Kinetics of Reduction of Hexachlororuthenate(IV) in Hydrochloric Acid Solutions

By **John A. Cook** and **David A. Rice,*** Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD

The reduction of $[RuCl_6]^{2-}$ by Br^- in 6.15 mol dm^{-3} HCl is first order in the concentrations of the reactants. At 298.1 K the second-order rate constant is $(7.24 \pm 0.25) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} and $\Delta H^‡ = 59.2 \pm 6.3$ kJ mol^{-1} and $\Delta S^‡ = -86.9$ J K^{-1} mol^{-1}. The products of the reaction are $[RuCl_6]^{3-}$ and bromine. The reaction proceeds to the equilibrium $[RuCl_6]^{2-} + Br^- \rightleftharpoons [RuCl_6]^{3-} + \frac{1}{2} Br_2$ whose constant at 298 K and in 6.15 mol dm^{-3} HCl is 1.06 ± 0.03 $dm^{\frac{3}{2}}$ $mol^{-\frac{1}{2}}$. In concentrated hydrochloric acid $[RuCl_6]^{2-}$ slowly and spontaneously reduces. The initial rate is proportional to the 0.6 power of the initial ruthenium concentration. The reduction process is complicated and appears to be catalysed by an unknown impurity in the concentrated acid.

ASSIGNMENTS have been made for the ultraviolet–visible spectra of the hexachloro-anions $[RuCl_6]^{2-}$ and $[RuCl_6]^{3-}$.[1] The spectra were obtained by measurements on concentrated hydrochloric acid solutions containing the appropriate hexachloro-salt. We observed that the u.v.–visible spectrum of an 11.3 mol dm^{-3} HCl solution containing $[RuCl_6]^{2-}$ changed over a period of days. Initially the spectrum resembled the diffuse-reflectance spectrum of the species $K_2[RuCl_6]$ which is known to contain $[RuCl_6]^{2-}$,[2] but ultimately the spectrum was that of $[RuCl_6]^{3-}$.[1,3] Other workers noted that the u.v.–visible spectrum of alcoholic solutions of $[RuCl_6]^{2-}$ changed with time [4] and they suggested that ruthenium(III) species were formed, the reduction being inhibited by the addition of chloride ion.[5]

We now report a kinetic study of the reduction of $[RuCl_6]^{2-}$ by bromide ion in 6.15 mol dm^{-3} HCl solutions and some observations on the spontaneous reduction of $[RuCl_6]^{2-}$ in AnalaR HCl solution. Under both sets of conditions, reactions involving the aquation of $[RuCl_6]^{2-}$ can be ignored.[5,6]

EXPERIMENTAL

Solvents and Reagents.—AnalaR hydrochloric acid was used as supplied. 6.15 mol dm^{-3} Hydrochloric acid was obtained by the appropriate dilution of AnalaR acid with distilled water. The resulting solution was distilled and the middle fraction collected. The samples of Group 1A halides were obtained by recrystallisation of AnalaR reagents.

---

[1] C. K. Jørgensen, *Mol. Phys.*, 1959, **2**, 309.

[2] D. A. Adams and D. P. Mellor, *Austral. J. Sci. Res.*, 1952, **5**, 577.

[3] M. G. B. Drew, D. A. Rice, and C. W. Timewell, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 59.

[4] N. K. Pshenitsyn and N. A. Ezerskaya, *Russ. J. Inorg. Chem.*, 1961, **6**, 312.

[5] K. A. Bolshakov, N. M. Sinitsyn, V. V. Borisov, and S. M. Vaseneva, *Russ. J. Inorg. Chem.*, 1971, **16**, 1047.

[6] K. A. Bolshakov, N. M. Sinitsyn, and V. V. Borisov, *Russ. J. Inorg. Chem.*, 1972, **17**, 1731.

Preparations.—$[NEt_4]_2[RuCl_6]$. A concentrated HCl solution of ruthenium(III) chloride was shaken with mercury to reduce any trace of Ru^{IV} that might be present as an impurity. The mixture was filtered and to the filtrate was added a 6 mol dm^{-3} excess of tetraethylammonium chloride. The resulting solution was allowed to evaporate on a water-bath until red-brown crystals were formed (Found: C, 33.6; H, 7.1; N, 4.8; Ru, 17.7. Calc. for $[NEt_4]_2[RuCl_6]$: C, 33.4; H, 7.0; N, 4.9; Ru, 17.6%).

