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Kinetic Study of the MnO_4^-–$Ru(CN)_6^{4-}$ Reaction in Acid Perchlorate Media

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The study of the MnO_4^-–$Ru(CN)_6^{4-}$ reaction in acid perchlorate media ($\mu = 1.02$) was investigated by stopped-flow techniques. The study showed a "bell-like" dependence of k_{obsd} on log $[H^+]^{-1}$ and a region in which k_{obsd} was independent of log $[H^+]^{-1}$. Equilibrium constants for the dissociation of two protonated forms of $Ru(CN)_6^{4-}$ ($K_4 = 0.002\,97$ and $K_3 = 0.003\,43$) were obtained from the kinetic data by conventional computer methods. The reaction is compared with the MnO_4^-–$Fe(CN)_6^{4-}$ reaction and several other MnO_4^-–reductant ion systems which have been shown to be of the outer-sphere type.

The reaction between the permanganate MnO_4^- and hexacyanoferrate(II), $Fe(CN)_6^{4-}$, has been shown to be a simple second-order process involving the outer-sphere interaction of these inert and stable ions.[1] Of particular interest was the distinctive dependence of the observed rate constant on pH. The plot of k_{obsd} vs. pH indicated two regions in which the reaction rate was independent of hydrogen ion. The results were interpreted in terms of the reaction between an unprotonated MnO_4^- ion and protonated and unprotonated species of $Fe(CN)_6^{4-}$.

As part of a study of the oxidation of various inert cyanometalate complexes, hexacyanoruthenate(II), $Ru(CN)_6^{4-}$, the second-row member of the iron family, was chosen to determine if a reaction pattern similar to that of the Fe(II) analogue was present in its reaction with MnO_4^-. This study would also provide further comparison of results obtained in the oxidation of $Mo(CN)_8^{4-}$[2] and $W(CN)_8^{4-}$[3] by MnO_4^-. Results from these studies showed the presence of the protonated and unprotonated forms of Mn(VII) and that the larger $W(CN)_8^{4-}$ ion was the more reactive.[3]

Experimental Section

$K_4Ru(CN)_6 \cdot 3H_2O$ was purchased from Ventron Chemical and used as received. Weighed samples of $K_4Ru(CN)_6 \cdot 3H_2O$ were dissolved in triple-distilled water and titrated spectrophotometrically with a standardized Ce(IV) solution. The analyses corresponded to a sample ~98.5% Ru(II). Molar absorption coefficients obtained from spectrophotometric titrations gave values for $Ru(CN)_6^{3-}$ in agreement with literature ($\lambda = 462$ nm, $\epsilon = 1005 \pm 56$ M^{-1} cm^{-1}; $\lambda = 325$ nm, $\epsilon = 2268 \pm 123$ M^{-1} cm^{-1}).[4,5] Analyses and all kinetic runs were performed under red-light conditions to avoid decomposition of the ruthenium compounds.

Preparation and standarization of stock solutions of $KMnO_4$, $HClO_4$, and $NaClO_4$ or $LiClO_4$, used to adjust the ionic strength, have been described previously.[2]

Kinetic Studies

The progress of the reaction was followed at $\lambda = 526$ and 310 nm, the major absorption peaks of MnO_4^- and $Ru(CN)_6^{3-}$, respectively, by using an Aminco-Morrow stopped-flow apparatus. Details of the equipment and treatment of the kinetic data have been previously described.[2]

Results and Discussion

$Ru(CN)_6^{4-}$ is quantitatively oxidized to $Ru(CN)_6^{3-}$ by MnO_4^- in acid perchlorate media in accordance with eq 1.

$$MnO_4^- + 5Ru(II) + 8H^+ \rightarrow Mn^{2+} + 5Ru(III) + 4H_2O \quad (1)$$

Table I. Rate Constants for the MnO_4^-–Ru(II) Reaction[a]

$10^5[MnO_4^-]$, M	$10^3[Ru(II)]$, M	k_{obsd}, M^{-1} s^{-1}
3.28	3.58	66.3
2.34	3.58	66.8
0.94	3.58	65.0
4.68	2.14	62.2
2.34	2.14	69.9
1.17	2.14	68.7
6.55	2.13	67.9
4.68	1.91	68.6
2.34	1.91	71.0
	av	67.4 ± 2.7

[a] $[H^+] = 0.36$ M; $\mu = 1.02$ ($NaClO_4$); $T = 25.0$ °C.

