Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99163

Kinetics of the Reaction of the 1,2-Diaminocyclohexanetetraacetatomanganate(III) Anion with Cyanide Ion

RANDALL E. HAMM* and J. CHARLES TEMPLETON[1]

Received September 29, 1972

Cyanide ion reacts with 1,2-diaminocyclohexanetetraacetatomanganate(III) ion to give hexacyanomanganate(III) ion as the final product. The kinetics of the reaction when studied over the temperature range 20–40° and a cyanide concentration range of 0.10–0.25 *M* at constant ionic strength of 0.25 *M* could be fitted by the mechanism

$$Mn^{III}CyDTAOH^{2-} + CN^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mn^{III}CyDTACN^{2-} + OH^-$$

$$Mn^{III}CyDTACN^{2-} + CN^- \xrightarrow{k_2} Mn^{III}CyDTA(CN)_2{}^{3-}$$

$$Mn^{III}CyDTA(CN)_2{}^{3-} + 4CN^- \xrightarrow{\text{fast}} Mn^{III}(CN)_6{}^{3-} + CyDTA^{4-}$$

At 25° values of $k_1 = 0.015\ M^{-1}\ \text{sec}^{-1}$ and $k_2 = 0.036\ M^{-1}\ \text{sec}^{-1}$ were obtained. The activation energies for these two reactions were 11.3 and 14.1 kcal mol^{-1}, respectively.

The reaction of the ethylenediaminetetraacetato complexes of nickel(II)[2] and cobalt(II)[3] and the reaction of the 1,2-diaminocyclohexanetetraacetatocobaltate(II) complex[4] with cyanide ion have been studied. The paramagnetic nickel(II) complex reacted much more slowly than the cobalt(II) complexes. This was explained by the requirement of a transition to a diamagnetic nickel(II)-tetracyano complex and the probable involvement of a seven-coordinate intermediate in the cobalt reaction. The ethylenediaminetetraacetato complexes reacted much more rapidly than the 1,2-diaminocyclohexanetetraacetato complexes. The mechanisms proposed were identical for both metals and both ligands, being third order in cyanide concentration and involving a very rapid formation of a 1:1 metal to cyanide intermediate.

The 1,2-diaminocyclohexanetetraacetatomanganate(III) ion has been reported to be seven-coordinate.[5] This complex, on reaction with cyanide, would be required to go from a high-spin state to the low-spin hexacyanomanganate(III) ion. In a basic solution a hydroxo-1,2-diaminocyclohexanetetraacetatomanganate(III) anion is formed instantaneously. The decomposition of this anion is much slower than the reaction with cyanide, but faster than the acid decomposition of the aquo compound.[5,6] In basic solution this hydroxo complex ion has been observed to give basic manganese precipitates in this laboratory, but in basic cyanide solution there is no indication of precipitation of manganese hydroxides.

Experimental Section

The potassium salt of *trans*-1,2-diaminocyclohexanetetraacetatomanganate(III) was prepared as reported previously[5] except that manganese acetate was used in place of manganese nitrate. Analytical grade sodium cyanide was used to prepare the 0.25 *M* stock solution, and this was analyzed by silver nitrate titration, using the Deniges modification of the Liebig method. The 0.25 *M* sodium perchlorate solution used to adjust the ionic strength was prepared by neutralization of perchloric acid with sodium carbonate followed by boiling to remove the carbon dioxide produced. The assay of this solution was performed by passing a quantity of the solution through a column of cation-exchange resin in the hydrogen ion form, followed by a distilled water wash and then base titration. The pH of the solution was measured at the end of each kinetic run with a Beckman Research pH meter.

The absorption spectra of quantities of 1,2-diaminocyclohexanetetraacetatomanganate(III) when dissolved in pH 11.0 sodium hydroxide solution and when dissolved in pH 11.0 sodium cyanide solution were identical immediately after the dissolution. From this experiment it was believed that no very rapid formation of a cyanide complex took place, but that the light absorption was due to the hydroxo species.