The corresponding potassium salt was prepared by the published method.[7]

Solution Preparation and Temperature Control.—The temperatures of the solutions were controlled with a conventional thermostatted water-bath to ±0.1 K. In the experiments in which the solvent was **11.3** mol dm^{-3} HCl the solvent was allowed to attain the bath temperature and a weighed sample of the solid containing $[RuCl_6]^{2-}$ was quickly added. When the bromide ion was the reducing agent the reaction solution was obtained by mixing thermostatted solutions of potassium bromide and $[RuCl_6]^{2-}$, both solutions being made up in 6.15 mol dm^{-3} HCl. The half-lives of the reactions were always such that mixing times were negligible.

TABLE 1

Spontaneous reduction of $[RuCl_6]^{2-}$ in hydrochloric acid

$10^4[RuCl_6^{2-}]_0$ / mol dm^{-3}	$10^9(-d[RuCl_6^{2-}]/dt)$ / mol dm^{-3} s^{-1}	T / K	Acid batch no.	[Acid] / mol dm^{-3}	10^6k [a] / (mol dm^{-3})$^{0.4}$ s^{-1}
3.89	12.23	298.1	1	11.3	
3.86	12.2	298.1	1	11.3	
3.28	11.0	298.1	1	11.3	
3.20	10.9	298.1	1	11.3	
2.78	9.9	298.1	1	11.3	
2.28	8.9	298.1	1	11.3	
1.73	7.5	298.1	1	11.3	
1.67	7.3	298.1	1	11.3	
1.07	5.6	298.1	1	11.3	
0.40	2.64	298.1	1	11.3	1.3 ± 0.05
1.00 – 4.00	*b*	298.1	2	11.3	0.24 ± 0.03
1.00 – 8.00	*b*	333.1	3	11.3	3.70 ± 0.35
0.54 – 4.50	*b*	333.1	3	6.15 [c]	0.098 ± 0.02
0.50 – 4.50	*b*	333.1	3	6.15 [d]	0.67 ± 0.03

[a] Defined by $-d[RuCl_6^{2-}]/dt = k[RuCl_6^{2-}]^{0.6}$. [b] Not applicable as the data refer to a range of concentrations. [c] Obtained by distillation of AnalaR acid batch 3. [d] Obtained by dilution of AnalaR acid batch 3.

Monitoring the Spontaneous Reduction of $[RuCl_6]^{2-}$ *and its Reduction by* Br^-.—The reduction reactions were followed by observing the decrease in intensity of the absorption band at 486 nm in the spectrum of $[RuCl_6]^{2-}$ with a Unicam SP 1800 spectrophotometer. At this wavelength $[RuCl_6]^{3-}$ and other likely products such as $[Br_2Cl]^-$ have negligible absorbance. The growth in concentration of $[RuCl_6]^{3-}$ was followed by monitoring the intensity of the absorbance at 349 nm, although a correction had to be applied for the absorbance of $[RuCl_6]^{2-}$ at this wavelength. In all the kinetics experiments, at any given time the sum of the concentrations of $[RuCl_6]^{2-}$ and $[RuCl_6]^{3-}$ was equal to the initial concentration of $[RuCl_6]^{2-}$. After the first half-life in the reduction of $[RuCl_6]^{2-}$ by Br^-, an absorption at 400 nm began to appear. This is attributable to $[Br_2Cl]^-$ whose formation is to be expected compared to $[Br_3]^-$ and $[BrCl_2]^-$ when the relative stability constants [8,9] and concentrations of the reacting species are considered.

The absorption coefficient of $[RuCl_6]^{2-}$ at 486 nm was obtained by monitoring the absorbance of a **11.3** mol dm^{-3} HCl solution of $[RuCl_6]^{2-}$ over a period of time. The reciprocal of absorbance at 486 nm was plotted against time and by extrapolation to zero time a value of 5 028 dm^3 mol^{-1} cm^{-1} was obtained for the absorption coefficient. This value is to be compared with the literature value of 4 400 dm^3 mol^{-1} cm^{-1} which was obtained without taking account of the spontaneous reduction of $[RuCl_6]^{2-}$ in 11.3 mol dm^{-3} HCl.[1]

Bromine concentrations were measured by extracting the solutions with a chlorinated hydrocarbon solvent followed by measurement of the u.v.–visible spectrum. The concentration of the chloride ion in the solvent medium was monitored throughout the reaction by the usual analytical techniques to verify that no loss of HCl had occurred.