Table II. k_{obsd} as a Function of Hydrogen Ion Concentration[b]

$[H^+]$, M	log $[H^+]^{-1}$	k_{obsd}, M^{-1} s^{-1}	$[H^+]$, M	log $[H^+]^{-1}$	k_{obsd}, M^{-1} s^{-1}
0.008	2.10	78.0[a]			
0.013	1.89	42.4 84.8[a]	0.16	0.80	106 ± 4.0
0.015	1.82	57.2 94.6	0.20	0.70	89.6 ± 3.7 87.2[a]
0.017	1.77	69.8	0.24	0.62	87.5 85.4[a]
0.0165	1.78	97.2	0.281	0.55	75.5 ± 3.0 76.1[a]
0.019	1.72	98.0	0.32	0.49	74.8
0.022	1.66	111.0	0.34	0.47	64.5
0.024	1.62	109 108 ± 3.2[a]	0.36	0.44	67.4 ± 2.7
0.026	1.59	118 ± 6.1	0.46	0.34	54.7
			0.48	0.32	69.2 ± 4.3[a]
0.029	1.54	125	0.50	0.30	40.4
			0.56	0.25	65.3[a]
0.033	1.48	142	0.62	0.21	37.8
0.037	1.43	144	0.64	0.19	42.5
0.040	1.40	133 ± 4.3[a]			
0.042	1.38	148	0.66	0.18	37.5
0.050	1.30	158	0.70	0.15	37.7
0.061	1.21	153 137[a]			
0.070	1.15	146	0.72	0.14	35.7
0.081	1.09	127[a]			
0.10	1.00	135	0.74	0.13	33.6
0.122	0.91	127 112[a]	0.78	0.108	37.1
0.13	0.89	117	0.90	0.06	35.7

[a] $LiClO_4$ media. [b] $T = 25$ °C; $\mu = 1.02$.

Spectrophotometric titration plots gave a value of 5.02 ± 0.11 for the ratio $[Ru(II)]_0/[MnO_4^-]_0$. The $[Ru(II)]_0$ was based on the sample weight. Decomposition of the reaction product $Ru(CN)_6^{3-}$ becomes more pronounced with high acid concentrations, and the stoichiometry experiments were run between 0.02 and 0.12 M $[H^+]$ without significant variation.

With use of pseudo-first-order reaction conditions, $[Ru(II)]_0 \geq 35[MnO_4]_0$, the observed spectral decay at $\lambda = 526$ nm, was found to follow the rate expression $-d[MnO_4^-]/dt = k_{obsd} \cdot$

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(1) M. A. Rawoff and J. R. Sutter, *J. Phys. Chem.*, **71**, 2767 (1967).
(2) L. Thomas and K. W. Hicks, *Inorg. Chem.*, **13**, 749 (1974).
(3) K. W. Hicks, *J. Inorg. Nucl. Chem.*, **38**, 1381 (1976).
(4) W. L. Waltz, S. S. Akhtar, and R. L. Eager, *Can. J. Chem.*, **51**, 2525 (1973).
(5) D. D. DeFord and A. W. Davidson, *J. Am. Chem. Soc.*, **73**, 1469 (1951).

0020-1669/80/1319-1623$01.00/0

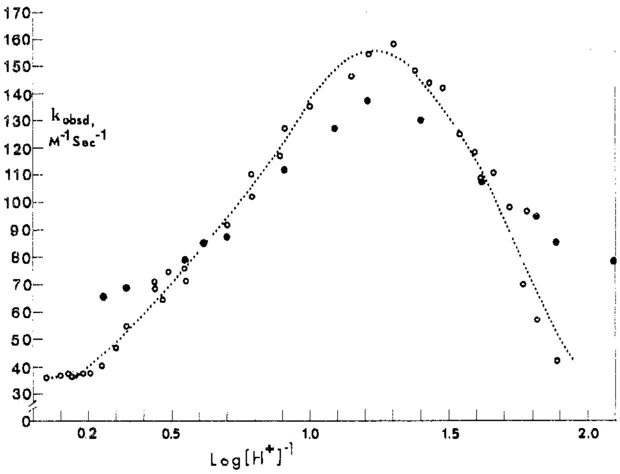

Figure 1. k_{obsd} vs. log $[H^+]^{-1}$ (T = 25.0 °C; μ = 1.02): Na^+, ○; Li^+, ●.

$[MnO_4^-][Ru(II)]$. The buildup of products toward the end of the reaction caused no apparent alteration of the reaction rate as plots of ln $(A_\infty - A_t)$ vs. time were linear for more than 3 half-lives. The data for the reaction in $NaClO_4$ media is presented in Table I.