For all kinetic runs the cell was filled with a solution having an ionic strength of 0.25 (mixture of appropriate quantities of the stock sodium cyanide and sodium perchlorate solutions). The cell was placed in the constant-temperature block of the Cary 14 spectrophotometer through which water from a thermostated water bath was being circulated with the temperature controlled to ±0.05°. After the cell and its contents had been temperature equilibrated, a small finely ground solid sample of $KMn^{III}CyDTA(H_2O)$ was added to the cell.[7] The cell was shaken (10 sec) and was replaced in the cell block, and the absorbance was measured as a function of time at either 448 or 470 nm. The absorption peak for the $Mn^{III}CyDTAOH^{2-}$ ion was found at 448 nm,[5] and a broad shoulder was located at 470 nm. The early kinetic runs were made at 470 nm to avoid any intrusion of the product absorption peak. Subsequent runs made at 448 nm gave apparent rate constants identical with those determined under the same conditions at 470 nm. Most runs were made in 1-cm cells. Variation of the hydroxide ion concentration was accomplished mainly through the variation of the cyanide ion concentration.

Discussion

Figure 1 is a plot of a typical kinetic run. In this figure the log (absorbance), log A_s, at 470 nm is plotted against time for the reaction of a 2.57×10^{-3} *M* solution of 1,2-diaminocyclohexanetetraacetatomanganate(III) ion in a 0.25 *M* sodium cyanide solution at 25°. The plot only becomes straight after a considerable induction period but then remains straight through about 4 half-lives. All runs showed this type of induction period. This indicates that there is a slow step which is first order in the complex ion but that the total reaction is not a simple process. It must involve at least two slow steps followed by some very rapid steps to give the final product.

The overall stoichiometry of the reaction was found to be represented by the equation

---

[1] Summer 1971 NSF College Teachers Research Participation Program.

[2] D. W. Margerum, T. J. Bydalek, and J. J. Bishop, *J. Amer. Chem. Soc.*, 83, 1371 (1961).

[3] S. Nakamura, Ph.D. Thesis, The University of Chicago, 1964.

[4] J. P. Jones and D. W. Margerum, *Inorg. Chem.*, **8**, 1486 (1969).

[5] R. E. Hamm and M. A. Suwyn, *Inorg. Chem.*, 6, 139 (1967).

[6] K. A. Schroeder and R. E. Hamm, *Inorg. Chem.*, 3, 391 (1964).

[7] $CyDTA^{4-}$ represents the 1,2-diaminocyclohexanetetraacetato ion.

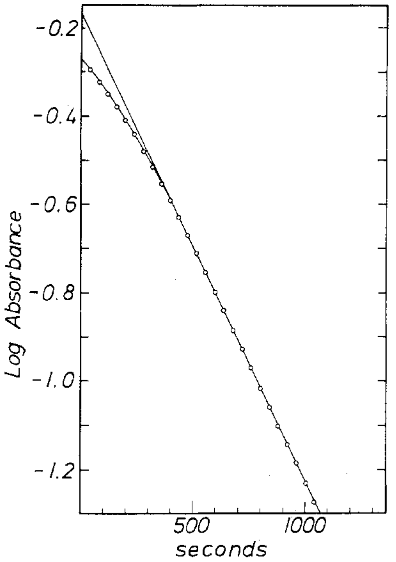

Figure 1. Log (absorbance) at 470 nm *vs.* time for the reaction of 2.57×10^{-3} *M* 1,2-diaminocyclohexanetetraacetatomanganate(III) in 0.25 *M* sodium cyanide at 25°.

$$\mathrm{Mn^{III}CyDTAOH^{2-} + 6CN^- \rightarrow Mn^{III}(CN)_6{}^{3-} + CyDTA^{4-} + OH^-}$$

The justification of this as the final kinetics was shown by the absorption spectra of the solutions after complete reaction: a single sharp peak was observed at 325 nm due to the $\mathrm{Mn^{III}(CN)_6{}^{3-}}$ ion that had been formed.[8] Chawla and Frank[9] agreed that the $\mathrm{Mn^{III}(CN)_6{}^{3-}}$ ion when dissolved in cyanide solution gives a single absorption peak at 325 nm but believed that it is due to some hydrolysis products rather than to its being the hexacyano compound. In this paper the products have been indicated as $\mathrm{Mn^{III}(CN)_6{}^{3-}}$ since this ion is the precursor of the species giving the 325-nm absorption peak and that species has not yet been identified. The rate of the reaction was followed by observing the increasing absorbance at 325 nm with the same results for the apparent rate constant as obtained at 470 nm. However, this is experimentally more difficult due to the fact that the $\mathrm{Mn^{III}}$-$\mathrm{CyDTAOH^{2-}}$ also absorbs at 325 nm, while at 470 nm the only important absorbers are the CyDTA complexes of manganese(III).

