complexes, but the nature of such interactions is not understood at present.

Conclusions

There remains little, if any, doubt that the monofluoride compexes are a clear and distinct exception to the Irving–Williams sequence. The use of methanol as an alternate solvent plays a crucial role in this conclusion and has proved to be an ideal choice for enhancing the anomalous aqueous sequence. These acceptors are distinctly "a" type in methanol, as in water. The predominance of electrostatic interactions in both solvents facilitates a direct and unambiguous comparison of stability data in these two solvents. Entropy control of these reactions is marked and overwhelms all other considerations.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. D.R.H. is grateful for a summer stipend provided by the Eastman Kodak scholarship program. We thank T. W. Kallen for helpful discussions. This paper was presented in part at the 10th Northeast Regional Meeting of the Americal Chemical Society, Potsdam, NY, June 1980, and at the 182nd National Meeting of the Americal Chemical Society, New York, Aug 1981.

Contribution from the Department of Chemistry,
University of Ottawa, Ottawa, Ontario K1N 9B4, Canada

The Nature of Selenium Dissolved in Hydrochloric Acid Containing Selenium Dioxide

MANI MAHADEVAN and JOHN MILNE*

Received August 4, 1982

Elemental selenium dissolved in solutions of SeO_2 in concentrated hydrochloric acid to a small extent, giving strongly yellow solutions. Gravimetric analysis and spectrophotometric study of these solutions show that the principal species in equilibrium with $SeOCl_2$ is Se_2Cl_2. A completely satisfactory interpretation of the results requires however the presence of $SeCl_2$ also. Formation constants and extinction coefficients at 25 °C for Se_2Cl_2 and $SeCl_2$ are given.

Introduction

It has been known for a long time that elemental selenium dissolves in concentrated hydrochloric acid containing SeO_2.[1] Concentrated solutions of this type are employed in the preparation of diselenium dichloride by a method first developed by Lenher and Kao.[2] Diselenium dibromide is prepared similarly. The nature of the dark yellow species formed when selenium is dissolved in SeO_2-containing solutions in hydrochloric acid was studied by Ullrich and Ditz.[3] They concluded that the species formed at low concentrations was diselenium dichloride on the basis of titration of Se(IV) in hydrochloric acid with tin(II) chloride to the point of precipitation of elemental selenium. However, on the basis of the solubility of selenium in the SeO_2 solutions, they showed that Se_2Cl_2 formation was not complete. The precise nature of the selenium species in these solutions was of interest to us as an extension of our work on solutions of SeO_2 in hydrochloric acid.[4] Of the three known chlorides of selenium, Se_2Cl_2, $SeCl_2$, and $SeCl_4$, only Se_2Cl_2 and $SeCl_4$ are known in condensed form while $SeCl_2$ is known only in the vapor phase[5] although Se(II)–halogen species are apparently stabilized by coordination of additional donor ligands.[6,7] A similar situation is found for the selenium bromides, and several studies of the equilibria between $SeBr_4$, Se_2Br_2, and $SeBr_2$ in nonaqueous solvents have been made.[8,9] In view of the possible existence of Se(II) in Se–SeO_2 mixtures in hydrochloric acid, a more precise study of such solutions by spectrophotometric and gravimetric means was considered of interest.

Experimental Section

Hydrochloric acid (J. T. Baker) was standardized against sodium carbonate by the usual procedures. All HCl solutions were then adjusted to 11.80 M. Selenium dioxide (Ventron) was analyzed for purity, and selenium (Baker AR) was finely ground before use.

Solutions, which were prepared from excess selenium and stock solutions of SeO_2 in hydrochloric acid, were stored in well-sealed flasks to minimize air oxidation. The solutions were shaken for 8 h at room temperature and then equilibrated overnight at 25 °C in a constant-temperature bath before study. Both spectrophotometric and gravimetric analytical methods showed no change in selenium solubility after 24 h of saturation.

Dissolved selenium was determined by simple dilution of 25-mL aliquots of the supernatant of the saturated acid solutions to 250 mL and weighing of precipitated elemental selenium. Analysis of total selenium in the saturated solutions by standard procedures[10] yielded the same value of the sum of original Se(IV) and dissolved elemental selenium, indicating that the dilution method is accurate and that no reduced selenium species, apart from Se(IV), remained dissolved after dilution.

