stable band (relative intensity (ri) = 0.022). The calculated mass of the parent ion was 428.6. In the benzyl compound, a similar strong transition was observed (ri = 0.055) for which the parent ion was calculated to be 504.2. The resolution of our instrument in this procedure did not allow the identification of the parent ion mass to better than about 1–2 mass units; however, there can be no doubt about the specific loss of methylamine and benzylamine, respectively, as structural units plus or minus a single proton.

The demonstration of the exceedingly facile loss of the alkylamine group in the mass spectrometer provides strong evidence in favor of structures III, since cleavage of the two N–P bonds with the subsequent re-formation of a P–P bond is highly unlikely. This was further confirmed by the observation that in the mass spectra of the parent amines, Ia and Ib, no significant M − RN or M − RNH peaks were observed. The possibility that the observed transition corresponds to a rearrangement in the molecular ion prior to fragmentation also appears remote, especially in view of the fact that *no other* metastable decomposition to mass 400 involving the separate losses of the R group and the nitrogen atom were observed. Further discussion of the mass spectra of these compounds will be reported elsewhere.

Migration of an alkyl group may occur either by breaking an R–N bond in a base-catalyzed reaction formally analogous to the Stevens rearrangement or by breaking an N–P bond *via* an intramolecular S_N2 type rearrangement. Investigations are under way to determine the stage in this multistep reaction sequence at which rearrangement occurs and to determine the mechanism of this rearrangement.

Acknowledgments.—D. F. Clemens gratefully acknowledges receipt of a grant from the North Carolina Board of Science and Technology. We also wish to acknowledge the Special Research Resources Branch, Division of Research Resources, NIH, for support, under Grant No. FR00330 for the Research Triangle Center for Mass Spectrometry.

CONTRIBUTION FROM THE ANALYTICAL CHEMISTRY LABORATORY,
FACULTY OF ENGINEERING,
HOKKAIDO UNIVERSITY, SAPPORO, JAPAN

The Mechanism of Oxygenation of Ferrous Ion in Neutral Solution

BY KATSUMI GOTO, HIROKI TAMURA, AND MASAICHI NAGAYAMA

Received July 28, 1969

As early as 1906, Just[1] had shown that the rate of oxidation of ferrous ion by dissolved oxygen in neutral solutions is expressed by

$$-\frac{\mathrm{d}[\mathrm{Fe(II)}]}{\mathrm{d}t} = k_0[\mathrm{Fe(II)}][\mathrm{O_2}][\mathrm{OH^-}]^2 \qquad (1)$$

More recently, Stumm and Lee[2] and Schenck and Weber[3] ascertained the validity of eq 1 from measurements under more carefully controlled conditions. The value of k_0 determined by the authors at 20° was $5.7 \times 10^{13}\ M^{-3}\ \mathrm{sec}^{-1}$.

Weiss[4] proposed the following radical mechanism to explain the first-order dependence of the rate both on dissolved oxygen and on ferrous ion

$$\mathrm{Fe^{2+} + O_2 \xrightarrow{\text{slow}} Fe^{3+} + O_2^-,\ O_2^- + H^+ \rightleftharpoons HO_2} \qquad (2a)$$

$$\mathrm{Fe^{2+} + HO_2 \longrightarrow Fe^{3+} + HO_2^-,\ HO_2^- + H^+ \rightleftharpoons H_2O_2} \qquad (2b)$$

$$\mathrm{Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH} \qquad (2c)$$

$$\mathrm{Fe^{2+} + OH \longrightarrow Fe^{3+} + OH^-} \qquad (2d)$$

However, since this does not explain the second-order dependence of the rate on hydroxyl ion concentration, Abel[5] proposed a somewhat different model

$$\left.\begin{aligned}\mathrm{O_2 + OH^-} &\rightleftharpoons \mathrm{O_2OH^-}\\ \mathrm{O_2OH^- + OH^-} &\rightleftharpoons \mathrm{O_3{}^{2-} + H_2O}\end{aligned}\right. \qquad (3)$$

$$\mathrm{Fe^{2+} + O_3{}^{2-} \xrightarrow{\text{slow}} Fe^{3+} + 3O^-,\ 3O^- + 3H^+ \rightleftharpoons 3OH} \qquad (4a)$$

$$\mathrm{3Fe^{2+} + 3OH \longrightarrow 3Fe^{3+} + 3OH^-} \qquad (4b)$$

The important assumption in his mechanism was that the $\mathrm{O_3{}^{2-}}$ ion which he named "peroxide-like oxygen" existed in the solution in equilibrium with the $\mathrm{O_2}$ molecule and $\mathrm{OH^-}$ ion. He considered that the $\mathrm{O_3{}^{2-}}$ ion is much more reactive toward Fe(II) than is the ordinary $\mathrm{O_2}$ molecule. This leads to the rate equation