Table II and Figure 1 show the results of the hydrogen ion experiments in both sodium and lithium perchlorate media. The experimental points for Na^+ and Li^+ are represented by the open and solid circles, respectively. The dotted line represents the best χ^2 fit (χ^2 = 62.4) of the data in sodium ion media to eq 2 by conventional nonlinear computer methods.[6]

$$k_{obsd} = \frac{k_2[H^+]^2 + k_1K_3[H^+] + K_0K_4K_3}{[H^+]^2 + K_3[H^+] + K_4K_3} \qquad (2)$$

The "bell-like" pH dependence of k_{obsd} can be explained by the presence of three reacting species that are coupled by pH-dependent equilibria.

The idea that the behavior of k_{obsd} was due to a medium effect, particularly in the high acid region ($[H^+] > 0.56$ M), and not due to protonic equilibria was considered. Butler and Taube and others[7] have shown that variations observed in $NaClO_4$ media can be ascribed to changes in the activity of the reacting species rather than being caused by a H^+-dependent path. The substitution of Li^+ for Na^+ was seen to remove the effect. Such was not the case with this reaction system.

An H_0 effect in the high acid region was considered because of a possible variation in the activity of the reactants[8,9] produced by changing the solvent from 1 M $NaClO_4$ (or $LiClO_4$) to 1 M $HClO_4$. Support for the interpretation that the variation in k_{obsd} with $[H^+]$ is due to a proton effect, and not one of the medium (Na^+/Li^+ or H_0), is taken from the observation that (1) a significant decrease in the rate constant occurs prior to $[H^+]$ = 0.56 M for both the Na^+ and Li^+ solutions (The decrease is greater than what one would attribute solely to a variation in activity. The activity coefficients of ionic species should be reasonably constant in $LiClO_4$–$HClO_4$ mixtures in this low acid region.), (2) the expected protonic equlibria of $Ru(CN)_6^{4-}$,[10] and (3) the similar behavior of k_{obsd} with $[H^+]$ when the reaction was run in lithium ion media.[7]

Table III. Dependence of k_{obsd} on Ionic Strength[a]

$[H^+]$ = 0.061 M				$[H^+]$ = 0.281 M			
Na^+ μ	k_{obsd}, $M^{-1} s^{-1}$	Li^+ μ	k_{obsd}, $M^{-1} s^{-1}$	Na^+ μ	k_{obsd}, $M^{-1} s^{-1}$	Li^+ μ	k_{obsd}, $M^{-1} s^{-1}$
0.31	78.3	0.30	96.2				
0.44	119	0.42	101			0.43	44.0
0.46	128						
		0.54	117	0.53	50.2	0.51	52.7
0.66	139	0.66	128	0.72	59.1	0.72	57.3
0.83	143	0.82	130	0.92	69.9	0.95	70.3
1.01	153	0.98	137	1.08	79.6	1.07	78.2

[a] T = 25.0 °C; ClO_4^- media.

Although the equilibrium constants for the protonation of $Ru(CN)_6^{4-}$ have not been reported, it is reasonable to expect a pattern similar to that of the H^+–$Fe(CN)_6^{4-}$ equilibria.[11] The equilibria

$$HRu(CN)_6^{3-} \rightleftarrows H^+ + Ru(CN)_6^{4-} \quad K_4 \qquad (3)$$

$$H_2Ru(CN)_6^{2-} \rightleftarrows H^+ + HRu(CN)_6^{3-} \quad K_3 \qquad (4)$$

can be used to account for the variation of k_{obsd} with H^+ and a rate law of the form

$$-d[MnO_4^-]/dt = (k_0 + k_1K_4[H^+] + k_2K_3K_4[H^+]^2)[Ru(CN)_6^{4-}][MnO_4^-] \qquad (5)$$

can be written where

$$MnO_4^- + Ru(CN)_6^{4-} \xrightarrow[k_0]{} \text{products} \qquad (6)$$

$$MnO_4^- + HRu(CN)_6^{3-} \xrightarrow[k_1]{} \text{products} \qquad (7)$$

$$MnO_4^- + H_2Ru(CN)_6^{2-} \xrightarrow[k_2]{} \text{products} \qquad (8)$$

The values obtained for the rate and equilibrium constants are $k_0 = 0.93$ $M^{-1} s^{-1}$, $k_1 = 5.03 \times 10^3$ $M^{-1} s^{-1}$, $k_2 = 15.4$ $M^{-1} s^{-1}$, $K_3 = 3.43 \times 10^{-3}$ M, and $K_4 = 2.97 \times 10^{-3}$ M. It is interesting to note that, although Schilt proposed an increase in proton affinity of $Ru(CN)_6^{4-}$ over $Fe(CN)_6^{4-}$ on the basis of the degree of π-bonding increase as determined from IR studies of $H_4M(CN)_6$ species,[12] the value of the dissociation constant for $HRu(CN)_6^{3-}$ is similar to that for $HFe(CN)_6^{3-}$ (K_4 = 0.0037 M), while the dissociation constant for $H_2Ru(CN)_6^{2-}$ is less than the value for its iron analogue $H_2Fe(CN)_6^{2-}$ (K_3 = 0.017 M) when literature values are extrapolated to μ = 1.02.[11]