Spectrophotometric measurements were made with a Varian DMS 90 UV–visible spectrophotometer using both 1 cm and 1 mm path length quartz cells. All measurements were blanked against air. The absorbances listed in this work are corrected for the hydrochloric acid background absorbance.

Results and Discussion

The results of the gravimetric determination of dissolved elemental selenium in various solutions of SeO_2 in 11.8 M hydrochloric acid are given in Table I. Elemental selenium

---

(1) Rose, H.; Finkener, R. "Handbuch der analytischen Chemie", 6th ed.; Springer Verlag: Berlin, 1867; Vol. I, p 596.

(2) Lenher, V.; Kao, C. H. *J. Am. Chem. Soc.* **1925**, *47*, 772.

(3) Ditz, H.; Ullrich, F. *Z. Anorg. Allg. Chem.* **1934**, *221*, 33.

(4) Milne, J.; Lahaie, P. *Inorg. Chem.* **1979**, *18*, 3180.

(5) Lundkvist, M.; Lellep, M. *Acta Chem. Scand.* **1968**, *22*, 291.

(6) Wynne, K. J.; Pearson, P. S. "Abstracts of Papers", 161st National Meeting of the American Chemical Society, Los Angeles, CA, 1971; American Chemical Society: Washington, DC, 1971; INOR 172.

(7) Wynne, K. J.; Golen, J. *Inorg. Chem.* **1974**, *13*, 185.

(8) Tideswell, N. W.; McCullough, J. D. *J. Am. Chem. Soc.* **1956**, *78*, 3026.

(9) Katsaros, N.; George, J. W. *Inorg. Chem.* **1969**, *8*, 759.

(10) Vogel, A. I. "Quantitative Inorganic Analysis", 3rd ed.; Longmans, Green and Co.: New York, 1961; p 508.

0020-1669/83/1322-1648$01.50/0

Table I. Gravimetric Results and Calculated Equilibrium Constants (c_{HCl} = 11.80 M)[a]

		equil 1[b]			equil 2[c]			equil 1 and 2 combined			
c_{IV}, M	$10^2 c_0$, M	[HCl], M	$10^6 \times (a_{H_2O}/a_{HCl}^2)$	$10^9 K$, M^{-1}	[HCl], M	$10^6 \times (a_{H_2O}/a_{HCl}^2)$	$10^9 K'$, M^{-1}	[HCl], M	$10^6 \times (a_{H_2O}/a_{HCl}^2)$	$10^9 K$, M^{-1}	$10^9 K'$, M^{-1}
0.005	0.56, 0.46	11.79	0.340	1.19	11.79	0.340		11.79	0.340	0.99	0.49
0.010	0.92, 0.93	11.77	0.355	1.99	11.76	0.360	44.6	11.78	0.347	1.55	0.78
0.020	1.39, 1.42	11.75	0.365	2.08	11.73	0.370	12.21	11.76	0.360	1.55	0.77
0.050	2.25, 2.27	11.68	0.403	2.82	11.65	0.418	11.29	11.70	0.395	1.53	0.76
0.100	2.87, 3.36, 3.03	11.58	0.460	2.21	11.54	0.487	6.82	11.61	0.441	1.53	0.77
0.200	4.15, 4.21	11.37	0.606	2.55	11.32	0.646	7.11	11.40	0.585	1.72	0.86

[a] c_{IV} = stoichiometric concentration of SeO_2 dissolved; c_0 = stoichiometric concentration of Se dissolved. [b] $3Se + SeOCl_2 + 2HCl = 2Se_2Cl_2 + H_2O$ (equil const = κ); $K = \kappa[Se]^3$. [c] $Se + SeOCl_2 + 2HCl = 2SeCl_2 + H_2O$ (equil const = κ'); $K' = \kappa'[Se]$.

is not soluble in solutions of concentrated hydrochloric acid or selenious acid alone and exhibits significant solubility in solutions of selenious acid only when the hydrochloric acid concentration reaches 10 M (0.4 mg of Se in 25 mL of 0.001 M SeO_2 in 10 M HCl).