A mechanism which fits the experimental data is[10]

$$\mathrm{Mn^{III}CyDTAOH^{2-} + CN^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Mn^{III}CyDTACN^{2-} + OH^-}$$

$$\mathrm{Mn^{III}CyDTACN^{2-} + CN^-} \xrightarrow{k_2} \mathrm{Mn^{III}CyDTA(CN)_2{}^{3-}}$$

$$\mathrm{Mn^{III}CyDTA(CN)_2{}^{3-} + 4CN^-} \xrightarrow{\text{fast}} \mathrm{Mn^{III}(CN)_6{}^{3-} + CyDTA^{4-}}$$

The rate expressions would be

$$\frac{d[\mathrm{B}]}{dt} = -k_1[\mathrm{B}][\mathrm{CN^-}] + k_{-1}[\mathrm{C}][\mathrm{OH^-}]$$

$$\frac{d[\mathrm{C}]}{dt} = k_1[\mathrm{B}][\mathrm{CN^-}] - k_{-1}[\mathrm{C}][\mathrm{OH^-}] - k_2[\mathrm{C}][\mathrm{CN^-}]$$

Table I. Reaction of 1,2-Diaminocyclohexanetetraacetatomanganate(III) with Cyanide at Ionic Strength 0.25 *M*[a]

[Cyanide], *M*	Temp, °C	$10^3[\mathrm{B}]_0$, *M*	10^3k, $\mathrm{sec^{-1}}$	Rate const, $M^{-1}\ \mathrm{sec^{-1}}$	
				k_2	k_1
0.25	25.0	4.38	2.55	0.034	0.013
		3.62	2.62	0.035	0.014
		2.57	2.48	0.033	0.014
0.20	25.0	4.19	2.18	0.036	0.016
		3.14	2.30	0.038	0.016
0.15	25.00	4.38	1.76	0.039	0.016
		3.76	1.60	0.036	0.017
0.10	25.0	4.05	1.01	0.034	0.016
		3.67	1.13	0.038	0.016
		4.10	1.14	0.038	0.017
0.25	20.0	3.28	1.70	0.022	0.009
	30.0	3.83	3.53	0.047	0.017
		4.93	3.42	0.045	0.018
	35.0	4.05	5.52	0.073	0.024
		5.99	5.10	0.068	0.023
		4.23	5.60	0.075	0.025
	40.0	3.81	7.93	0.106	0.034
		3.95	7.95	0.104	0.035

[a] Sodium perchlorate used to maintain ionic strength.

Before the completion of the induction time the integration of the rate equation for [C] assuming [B] to be constant gives

$$[\mathrm{C}] = \frac{k_1[\mathrm{B}][\mathrm{CN^-}]}{k_{-1}[\mathrm{OH^-}] + k_2[\mathrm{CN^-}]}\{1 - \exp(-(k_{-1}[\mathrm{OH^-}] + k_2[\mathrm{CN^-}])t)\} \tag{1}$$

After the attainment of the steady state as shown by the straight-line portion of the plot in Figure 1, equations can be obtained by a steady-state treatment

$$[\mathrm{B}] = [\mathrm{B}]_0 \exp \frac{-k_1k_2[\mathrm{CN^-}]^2t}{k_{-1}[\mathrm{OH^-}] + k_2[\mathrm{CN^-}]} \tag{2}$$

$$[\mathrm{C}] = \frac{k_1[\mathrm{B}][\mathrm{CN^-}]}{k_{-1}[\mathrm{OH^-}] + k_2[\mathrm{CN^-}]} \tag{3}$$