RESULTS AND DISCUSSION

(a) *The Spontaneous Reduction of* $[RuCl_6]^{2-}$ *in* **11.3** *mol dm*$^{-3}$ HCl *Solution*.—The spontaneous reduction of $[RuCl_6]^{2-}$ to $[RuCl_6]^{3-}$ in **11.3** mol dm^{-3} HCl was followed by observing the changes in the u.v.–visible spectrum of the solution with time. Two isosbestic points at 320 (ε 2 300) and 375 nm (ε 2 750 dm^3 mol^{-1} cm^{-1}) were detected, thus indicating the reduction to be a simple process and that no long-lived intermediates were formed.

Summarised in Table 1 are the results obtained from studying the kinetics of the spontaneous reduction of $[RuCl_6]^{2-}$ in concentrated HCl. The initial rate of reduction was dependent on the 0.6 power of the initial ruthenium concentration, and the rate constant was the same for the tetraethylammonium and potassium salts. The rate constant, however, varied with the batch of acid employed as solvent, thus suggesting the interference of some impurity in the acid. Unsuccessful attempts were made to try and identify the impurity by monitoring the reduction in acid solutions to which various ions known to catalyse reduction reactions [such as sulphate, mercury(II), and lead(II), *etc.*] had been added. The most probable oxidation product from the reduction of $[RuCl_6]^{2-}$ was thought to be chlorine, but all attempts to detect it by extraction with chlorinated solvents failed, although heating of powdered $K_2[RuCl_6]$ is known to lead to the formation of chlorine and $K_2[RuCl_5]$.[10]

---

[7] J. L. Howe, *J. Amer. Chem. Soc.*, 1904, **26**, 543.

[8] R. P. Bell and M. Pring, *J. Chem. Soc.* (*A*), 1966, 1607.

[9] D. B. Scaife and J. J. V. Tyrrell, *J. Chem. Soc.*, 1958, 386.

[10] J. L. Howe, *J. Amer. Chem. Soc.*, 1927, **49**, 2381.

The spontaneous reduction was also studied in distilled 6.15 mol dm^{-3} HCl solutions of $[RuCl_6]^{2-}$. The rate of reaction was so slow at 298.1 K that meaningful measurements could only be obtained at 333.1 K. The reduction still depended on the 0.6 power of the initial $[RuCl_6]^{2-}$ concentration, but comparison of the value of the rate constant [9.8×10^{-8} (mol dm^{-3})$^{0.4}$ s^{-1}] with that obtained for a 6.15 mol dm^{-3} HCl solution obtained by dilution of a sample of AnalaR HCl [6.7×10^{-7} (mol dm^{-3})$^{0.4}$ s^{-1}] revealed the influence of the unknown impurity (Table 1).

TABLE 2

Equilibrium constant for the reaction $[RuCl_6]^{2-} + Br^- \rightleftharpoons [RuCl_6]^{3-} + \frac{1}{2}Br_2$ at 298.1 K

$10^4[RuCl_6^{2-}]$ / mol dm^{-3}	$10^4[RuCl_6^{3-}]$ / mol dm^{-3}	$10^2[Br^-]$ / mol dm^{-3}	$10^2[Br_2]^{\frac{1}{2}}$ / mol$^{\frac{1}{2}}$ dm$^{-\frac{3}{2}}$	K_2 / dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$	
(*a*) in 6.15 mol dm^{-3} distilled HCl					
0.66	3.20	5.98	1.26	1.03	
0.84	2.00	4.00	1.22	1.09	
0.71	2.20	3.03	1.05	1.08	
0.23	1.61	6.00	0.90	1.06	
0.37	1.40	2.99	0.84	1.07	
0.19	1.70	8.02	0.92	1.04	
0.21	1.71	7.00	0.92	1.06	
(*b*) In mixed LiCl and distilled HCl such that $[Cl^-]_T$ = 6.15 mol dm^{-3}					$[H^+]$ / mol dm^{-3}
0.12	2.06	5.00	1.00	3.24	0.18
0.11	1.83	5.00	0.96	3.24	0.49
0.12	1.87	4.99	0.97	3.03	1.04
0.14	1.79	4.00	0.90	3.02	3.05
0.10	1.85	4.97	0.97	3.20	4.04
0.11	1.91	5.00	0.98	3.26	5.12