The kinetic results for the Ru(II) reaction with MnO_4^- appear to parallel the analogous $Fe(CN)_6^{4-}$ reaction system and vary from that found for the oxidation of $Mo(CN)_8^{4-}$ and $W(CN)_8^{4-}$. Both the Ru(II) and Fe(II) reactions show regions in which k_{obsd} is independent of $[H^+]$ and a region where the reaction rate is governed by the protolytic equilibria of the reductant ion species rather than the oxidant. The rate law for the outer-sphere reactants, $Mo(CN)_8^{4-}$ and $W(CN)_8^{4-}$, showed the presence of only one reacting form of the cyanometalate reductant ion. The expression for the hydrogen ion dependence in their oxidation by MnO_4^-, $k_{obsd} = k_0 + k_1[H^+]$, was interpreted in terms of two reacting forms of Mn(VII) (MnO_4^- and $HMnO_4$).

The ionic strength studies (Table III) at $[H^+]$ = 0.061 and 0.281 M showed an increase in k_{obsd} with increasing μ for both the Na^+ and Li^+ solutions. The slope obtained from plots of ln k_{obsd} vs. $\mu^{1/2}$ gave positive but different values, with the

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(6) P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences", McGraw-Hill, New York, 1969.
(7) R. D. Butler and H. Taube, *J. Am. Chem. Soc.*, **87**, 5597 (1965); J. Doyle and A. G. Sykes, *J. Chem. Soc. A*, 795 (1967).
(8) K. Yates and H. Wai, *J. Am. Chem. Soc.*, **86**, 5408 (1964).
(9) T. C. Templeton and E. L. King, *J. Am. Chem. Soc.*, **93**, 7160 (1971).
(10) J. Birk reached a similar conclusion in his investigation of this reaction system (pesonal communications and unpublished results).
(11) J. Jordan and G. J. Ewing, *Inorg. Chem.*, **1**, 587 (1962).
(12) A. A. Schilt, *J. Am. Chem. Soc.*, **85**, 904 (1963).

reaction at $[H^+] = 0.281$ having the larger value. These qualitative results are in keeping with both reactants being of the same charge and not a reaction between a neutral Mn(VII) species and a protonated Ru(II) ion.

The results of this study demonstrate that the various Ru(II) ions present in acidic perchlorate media are considerably less reactive with Mn(VII) than the corresponding Fe(II) complexes. The observation that the unprotonated Ru(II) ion is considerably less reactive that the monoprotonated Ru(II) ion once again points to the importance of a proton in the activated complex in the conversion of Mn(VII) to Mn(VI) when the E° of the reductant ion is greater than 0.56 V.[2,3,13] Perhaps the proton can more effectively reduce the repulsive charge between the negatively charged MnO_4^- and the smaller Fe(II) ions than the larger Ru(II) ions.

Our results and those of Sutter indicate that the proton needed in the reaction of MnO_4^- with $Ru(CN)_6^{4-}$ and $Fe(CN)_6^{4-}$ is brought into the activated complex by the reductant ion rather than the oxidant. The other MnO_4^-–inorganic reductant ion systems that have been investigated ($Mo(CN)_8^{4-}$, $W(CN)_8^{4-}$, VO^{2+}) show the opposite trend, and the oxidant is the protonated species.

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Registry No. MnO_4^-, 14333-13-2; $Ru(CN)_6^{4-}$, 21029-33-4.

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[13] F. M. Moore and K. W. Hicks, *Inorg. Chem.*, **14**, 413 (1975).

