_6]^{2-}$, proceeds at a convenient rate at 30° , giving reducing molybdenum(II) species. The rate of replacement was followed at early reaction times by argentimetric assay of released chloride, and over the whole reaction time by permanganate titration of the molybdenum(II) products. In both cases the rate follows second-order kinetics, being dependent on chloromolybdate(II) and hydroxide ion concentration. A bimolecular process is shown to be reasonable for replacement in the chloromolybdenum(II) group since its structure can be regarded as rigid and a unimolecular rate-determining step would involve very high activation energy.

This investigation is part of a study of the chemistry of octa- μ_3 -halogenohexamolybdenum(II) compounds, referred to below in short as halogenomolybdenum(II) compounds, which contain polynuclear groups (Mo_6X_8). These compounds provided early examples of "kinetically inert" complexes since it was known in 1859¹ that hydroxide ions would replace only one-third of the halogen atoms of molybdenum(II) chloride and bromide with any rapidity. The reaction can be written, $(\text{Mo}_6\text{X}_8)\text{X}_4 + 4\text{OH}^- \longrightarrow \text{Mo}_6\text{X}_8(\text{OH})_4 + 4\text{X}^-$. Since the remaining bound halogen is replaced by hydroxide at a low rate quite convenient for kinetic study, it has been the object of the present kinetic investigation.

The Chemistry of the Alkaline Hydrolysis of the Chloromolybdenum(II) Groups.—Chloromolybdenum(II) tetrahydroxide, $\text{Mo}_6\text{Cl}_8(\text{OH})_4 \cdot 14\text{H}_2\text{O}$, is freely soluble in 0.01–2M-sodium hydroxide, forming the hexahydroxo-octachlorohexamolybdate(II) ion: $\text{Mo}_6\text{Cl}_8(\text{OH})_4 + 2\text{OH}^- \rightleftharpoons [\text{Mo}_6\text{Cl}_8(\text{OH})_6]^{2-}$.² Preliminary results of the photolysis of alkaline chloromolybdate(II) solutions by visible and ultraviolet light indicate that the thermal hydroxide-chloromolybdate(II) reaction is the only process likely in shaded roomlight. The products of the alkaline hydrolysis are not completely known but a reasonable working hypothesis is that the $[\text{Mo}_6\text{Cl}_8(\text{OH})_6]^{2-}$ ion suffers stepwise introduction of hydroxyl with simultaneous release of chloride, to give successive products of the type $\{[\text{Mo}_6\text{Cl}_{8-n}(\text{OH})_n](\text{OH})_6\}^{2-}$ where n is 1, 2, 3, etc. It is known that the μ_3 -hydroxochloromolybdenum(II) products with $n \geq 4$ are insoluble in alkali and that the eventual product of alkaline hydrolysis is a precipitate, probably best formulated as $\{[\text{Mo}_6\text{Cl}_{8-n}(\text{OH})_n](\text{OH})_4\} \cdot m\text{H}_2\text{O}$.³ This precipitate and one or more of the soluble μ_3 -hydroxochloromolybdate(II) products, *i.e.*, those with $n \leq 4$, are strong reducing agents.

Table I reports the hydrolysis of hexahydroxochloromolybdate(II) by M-hydroxide at 30° ; its progress was followed by titrating acidified aliquot parts with permanganate solution. The number of equivalents of permanganate required per mole of chloromolybdate(II) approaches a limit of 24. This establishes that the reaction products contain only molybdenum(II) since $\text{Mo}_6^{\text{II}} \longrightarrow 6\text{Mo}^{\text{VI}} + 24\text{e}$.

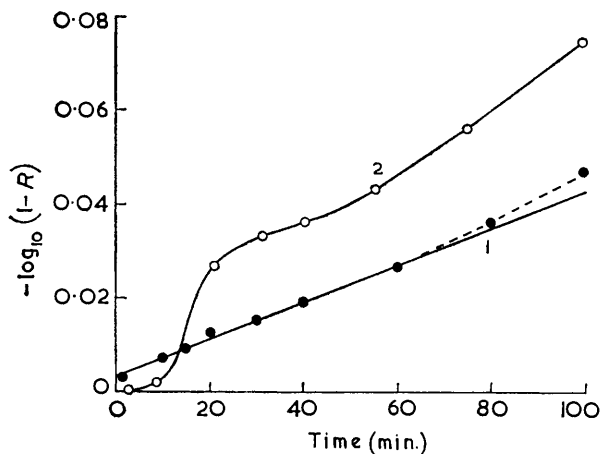
TABLE I.