It is known from earlier work[4] that Se(IV) in concentrated HCl is present mainly as $SeOCl_2$, and a Raman spectrum of a 0.2 M Se(IV) solution in 11.80 M HCl saturated with elemental selenium shows only the characteristic bands of $SeOCl_2$, indicating this to be the principal species in this solution. Two equilibria are possible

$$3Se + SeOCl_2 + 2HCl = 2Se_2Cl_2 + H_2O \quad (1)$$

$$Se + SeOCl_2 + 2HCl = 2SeCl_2 + H_2O \quad (2)$$

governed, for solutions saturated in Se, by the expressions

$$K = \frac{[Se_2Cl_2]^2 a_{H_2O}}{[SeOCl_2] a_{HCl}^2} \quad (3)$$

$$K' = \frac{[SeCl_2]^2 a_{H_2O}}{[SeOCl_2] a_{HCl}^2} \quad (4)$$

respectively, where a_{H_2O} and a_{HCl} are the activities of H_2O (mole fraction scale) and HCl (molar scale) and all other activity coefficients are assumed to be unity, which is a good approximation at the concentrations of selenium species studied. The concentration of Se, [Se], in these solutions is constant, and equilibrium constants given in eq 3 and 4 are related to the thermodynamic constants, κ and κ', by the expressions $K = \kappa[Se]^3$ and $K' = \kappa'[Se]$. The factor a_{H_2O}/a_{HCl}^2 will vary as [HCl] varies; the latter depends upon selenium solute concentration according to

$$[HCl] = 11.80 - 2c_{IV} - 2c_0/3 \quad (5)$$

for equilibrium 1 and

$$[HCl] = 11.80 - 2c_{IV} - 2c_0 \quad (6)$$

for equilibrium 2 where c_{IV} is the stoichiometric concentration of SeO_2 dissolved in the solution and c_0 is the concentration of dissolved elemental selenium. The valence and mass balance equations for equilibria 1 and 2 respectively, are

$$4c_{IV} = 2[Se_2Cl_2] + 4[SeOCl_2] \qquad c_0 = 3[Se_2Cl_2]/2 \quad (7)$$

$$4c_{IV} = 2[SeCl_2] + 4[SeOCl_2] \qquad c_0 = [SeCl_2]/2 \quad (8)$$

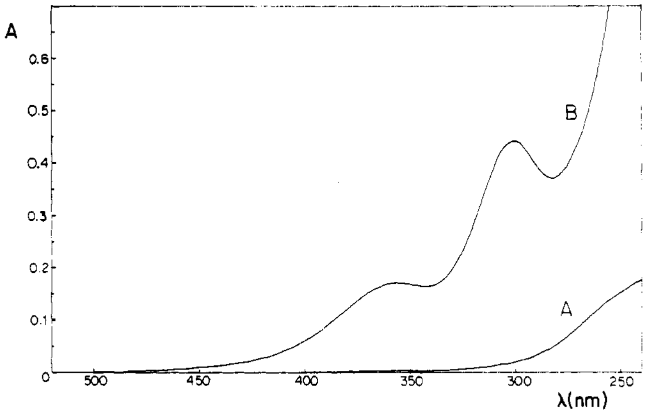

Figure 1. UV-visible spectrum of (A) 0.0001 M SeO_2 in 11.80 M HCl (1 mm cell) and (B) 0.0001 M SeO_2 in 11.80 M HCl saturated with Se (1 cm cell).

From these equations, in conjunction with the equilibrium constant expressions (3) and (4), the c_0 (mean values) vs. c_{IV} data in Table I, and a_{H_2O}/a_{HCl}^2 quotients calculated via (5) and (6) from activities in ref 11 and 12, equilibrium constants K and K' were calculated at each concentration for both possible equilibria, and these are given in Table I. For purposes of these calculations [Se] in the mass balance equation is negligible and may be ignored. Although the constancy of K (Se_2Cl_2 formation) is better than that of K' ($SeCl_2$ formation), neither equilibrium accounts for the gravimetric data satisfactorily and a quantitative description of the system requires the presence of both lower selenium chlorides.