When the rate of the reaction is determined by the absorbance of the solution in a 1-cm cell at a wavelength where the $\mathrm{Mn^{III}}$ species absorb

$$(A_\mathrm{s})_\mathrm{t} = \epsilon_\mathrm{B}[\mathrm{B}] + \epsilon_\mathrm{C}[\mathrm{C}]$$

where $(A_\mathrm{s})_\mathrm{t}$ represents total absorbance at time t. Substituting from eq 2 and 3 and taking the logarithm

$$\log(A_\mathrm{s})_t = \log\left(\epsilon_\mathrm{B} + \frac{\epsilon_\mathrm{C}k_1[\mathrm{CN^-}]}{k_{-1}[\mathrm{OH^-}] + k_2[\mathrm{CN^-}]}\right) + \log[\mathrm{B}]_0 - \left\{\frac{k_1k_2[\mathrm{CN^-}]^2}{2.3(k_{-1}[\mathrm{OH^-}] + k_2[\mathrm{CN^-}])}\right\}t \tag{4}$$

When $\log(A_\mathrm{s})_t$ is plotted against time, the slope is equal to the coefficient of t in eq 4 and the intercept is given by the first and second terms on the right in eq 4. Further equations can then be written

$$\frac{\text{antilog (intercept)} - (A_\mathrm{s})_0}{\epsilon_\mathrm{C}[\mathrm{B}]_0} = \frac{k_1[\mathrm{CN^-}]}{k_{-1}[\mathrm{OH^-}] + k_2[\mathrm{CN^-}]} = \Delta$$

$$k_2 = \frac{2.3 \times \text{slope}}{\Delta[\mathrm{CN^-}]}$$

Equation 1 reduces to eq 3 as the exponential term in eq 1 approaches zero. For the purpose of evaluation, the induction time was taken to be the time at which the exponential term in eq 1 is equal to 0.01. This permits the evaluation of

---

[8] A. W. Adamson, J. P. Welker, and W. B. Wright, *J. Amer. Chem. Soc.*, 73, 4786 (1951).

[9] I. D. Chawla and M. J. Frank, *J. Inorg. Nucl. Chem.*, 32, 555 (1970).

[10] In the derivations which are given in this paper $\mathrm{Mn^{III}}$-$\mathrm{CyDTAOH^{2-}}$ is represented by B and $\mathrm{Mn^{III}CyDTACN^{2-}}$ is represented by C. The species $\mathrm{Mn^{III}CyDTA(CN)_2{}^{3-}}$ is considered to be one in which one arm of the CyDTA has been replaced from its coordinating position by a cyanide.

k_{-1} by means of the equation $(k_{-1}[OH^-] + k_2[CN^-]) = 4.6/$(induction time in seconds).

Given in Table I are the results of the kinetic investigation along with the rate constants calculated.

The average value obtained for k_2 at 25° was $0.036 \pm 0.0021\ M^{-1}\ sec^{-1}$ and the average for k_1 at 25° was $0.015 \pm 0.0017\ M^{-1}\ sec^{-1}$. The uncertainties given are standard deviations. The estimated value of k_{-1} at 25° was $4\ M^{-1}\ sec^{-1}$. This is only a crude estimate at the best because the determination of the induction time can only be approximated to and within 20 sec, and the calculation of k_{-1} involves the difference of two terms which have about the same magnitude.

Least-squares treatment of the plot of log k *vs.* $1/T$ for k_1 and k_2 gave 11.3 ± 0.5 kcal mol^{-1} and 14.1 ± 0.4 kcal mol^{-1}, respectively, as the activation energies and standard deviations of the two rate processes. These activation energies are much larger than that reported for the similar cobalt(II) complex in its reaction with cyanide.[5] Also, the mechanism of the reaction is totally different since only two cyanides are involved through the slow step in the manganese(III) reaction while three cyanides were found to be involved in the case of the cobalt(II) reaction. The higher activation energy in the manganese(III) reaction may be because the manganese(III) is in a seven-coordinate hydroxo form and there is only an exchange of cyanide for the hydroxide.

The reactions of EDTA complexes of nickel(II) and cobalt(II) were found to be much faster than the CyDTA complexes.[5] Simple observation of the rate of reaction of Mn^{III}-EDTA with cyanide showed that at 25° it appeared to have an apparent half-life of less than 10 sec. While this is too fast to make investigation practical by the technique used in this investigation, it is in agreement with the observation that ligand replacement reactions for EDTA complexes are much faster than those for CyDTA complexes.

Registry No. Potassium salt of *trans*-1,2-diaminocyclohexanetetraacetatomanganate(III), 38127-69-4; sodium cyanide, 143-33-9.