Time (min.)	1.5	8.5	17.5	29.0	41.5	74	290
Equivs. of MnO_4^- per mole of $[\text{Mo}_6\text{Cl}_8(\text{OH})_6]^{2-}$	2.1	8.8	14.3	17.9	20.4	21.6	23.1

The Kinetics of Introduction of Hydroxyl into Chloromolybdenum(II) Groups.—(i) *Chloride release.* The hydroxide ion concentration employed was a hundred to a thousand times that of chloromolybdate(II) in order to obtain prompt solution of the chloromolybdenum(II)

¹ Blomstrand, *J. prakt. Chem.*, 1859, **77**, 88.² Sheldon, *Nature*, 1959, **184**, 1210.³ Sheldon, *Chem. and Ind.*, 1961, 323.

tetrahydroxide at the commencement of a kinetic run and to simplify the interpretation of the rate data. The data were treated on the assumption that the rate has first-order dependence on the chloromolybdate(II) concentration and is pseudo-independent of hydroxide concentration. There are probably successive reactions of differing rates, but analysis of the results in terms of successive rate constants is here impossible. Nevertheless an *apparent* rate constant which serves as a useful relative measure of rate can be derived for early reaction times from the plot of $-\log_{10}(1-R)$ (where R is the fraction of initially combined chloride that is released in time t) against t , since this produces curves with a nearly linear initial portion, though they later develop pronounced curvature. An example is curve 1 in the Figure. Plotting the data on pseudo-second-order kinetics was less satisfactory. It should be noted that these apparent rate constants are properly expressed in terms of moles of hexahydroxochloromolybdate(II) ion since no attempt is, or can be, made to express the rate in terms of individual chlorine-atom replacements.



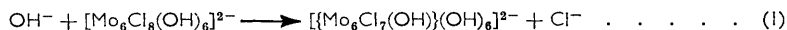
First-order rate plots of chloride release at 30° in 0.05M-hydroxide. (1) Normal form. (2) Abnormal form.

Sixteen runs were carried out at 30° at a constant ionic strength (molar in uni-univalent electrolyte) with a twelve-fold variation of chloromolybdate(II) concentration and a twenty-fold variation of hydroxide ion concentration. Four of these runs were rejected since they showed unsatisfactory features. A further seven runs were carried out at lower ionic strength and one run rejected. The pseudo-first-order rate constants (apparent) obtained from the initial slopes of the rate curves show a proportional dependence on the hydroxide ion concentration, and the second-order constant is thus obtained by dividing the former constant by the hydroxide ion concentration. Table 2 sets out the apparent second-order constants (k_{app}) obtained against the concentration of reactants and uni-univalent electrolyte at 30° . At constant ionic strength of 1.0 there is a $\pm 20\%$ variation shown about the mean value of 1.7×10^{-2} mole $^{-1}$ min. $^{-1}$ of the apparent rate

TABLE 2.

Concn. (mole l. $^{-1}$) [(Mo $_6$ Cl $_8$)(OH) $_6$] $^{2-}$	OH $^-$	Uni-univalent electrolyte	$10^2 k_{app}$ (mole $^{-1}$ min. $^{-1}$)	Concn. (mole l. $^{-1}$) [(Mo $_6$ Cl $_8$)(OH) $_6$] $^{2-}$	OH $^-$	Uni-univalent electrolyte	$10^2 k_{app}$ (mole $^{-1}$ min. $^{-1}$)
0.0017	1.0	1.0	1.5	0.0007	0.1	1.0	1.6
0.0017	1.0	1.0	1.7	0.0016	0.1	1.0	2.1
0.0020	1.0	1.0	1.6	0.0007	0.05	1.0	1.7
0.0024	1.0	1.0	1.7	0.0008	0.1	0.1	0.8
0.0044	1.0	1.0	1.5	0.0020	0.1	0.1	0.5
0.0048	1.0	1.0	1.9	0.0022	0.1	0.1	0.7
0.0004	0.5	1.0	1.4	0.0025	0.1	0.1	0.7
0.0016	0.5	1.0	2.1	0.0050	0.1	0.1	0.8
0.0025	0.5	1.0	1.4	0.0020	0.02	0.02	0.8

constant. This is considered to be of small significance in view of the difficulty of deriving constants from initial slopes, and of the possibilities of unknown minor factors, *e.g.*, catalysis or variable degrees of precipitation of products, in a little studied system. The rates are thus reasonably explained in terms of second-order kinetics and suggest a bimolecular process,



The dependence of the rate constant on ionic strength is a further indication that the reacting species are ions, as required by the above equation.

It was stated above that a number of runs were rejected and the reason is that the rate curves displayed a curious form. The Figure shows two pseudo-first-order rate plots for chloride release at 30° with 0.05M hydroxide. Curve 1 is typical of most of the experimental curves and yields an acceptable apparent rate constant. Curve 2 displays an initially sigmoid curve, followed by a straight-line portion of greater than normal slope. Such results were rare and the case described is an extreme example. The sigmoid curve is suggestive of autocatalysis, but no explanation of the phenomenon has yet been evolved.