(b) *The Reduction of* $[RuCl_6]^{2-}$ *by* Br^-.—As stated earlier we believe that the primary product of the spontaneous reduction of $[RuCl_6]^{2-}$ in concentrated HCl is chlorine, although no experimental proof has been obtained. Accordingly, we tested the effect of the addition of iodide and bromide ions to concentrated HCl solutions of $[RuCl_6]^{2-}$. Iodide ion caused instantaneous reduction of $[RuCl_6]^{2-}$ to $[RuCl_6]^{3-}$, the other product being iodine, while bromide ion caused a slow reduction. Preliminary experiments showed that the reduction of $[RuCl_6]^{2-}$ in distilled 6.15 mol dm^{-3} HCl by bromide ion leads to the formation of bromine and $[RuCl_6]^{3-}$. In the reaction an equilibrium is established in accordance with equation (1). Recorded in Table 2

$$[RuCl_6]^{2-} + Br^- \rightleftharpoons [RuCl_6]^{3-} + \tfrac{1}{2}Br_2 \qquad (1)$$

are the values for the equilibrium constant which varied with the medium. Thus in 6.15 mol dm^{-3} HCl the constant was 1.06 ± 0.03 dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$ at 298.1 K, while in HCl–LiCl where the chloride concentration was kept at 6.15 mol dm^{-3} (that is, constant ionic strength) the value was 3.1 ± 0.1 dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$. From the value of the equilibrium constant it can be seen that the couple $[RuCl_6]^{2-}$–$[RuCl_6]^{3-}$ in 6.15 mol dm^{-3} HCl must be close to 1.085 V, the potential of the Br_2–Br^- couple under standard conditions.[11]

The kinetics of the reduction of $[RuCl_6]^{2-}$ by bromide ion were studied in 6.15 mol dm^{-3} HCl solutions where the bromide concentration greatly exceeded the concentration of $[RuCl_6]^{2-}$. Thus under these conditions the rate of the reverse reaction, *i.e.* the oxidation of $[RuCl_6]^{3-}$ by bromine, was negligible and the bromide concentration was effectively constant. By keeping the initial bromide concentration constant and varying the initial concentration of $[RuCl_6]^{2-}$, it was shown the rate of reduction followed the rate equation (2). Repeating

$$\frac{-d[RuCl_6^{2-}]}{dt} = k_1[RuCl_6^{2-}] \qquad (2)$$

the experiments with a range of initial bromide concentrations (see Table 3) showed k_1 to be a pseudo-first-order rate constant and that the true rate equation is as in (3).

$$\frac{-d[RuCl_6^{2-}]}{dt} = k_2[Br^-][RuCl_6^{2-}] \qquad (3)$$

TABLE 3

Determination of the order of the reaction between $[RuCl_6]^{2-}$ and Br^- in medium-distilled 6.15 mol dm^{-3} HCl at 298.1 K

$10^4[RuCl_6^{2-}]$ / mol dm^{-3}	$10^2[Br^-]$ / mol dm^{-3}	10^4k_1 * / s^{-1}	10^3k_2 * / dm^3 mol^{-1} s^{-1}
3.86	3.00	2.14	7.12
2.91	3.03	2.14	7.09
1.77	2.99	2.12	7.12
1.77	4.01	2.84	7.08
3.79	4.01	2.97	7.41
1.92	4.99	3.61	7.23
1.84	6.00	4.35	7.25
1.92	7.00	5.28	7.54
1.89	8.02	5.85	7.29

* Defined by $-d[RuCl_6^{2-}]/dt = k_2[Br^-][RuCl_6^{2-}]$ and k_1 (the pseudo-first-order constant) $= k_2[Br^-]$.

Having observed the change in equilibrium constant for (1) caused by replacing hydrogen ion by lithium ions (Table 1), the kinetics of the reduction reaction were investigated in a range of HCl–LiCl mixtures (Table 4). The order of the reaction was identical to that observed in 6.15 mol dm^{-3} HCl; however, the rate constant

---

[11] G. Charlot, 'Selected Constants: Oxidation–Reduction Potentials of Inorganic Substances in Aqueous Solution,' I.U.P.A.C., Butterworths, 1971.

varied with hydrogen-ion concentration, being largely constant in the range $[H^+] = 0.18—3.05$ mol dm^{-3} and then increasing with $[H^+]$ to $(7.24 \pm 0.25) \times 10^{-3}$ mol dm^{-3} s^{-1} at 298 K in 6.15 mol dm^{-3} HCl. The increase in rate constant over the range $[H^+] = 5.4—5.7$ mol dm^{-3} was quite large. However, the reported change was reproducible.