With use of the valence and mass balance equations

$$\begin{aligned} 4c_{IV} &= 2[Se_2Cl_2] + 2[SeCl_2] + 4[SeOCl_2] \\ c_0 &= 3[Se_2Cl_2]/2 + [SeCl_2]/2 \end{aligned} \quad (9)$$

eq 3 and 4 and

$$[HCl] = 11.80 - 2[SeOCl_2] - 2[Se_2Cl_2] - 2[SeCl_2] \quad (10)$$

and with the factor a_{H_2O}/a_{HCl}^2 redefined as Q for brevity, the following expression may be derived:

$$c_{IV} = \tfrac{1}{2}[K/Q + K'/Q]\left[\frac{c_0}{\tfrac{3}{2}(K/Q)^{1/2} + \tfrac{1}{2}(K'/Q)^{1/2}}\right] + \frac{c_0^2}{[\tfrac{3}{2}(K/Q)^{1/2} + \tfrac{1}{2}(K'/Q)^{1/2}]^2} \quad (11)$$

For each point, K/Q and K'/Q values were found that fit the c_{IV}–c_0 data (average values) in Table I, [HCl] was then calculated, and Q was determined. From the Q values, K and K' were found. The smallest average deviation amongst the series of K and K' values was found for $K = (1.48 \pm 0.16) \times 10^{-9}$ mol^{-1} L and $K' = (0.74 \pm 0.08) \times 10^{-9}$ mol^{-1} L.

The gravimetric analysis of selenium involves the weighing of relatively small amounts of elemental selenium (10–83 mg), which can lead to uncertainty in the calculations. Furthermore, the relatively high concentrations of Se(IV) (c_{IV}) cause significant changes in HCl activity, which will affect the concentration of $SeOCl_2$ in equilibrium with H_2SeO_3.[4] For these reasons the spectrophotometric method is more attractive

---

(11) Randall, M.; Young, L. E. *J. Am. Chem. Soc.* **1928**, *50*, 1002.

(12) Robinson, R. A.; and Stokes, R. H. "Electrolyte Solutions", 2nd ed.; Butterworths: London, 1959; Appendix 8.10.

Table II. Spectrophotometric Measurements at 300 nm for Solutions of Se in 11.80 M HCl Solutions of SeO_2

10^3c_{IV},[a] M	A_{300}[b]	10^3c_{IV},[a] M	A_{300}[b]
0.10	0.353	3.00	8.97, 8.60
0.20	0.774	4.00	11.2, 10.9
0.30	1.034	4.50	12.85
0.40	1.348	5.00	13.13
0.50	1.760	5.50	14.91
0.60	2.08	6.00	15.35
0.70	2.49	6.40	15.41
0.80	2.73	7.00	17.9, 17.3
1.00	3.22, 3.30	8.00	19.81
2.00	6.26		

[a] c_{IV} represents the stoichiometric concentration of SeO_2 dissolved. [b] All results are given for 1 cm path length, corrected for HCl absorbance at 300 nm.

since lower c_{IV} solutions may be studied in this way and these effects overcome. Figure 1 shows the electronic spectra of 0.0001 M SeO_2 (trace A) and 0.0001 M SeO_2 saturated with selenium (trace B) in 1 mm and 1 cm path length cells, respectively. The spectrum of SeO_2 in concentrated HCl has a strong peak at 195 nm with a shoulder at 260 nm, and as selenium is dissolved in the solution, peaks at 300 and 360 nm grow into the spectrum. These peaks are at the same wavelength as those of Se_2Cl_2 in acetonitrile,[13] suggesting the presence of Se_2Cl_2 in the solution. The peak at 300 nm was used to evaluate the formation constants. The weaker peak at 360 nm yielded similar but less precise formation constants. Table II shows the absorbances at 300 nm for solutions of SeO_2 in 11.80 M HCl saturated with selenium. It is not possible to differentiate between Se_2Cl_2 and $SeCl_2$ as a product from these data alone since the expressions derived for the dependence of absorbance on c_{IV} are identical in form for each product. Only a comparison of the calculated c_0 assuming either product, with those observed in the gravimetric work permits differentiation between the two. Interpretation in terms of either Se_2Cl_2 or $SeCl_2$ alone does not account satisfactorily for the observed c_0 values, and the data are best explained by the presence of both lower chlorides of selenium.