(ii) *Oxidimetrically determined rates.* The progress of hydrolysis may be followed over the whole reaction time by permanganate titration of the products. It was again assumed that the rate showed first-order dependence on chloromolybdate(II) and pseudo-independence of hydroxide ion concentration. Plots of $-\log(1 - R')$ (where R' is the fraction of permanganate required at time t of the total theoretically required at infinite time) against t are linear up to at least 70% reaction. Thereafter, deviation from linearity is observed and is probably due to atmospheric or aqueous oxidation [hydrogen is evolved from warm hydrolysing chloromolybdate(II) solutions] of the products. That the rate obeys a simple first-order rate law indicates that only one rate-determining step is involved in the production of reducing molybdenum(II) species. Since hydrolysing chloromolybdate(II) solution gives a detectable permanganate titre even at the earliest reaction times (*i.e.*, there is no induction period), it follows that the reducing molybdenum(II) species are formed swiftly after the primary substitution [*i.e.*, eqn. (1)] or possibly by this step alone. In either case it is reasonable that eqn. (1) represents the rate-determining step for oxidimetrically determined rates. The second-order rate constants obtained from six out of eight runs at 30° and in molar uni-univalent electrolyte are given in Table 3.

TABLE 3.

Concn. (mole l. ⁻¹)		10 ² <i>k</i> (mole ⁻¹ min. ⁻¹)	Concn. (mole l. ⁻¹)		10 ² <i>k</i> (mole ⁻¹ min. ⁻¹)
[(M ₆ Cl ₈)(OH) ₆] ²⁻	OH ⁻		[(M ₆ Cl ₈)(OH) ₆] ²⁻	OH ⁻	
0.0007	1.0	5.0	0.0013	0.1	4.8
0.0020	1.0	4.9	0.0015	0.1	4.8
0.0038	1.0	4.1			

A restricted number of runs was carried out at the additional temperatures of 20°, 40°, and 50° and the rate constants were 1.3, 13, and 34 (all $\times 10^{-2}$, mole⁻¹ min.⁻¹), respectively. The Arrhenius activation energy was about 21 kcal. mole⁻¹.

Discussion.—The second-order dependence of the rate is significant and in contrast to the alkaline hydrolysis of chloroplatinate(II) complexes which proceeds by first-order kinetics. Although chlorocobalt(III) complexes undergo hydroxide attack with second-order kinetics, there has been an inclination to interpret this by a unimolecular conjugate-base reaction path. Since reactions of the chloromolybdate(II) ion can hardly be assigned such a mechanism, as this ion contains no aquo- or amino-groups, S_N2 hydroxide attack remains the best account of the present results. This mechanism is all the more probable in view of the likely nature of the activated complex for an S_N1 process. It is usually granted that a reaction intermediate of lower co-ordination number than the initial and the final compound may be stabilised and formed at a lower energy of activation by stereochemical rearrangement. For example, it is reasonable that a five-co-ordinate intermediate

in octahedral substitution should be a trigonal-bipyramid. Since the bonding within the Mo_6Cl_8 group provides what appears to be a unique and effective type of bracing, this group ought to be too rigid to be distorted to a less energetic activated complex of reduced co-ordination number. An S_N1 process would probably involve removal of a chloro-group, creating a complete vacancy and requiring a greater expenditure of energy than the synchronised bond-making and -breaking of the S_N2 mechanism.

Experimental.—Octa- μ_3 -chlorohexamolybdenum(II) tetrahydroxide-14-water was prepared as previously described.⁴ The kinetic procedure was as follows. The prepared solution of known hydroxide ion concentration and total uni-univalent electrolyte strength (by appropriate addition of sodium perchlorate) was equilibrated to the desired temperature. The approximate amount of powdered chloromolybdenum(II) tetrahydroxide was added to the solution at zero time, and complete dissolution of the tetrahydroxide could usually be obtained in $\frac{1}{4}$ — $\frac{3}{4}$ min. by swirling the solution. The concentration of chloromolybdate(II) was determined by estimation of chloride in an aliquot part of solution after decomposition of the chloromolybdate(II) by boiling hydrogen peroxide. In general, aliquot parts for assay of the reaction progress were discharged into an excess of ice-cold acid and analysed in the normal manner with silver nitrate (potentiometrically with silver and glass electrodes) or potassium permanganate.

DEPARTMENT OF PHYSICAL AND INORGANIC CHEMISTRY,
THE UNIVERSITY OF ADELAIDE,
ADELAIDE, SOUTH AUSTRALIA.

[Received, November 12th, 1962.]

⁴ Sheldon, J., 1960, 1007.