The reduction of $[RuCl_6]^{2-}$ by bromide ion was studied over a temperature range using two solvents (Table 5). With distilled 6.15 mol dm^{-3} HCl as solvent the enthalpy of activation was 59.2 ± 6.3 kJ mol^{-1} and the entropy of activation -86.9 ± 17.0 J K^{-1} mol^{-1}. The comparable values with a solvent consisting of 2.47 mol dm^{-3} HCl and 3.68 mol dm^{-3} LiCl were $\Delta H^\ddagger = 68.2 \pm 3.0$ kJ mol^{-1} and $\Delta S^\ddagger = -60.6 \pm 8.8$ J K^{-1} mol^{-1}. These values are in the same range as those obtained for other metal-ion–ligand redox reactions where the metal ion does not undergo a change in its co-ordination sphere. Examples are the reactions of $[Fe(CN)_6]^{2-}$ with $[S_2O_8]^{2-}$ ($\Delta H^\ddagger = 63.1$ kJ mol^{-1}, $\Delta S^\ddagger = -114.9$ J K^{-1} mol^{-1}),[12] $[LiFe(CN)_6]^{2-}$ with $[S_2O_8]^{2-}$ ($\Delta H^\ddagger = 42.4$ kJ mol^{-1}, $\Delta S^\ddagger = -118.2$ J K^{-1} mol^{-1}),[12] and $[Fe(phen)_3]^{2+}$ with $[ClO]^-$ ($\Delta H^\ddagger = 105.3$ kJ mol^{-1}, $\Delta S^\ddagger = -58.9$ J K^{-1} mol^{-1}; phen = 1,10-phenthroline).[13]

TABLE 4

Effect of variation of hydrogen-ion concentration on the rate constant for the reaction between $[RuCl_6]^{2-}$ and Br$^-$. Total concentration of HCl and LiCl kept at 6.15 mol dm^{-3}, 298.1 K

$10^4[RuCl_6^{2-}]$ / mol dm^{-3}	$10^2[Br^-]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	10^3k_2 / dm^3 mol^{-1} s^{-1}
2.18	5.01	0.18	5.12
1.94	5.00	0.49	5.01
1.99	4.90	1.04	5.13
1.93	4.00	3.05	5.06
1.95	4.97	4.04	5.23
2.02	5.01	5.12	5.65
2.04	5.01	5.44	5.68
1.92	5.02	5.73	7.30

TABLE 5

Effect of temperature on the second-order rate constants for the reaction of $[RuCl_6]^{2-}$ with Br$^-$

T / K	$10^2[Br^-]$ / mol dm^{-3}	10^3k_2 / dm^3 mol^{-1} s^{-1}
(*a*) in 6.15 mol dm^{-3} distilled HCl, $[RuCl_6^{2-}] = 2 \times 10^{-4}$ mol dm^{-3}		
303	3.00	8.42
308	3.00	13.59
313	2.25	19.97
318	1.52	29.66
323	0.99	38.57
$\Delta H^\ddagger = 59.2 \pm 6.1$ kJ mol^{-1}, $\Delta S^\ddagger = -86.9 \pm 17.0$ J K^{-1} mol^{-1}, $E^\ddagger = 63.7 \pm 5.1$ kJ mol^{-1}, $A = 10^{8.74}$ dm^3 mol^{-1} s^{-1}.		
(*b*) In a solution containing 2.47 mol dm^{-3} HCl and 3.68 mol dm^{-3} LiCl		
303	3.00	7.74
308	3.00	12.00
313	2.24	18.56
318	1.50	28.33
323	1.00	44.20
$\Delta H^\ddagger = 68.2 \pm 3.0$ kJ mol^{-1}, $\Delta S^\ddagger = -60.6 \pm 8.8$ J K^{-1} mol^{-1}, $E^\ddagger = 70.8 \pm 2.0$ kJ mol^{-1}, $A = 10^{10.1}$ dm^3 mol^{-1} s^{-1}.		

The role of the cation in the reduction is presumably to act as a bridge between the two reacting anions $[RuCl_6]^{2-}$ and Br$^-$. In solutions of such high concentrations of LiCl and HCl as were necessary to prevent aquation reactions, it is possible that $[MRuCl_6]^-$ could be present and take part in the reduction process. A related species, $[HFe(CN)_6]^{3-}$, is thought to be involved at high acid concentrations in the reaction between $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$.[14]

[6/911 *Received*, 13*th May*, **1976**]

---

[12] R. W. Chlebek and M. W. Lister, *Canad. J. Chem.*, 1971, **49**, 2943.

[13] M. G. Ondras and G. Gordon, *Inorg. Chem.*, 1971, **10**, 474.

[14] M. Shporer, G. Ron, A. Loewenstein, and G. Wavon, *Inorg. Chem.*, 1965, **4**, 361.