The absorbance of these solutions is then given by

$$A_{300} = \epsilon_{Se_2Cl_2}[Se_2Cl_2] + \epsilon_{SeCl_2}[SeCl_2] + \epsilon_{SeOCl_2}[SeOCl_2] \tag{12}$$

where the ϵ values represent the extinction coefficients at 300 nm. Equation 12, along with eq 3, 4, and 9, may be combined to give

$$\epsilon_{SeOCl_2} = \left[2\left\{\left[\frac{\epsilon_{SeCl_2}}{(K/K')^{1/2}} + \epsilon_{Se_2Cl_2}\right]^2 + \frac{4A\epsilon_{SeOCl_2}}{K/Q}\right\}^{1/2} - \left\{\frac{\epsilon_{SeCl_2}}{(K/K')^{1/2}} + \epsilon_{Se_2Cl_2}\right\}\right] \Bigg/ \left[\left\{[(K'/K)^{1/2} + 1]^2 + \frac{16Qc_{IV}}{K}\right\}^{1/2} - [(K'/K)^{1/2} + 1]\right] \tag{13}$$

Various values of K, K', $\epsilon_{Se_2Cl_2}$, and ϵ_{SeCl_2} were tried to satisfy this equation for the data given in Table II. Initially $\epsilon_{Se_2Cl_2}$ was taken to be equal to the value of acetonitrile solutions. ϵ_{SeOCl_2} was measured independently and found to be 810 cm^{-1} mol^{-1} L. Changes in [HCl] and $a_{H_2O}/a_{HCl}{}^2$ (=Q) in the c_{IV} range studied are small and for purposes of these calculations have been ignored. The quotient, Q, has the value 0.342×10^{-6} in 11.80 M HCl. The calculations were found to be more sensitive to values chosen for $\epsilon_{Se_2Cl_2}$ and K than ϵ_{SeCl_2} and K', which is expected, since the absorbances were taken at the wave length of maximum absorbance for Se_2Cl_2 and since Se_2Cl_2 is also the predominant lower chloride of the two ac-

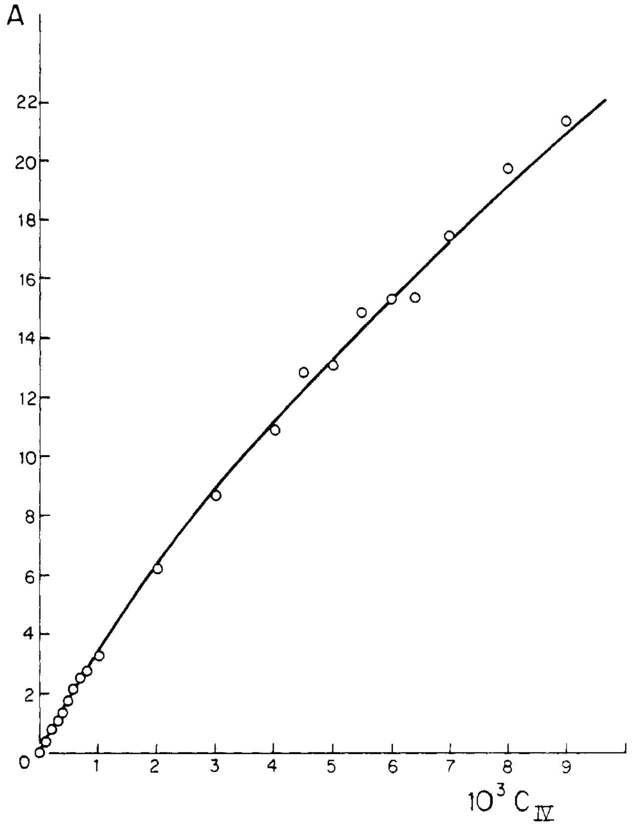

Figure 2. Plot of absorbance vs. stoichiometric SeO_2 concentration (c_{IV}) in 11.80 M HCl for solutions saturated in Se: (○) observed points; (—) theoretical curve for $K = 1.46 \times 10^{-9}$ mol^{-1} L, $K' = 0.748 \times 10^{-9}$ mol^{-1} L, $\epsilon_{Se_2Cl_2}(300) = 3300$ cm^{-1} mol^{-1} L, and $\epsilon_{SeCl_2}(300) = 500$ cm^{-1} mol^{-1} L.