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Solution Equilibria of Copper(II) Chloride in Pyridine and Pyridine–Diluent Mixtures

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The concentration-independent visible absorption spectrum and lack of electrical conductance of $CuCl_2$ in pyridine both indicate existence of a single solution complex, $CuCl_2(py)_n$, generally believed to be six-coordinate pseudooctahedral. However, the solubility data for the $CuCl_2 \cdot 2py$ solid compound in pyridine–aprotic diluent mixtures of varying composition can best be rationalized in terms of the equilibrium $CuCl_2(py)_4 \rightleftharpoons CuCl_2(py)_3 + py$. At the same time the diluents exert but a very small effect on the visible absorption band of $CuCl_2$, indicating essential lack of changes in the coordination sphere of copper(II) upon dilution. Exceptional in this respect is chloroform whose additions result in decreasing intensity and a blue shift of the band, consistent with the formation of a centrosymmetrical octahedral complex, except at low pyridine concentrations where the spectral changes become reversed. This effect agrees with the expected stabilization of the octahedral complex by the protic solvent due to its $H \cdots \pi$-type interaction with the coordinated pyridine molecules enhancing the d_π-electron back-donation from the central metal atom. At the same time it shows existence of a different, less symmetrical environment of the Cu^{2+} cation in the $CuCl_2$ solutions in pure pyridine or in mixtures thereof with the aprotic diluents. In an apparent contradiction to these inferences are the ESR spectra of frozen solutions showing axial symmetry of the complex as well as interaction of the unpaired electron with four equivalent nitrogen nuclei. An explanation is provided by the observation that decreasing temperature induces changes in the visible spectrum of $CuCl_2$ paralleling those induced by chloroform additions, thus showing a drastic change in structure of the solution complex upon freezing. The following scheme of solution equilibria of $CuCl_2$ is proposed in conclusion: $CuCl_2(py)_3 + py \rightleftharpoons CuCl_2(py)_4\ (C_{2v}) \rightleftharpoons CuCl_2(py)_4\ (D_{4h})$, the C_{2v} complex involving essentially five-coordinate copper(II) and one weakly bound pyridine molecule predominating in pure pyridine at room temperature, while decreasing temperature or chloroform additions to pyridine induce formation of the $CuCl_2(py)_4$ centrosymmetrical complex.

Introduction

The well-known crystalline compound $CuCl_2 \cdot 2py$[1,2] dissolves in pyridine (py) to give a nonconducting solution, whose relatively intense absorption band at 775 nm ($\epsilon_{max} = 140$) is independent of concentration.[3] Additions of a noncoordinating solvent (diluent) like chlorobenzene to pyridine result in a sharp decrease in solubility of $CuCl_2 \cdot 2py$ and but a very small change in intensity of the visible absorption band of the solution. The single solution complex indicated by these facts was believed to be six-coordinate pseudooctahedral.[3] However, after pyridine activities had been determined, the solvent activity coefficient calculated as

$$y^\circ = s^* a_{py}^{\,n-2}/s \qquad (1)$$

where s and s^* denote solubilities of $CuCl_2 \cdot 2py$ in the given mixed solvent and in pure pyridine, respectively, and a_{py} is the activity of pyridine, was found to be a reasonable function of solvent composition under the assumption that $n = 3$.[4,5] Supported by the above-mentioned relatively high intensity of the ligand field band, this result indicated existence of the $CuCl_2(py)_3$ complex in the respective solutions. Following our work, Uruska and Szpakowska applied the same argumentation to show formation of the $CuCl_2(iq)_3$ complex in $CuCl_2$ solutions in isoquinoline–chlorobenzene mixtures.[6] In the latter work the ESR spectra of frozen solutions were also determined, and two local environments of the Cu^{2+} ion involving two and three nitrogen atoms of D_{4h} and C_{4v} effective symmetries, respectively, were inferred from the observed superhyperfine lines due to the interaction of the unpaired electron with the nitrogen nuclei. The ESR spectra of the $CuCl_2$ solutions in pyridine[7] and pyridine–diluent mixtures[8,9]

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[1] L. E. Orgel and J. Dunitz, *Nature (London)*, **179**, 462 (1957).
[2] J. Dunitz, *Acta Crystallogr.*, **10**, 307 (1957).
[3] W. Libuś and I. Uruska, *Inorg. Chem.*, **5**, 256 (1966).
[4] H. Berek, M. Kluczkowski, and W. Libuś, *Proc. Int. Conf. Coord. Chem., 13th, 1970*, **2**, 221 (1970).
[5] W. Libuś, M. Kluczkowski, A. Klonkowski, and W. Nierzwicki, *J. Chem. Soc., Faraday Trans. 1*, **72**, 2552 (1976).
[6] I. Uruska and M. Szpakowska, *J. Chem. Soc., Faraday Trans. 1*, **72**, 2545 (1976).
[7] W. Schubel and E. Lutze, *Z. Angew. Phys.*, **17**, 332 (1961).
[8] H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962).

0020-1669/80/1319-1625$01.00/0