Acknowledgment. The authors wish to thank the National Science Foundation for financial support which made the work on this research possible.

Contribution from the Department of Chemical Engineering,
University of Waterloo, Waterloo, Ontario, Canada

Activation of Hydrogen by Bridged Transition Metal Carboxylates. Rhodium(II) Acetate Catalyzed Hydrogenation of Olefins

B. C. Y. HUI, W. K. TEO, and G. L. REMPEL*

Received August 8, 1972

Dimeric rhodium(II) acetate, $Rh_2(OCOMe)_4$, functions as an efficient and selective catalyst for the hydrogenation of terminal olefins in a variety of solvent media. The detailed kinetics are reported for the hydrogenation of dec-1-ene in *N,N'*-dimethylformamide solution under mild conditions. These studies indicate that the initial step of the hydrogenation mechanism involves activation of hydrogen at only one of the metal centers of the dimer. The hydrogen activation process, which involves heterolytic splitting of hydrogen, leads to the formation of an intermediate metal hydride, $HRh_2(OCOMe)_3$, which undergoes a subsequent reaction with the olefinic substrate. Insertion of the olefin into the metal–hydride bond followed by proton attack on the intermediate metal alkyl completes the catalytic cycle.

Introduction

The hydrogenation of simple olefins catalyzed by carboxylate complexes of the first-row transition elements scandium(III) to zinc(II) has been extensively studied.[1] The general mechanism proposed for these catalysts involves dimeric catalytic species. A recent series of publications[2] has reported that dimethylformamide solutions of rhodium(I) complexes with tyrosine, anthranilic acid, or phenylacetic acid are excellent catalysts for the hydrogenation of olefins. Although the structure of these complexes is not clear, they have been represented as $H[Rh_2(PhCH_2COO)_2Cl]$. The RCOO groups appear to function as bridges or chelates and it has been suggested that the rhodium interacts with the π electrons of the phenyl ring.[2] The systems using $H[Rh_2(PhCH_2COO)_2Cl]$ are discussed by Khidekel, *et al.*,[2] as involving the monomeric catalytic species, $HRh(PhCH_2CO_2)^-$. Protonation of rhodium(II) acetate by noncomplexing, nonoxidizing acids has led to the formation of Rh_2^{4+} which in the presence of triphenylphosphine is an active hydrogenation catalyst.[3] The catalytic species in these systems, however, appear to be monomeric Rh(I) complexes. We have noted previously[4] that certain second-row transition metal acetates, including the dimeric rhodium(II) acetate, $Rh_2(OCOMe)_4$, function as homogeneous catalysts for the hydrogenation of olefins in a wide variety of solvent media.

The tetrabridged dimeric rhodium(II) acetate, $Rh_2(OCOMe)_4$, has a Rh-Rh separation of 2.45 Å which suggests a significant Rh-Rh interaction.[5] A number of adducts of the type $Rh(OCOMe)_2L$ have been prepared[6-8] and in most cases it is probable that these complexes are also dimeric

---

(1) V. A. Tulupov, *Russ. J. Phys. Chem.*, 39, 1251 (1965); 41, 456 (1967).

(2) N. V. Borunova, L. Kh. Friedlin, M. L. Khidekel, S. S. Danielova, V. A. Avilov, and P. S. Chekrii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 434 (1968); V. A. Avilov, Yu. G. Brod'ko, V. B. Panov, M. L. Khidekel, and P. S. Chekrii, *Kinet. Catal. (USSR)*, 9, 582 (1968); O. N. Efimov, M. L. Khidekel, V. A. Avilov, P. S. Chekrii, O. N. Eremenko, and A. G. Ovcharenko, *J. Gen. Chem. USSR*, 38, 2581 (1968).

(3) P. Legzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc. A*, 3322 (1970).

(4) B. C. Hui and G. L. Rempel, *Chem. Commun.*, 1195 (1970).

(5) L. Dubicki and R. L. Martin, *Inorg. Chem.*, 9, 673 (1970).

(6) S. A. Johnson, H. R. Hunt, and H. M. Neumann, *Inorg. Chem.*, 2, 960 (1963).

(7) T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 3632 (1965).

(8) L. A. Nazarova, I. I. Chernyaev, and A. S. Morozova, *Russ. J. Inorg. Chem.*, 11, 1387 (1966).