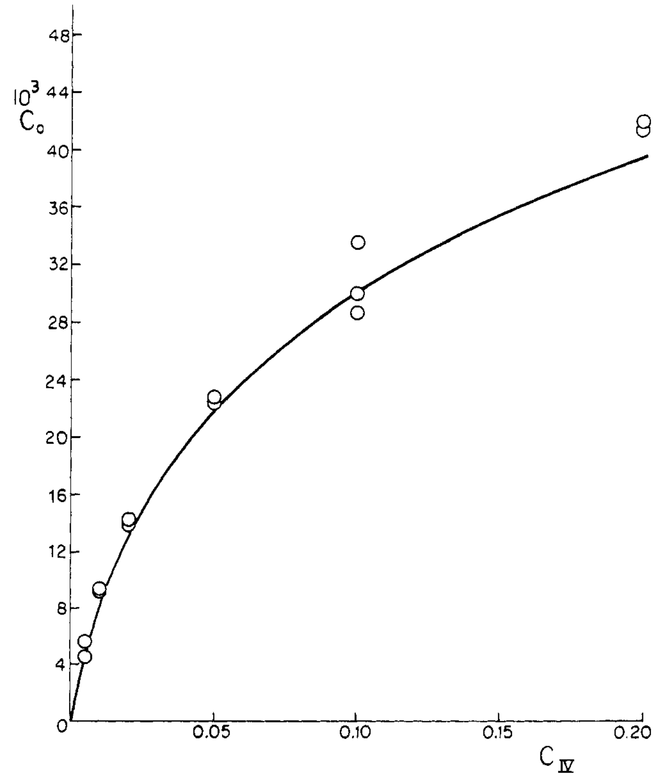

Figure 3. Plot of dissolved Se (c_0) vs. stoichiometric SeO_2 concentration (c_{IV}) in 11.80 M HCl: (○) observed points; (—) theoretical curve for $K = 1.46 \times 10^{-9}$ mol^{-1} L and $K' = 0.748 \times 10^{-9}$ mol^{-1} L.

---

(13) Mahadevan, M.; Milne, J. B., unpublished results.

cording to the gravimetric results. The optimum fit to the absorbance data, which is based upon a minimum average deviation of eq 13 for all experimental points, and which is shown in Figure 2, is found for $K = (1.46 \pm 0.13) \times 10^{-9}$ mol^{-1} L, $K' = (0.75 \pm 0.11) \times 10^{-9}$ mol^{-1} L, $\epsilon_{Se_2Cl_2} = 3300$ cm^{-1} mol^{-1} L, and $\epsilon_{SeCl_2} = 500$ cm^{-1} mol^{-1} L. The agreement with the gravimetric equilibrium constants is excellent. However, for reasons given above, the spectrophotometric equilibrium constants are preferred. Moreover, the fit of these constants to the gravimetric results is within the error of the gravimetric analysis as shown in Figure 3. Unfortunately the c_0 data are of insufficient precision to determine the solubility of elemental selenium in hydrochloric acid.

Conclusion

Although the presence of Se_2Cl_2 in concentrated HCl solutions is not unexpected at these concentrations, the presence of $SeCl_2$ has not yet been reported. The precise nature of the Se(I) and Se(II) species in these solutions is not known, but in view of the weak chloride acceptor power of $SeOCl_2$ in aqueous solution,[4] it is unlikely that the lower oxidation state species would form $Se_2Cl_3^-$, $SeCl_3^-$, or similar anions. The existence of species such as ClSeSe(OH) or ClSe(OH) is a possibility however.

Resolution of the electronic spectrum of the Se(II) species is made difficult by the strong absorbance of $SeOCl_2$ and Se_2Cl_2 in the spectra, but work is continuing in this direction for both aqueous and nonaqueous media.

Acknowledgment. Francine Bouchard is thanked for some preliminary experiments, and the NSERC of Canada, for financial support.

Registry No. SeO_2, 7446-08-4; $SeCl_2$, 14457-70-6; Se_2Cl_2, 10025-68-0; HCl, 7647-01-0; Se, 7782-49-2.

Contribution from Ames Laboratory and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Kinetics and Mechanism of the Oxidation of Hexaaquovanadium(II) Ions by Aliphatic Radicals[1]

JWU-TING CHEN and JAMES H. ESPENSON*

Received August 17, 1982

$V(H_2O)_6^{2+}$ is oxidized to V^{3+} by $\cdot C(CH_3)_2OH$ and by $\cdot CH(CH_3)OC_2H_5$ with formation of $(CH_3)_2CHOH$ and $(C_2H_5)_2O$, respectively. The rate constants were determined by kinetic competition methods based on the homolytic decomposition of organopentaaquochromium(III) cations. The rate constants for the respective reactions are 2.1×10^5 and 5.9×10^4 M^{-1} s^{-1} (at 25 °C, 0.2–1.0 M H$^+$). The former reaction has $k = 3.6 \times 10^4$ M^{-1} s^{-1} in 92% D_2O. The mechanisms considered are (1) rate-limiting acidolysis of a seven-coordinate organovanadium species present in steady-state equilibrium with the reactants and (2) abstraction by the aliphatic radical of a hydrogen atom from a water molecule coordinated to vanadium(II). These possibilities are considered in light of data on the oxidation of $(CH_3)_2CHOH$ by Co^{3+} and Mn^{3+}.

Introduction

To the best of our knowledge no kinetic or other studies of the reactions of vanadium(II) complexes with aliphatic radicals have been reported. Generation of $\cdot CH_3$ in the presence of $V(H_2O)_6^{2+}$ results in the formation of methane,[2] suggesting a direct reaction of V^{2+} and the free radical, lest the latter dimerize.

We earlier found that a large number of organochromium cations $(H_2O)_5CrR^{2+}$ undergo homolytic decomposition in aqueous acidic solution.[3] This opened the door to a new method for evaluating free-radical rate constants, not just because the decomposition of the CrR^{2+} complexes generates the free radical by the reaction $CrR^{2+} \rightleftarrows Cr^{2+} + \cdot R$ but because (a) the slowness of this reaction keeps the free-radical concentration at a low, steady-state value, preventing its dimerization or disproportionation, and (b) its reversibility by addition of Cr^{2+} occurs at a known rate for a large number of radicals.[4] This method[5] relies on the competitive fate of the radical between its return to CrR^{2+} by reaction with Cr^{2+} vs. its reaction with the substrate of interest, $V(H_2O)_6^{2+}$ in the present case.

We chose to examine the reactions of $V(H_2O)_6^{2+}$ and two aliphatic radicals—$\cdot C(CH_3)_2OH$ and $\cdot CH(CH_3)OC_2H_5$—in aqueous perchloric acid solutions, pH 0–3. These widely investigated radicals typically act as thermodynamically powerful and kinetically reactive reducing agents. $E°$ has been estimated[6] as ~−1.2 V vs. NHE for $(CH_3)_2CO + H^+ + e^- = \cdot C(CH_3)_2OH$. Although much less often exemplified in practice, these free radicals may also function as oxidizing agents, e.g., $\cdot C(CH_3)_2OH + H^+ + e^- = (CH_3)_2CHOH$. Relatively few examples of the latter have been reported, however, especially for transition-metal complexes. Of the few cases examined, the reactions appear to involve metastable organometallic intermediates. Such reactions include Cr^{2+},[4,7] Fe^{2+},[8] Ni^+,[9] Zn^+,[10] Cd^+,[11] Pb^+,[12] Ti^{3+},[13] and possibly Cu^+.[14]

---

(1) Based on the Ph.D. thesis of J.T.C., Iowa State University, 1982.

(2) Gold, V.; Wood, D. L. *J. Chem. Soc., Dalton Trans.* **1982**, 2462.

(3) Kirker, G. W.; Bakač, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 1249.

(4) Cohen, H.; Meyerstein, M. *Inorg. Chem.* **1974**, *13*, 2434.

(5) Espenson, J. H.; Shimura, M.; Bakač, A. *Inorg. Chem.* **1982**, *21*, 2537.

(6) Endicott, J. F. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; pp 90–92.

(7) Schmidt, W. A.; Swinehart, J. H.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 1116.

(8) Pribush, A. G.; Brusentseva, S. A.; Shubin, V. N.; Dolin, P. I. *High Energy Chem. (Engl. Transl.)* **1975**, *9*, 206.

(9) Rabani, J.; Mulac, W. A.; Matheson, M. S. *J. Phys. Chem.* **1977**, *81*, 99.

(10) Kelm, M.; Lilie, J.; Henglein, A.; Janata, E. *J. Phys. Chem.* **1974**, *78*, 882.

(11) Kelm, M.; Lilie, J.; Henglein, A. *J. Chem. Soc., Faraday Trans. 1* **1975**, *5*, 1132.

(12) Breitenkamp, M.; Henglein, A.; Lilie, J. *Ber. Bunsenges. Phys. Chem.* **1976**, *80*, 973.

(13) Behar, D.; Samuni, A.; Fessenden, R. W. *J. Phys. Chem.* **1973**, *77*, 2055.