$$-\frac{\mathrm{d}[\mathrm{Fe(II)}]}{\mathrm{d}t} = 4k\beta_{\mathrm{O_3{}^{2-}}}[\mathrm{Fe^{2+}}][\mathrm{O_2}][\mathrm{OH^-}]^2 \qquad (5)$$

where $\beta_{\mathrm{O_3{}^{2-}}}$ designates the overall stability constant of $\mathrm{O_3{}^{2-}}$. The value of k in eq 5 is considered to be smaller than $1.4 \times 10^{11}\ M^{-1}\ \mathrm{sec}^{-1}$, the rate constant[6] of the reaction $\mathrm{H^+ + OH^- \rightarrow H_2O}$. Considering that $k_0 = 5.7 \times 10^{13}$ is equal to $4k\beta_{\mathrm{O_3{}^{2-}}}$ and the value of k is smaller than 1.4×10^{11}, the value of $\beta_{\mathrm{O_3{}^{2-}}}$ should be larger than 1.0×10^2. However, this seems unlikely when the solubility of oxygen is taken into consideration. If $\beta_{\mathrm{O_3{}^{2-}}} = [\mathrm{O_3{}^{2-}}]/[\mathrm{O_2}][\mathrm{OH^-}]^2 = 1.0 \times 10^2$ is the case, the equilibrium concentration of $\mathrm{O_3{}^{2-}}$ would be equal to that of the ordinary oxygen molecule $\mathrm{O_2}$ at a pH of about 13. This means that the $[\mathrm{O_3{}^{2-}}]$, hence the total concentration of oxygen $[\mathrm{O_2}] + [\mathrm{O_2OH^-}] + [\mathrm{O_3{}^{2-}}]$, will change remarkably around this pH. Since the value of $\beta_{\mathrm{O_3{}^{2-}}}$ given above is the maximum possible value, the change of the solubility of oxygen should occur around a lower pH value. This conflicts with the experimental fact that there is no appreciable change in the solubility of oxygen over a wide range of pH's from strongly acidic to strongly alkaline.[7] It is therefore clear that the assumption adopted in Abel's mechanism is inadequate.

---

(1) G. Just, *Z. Physik. Chem.*, **63**, 385 (1908).

(2) W. Stumm and G. F. Lee, *Ind. Eng. Chem.*, **53**, 143 (1961).

(3) J. E. Schenk and W. J. Weber, Jr., *J. Am. Water Works Assoc.*, **60**, 199 (1968).

(4) J. Weiss, *Naturwissenschaften*, **23**, 64 (1935).

(5) E. Abel, *Z. Elektrochem.*, **59**, 903 (1955).

(6) M. Eigen and L. DeMaeyer, *ibid.*, **59**, 986 (1955).

(7) F. Linke, "Solubilities of Inorganic and Metal Organic Compounds," Vol. 2, 4th ed, American Chemical Society, Washington, D. C., 1965, p 1229.

A new mechanism is proposed in this paper to overcome these difficulties. As can be seen below, the rate-determining step is assumed to be the reaction between $FeOH^+$ and O_2OH^-, the latter species being the intermediate to form the "peroxide-like oxygen" as can be seen in eq 3.

$$Fe^{2+} + OH^- \rightleftharpoons FeOH^+, \quad K_{FeOH^+} = \frac{[FeOH^+]}{[Fe^{2+}][OH^-]}$$
$$O_2 + OH^- \rightleftharpoons O_2OH^-, \quad K_{O_2OH^-} = \frac{[O_2OH^-]}{[O_2][OH^-]} \qquad (6)$$

$$FeOH^+ + O_2OH^- \xrightarrow{\text{slow}} Fe(OH)_2{}^+ + O_2{}^-, \quad O_2{}^- + H^+ \rightleftharpoons HO_2 \qquad (7)$$

The rate equation will be

$$-\frac{d[Fe(II)]}{dt} = 4k[FeOH^+][O_2OH^-]$$
$$= 4kK_{FeOH^+}K_{O_2OH^-}\frac{[Fe(II)]}{1 + K_{FeOH^+}[OH^-]} \times \frac{[O_2]_{total}}{1 + K_{O_2OH^-}[OH^-]}[OH^-]^2 \qquad (8)$$

where $[Fe(II)] = [Fe^{2+}] + [FeOH^+]$ and $[O_2]_{total} = [O_2] + [O_2OH^-]$. Calculations with $K_{FeOH^+} = 10^{4.5}$ reported by Hedström[8] indicated that, at pH's below 7.5, the term $K_{FeOH^+}[OH^-]$ in eq 8 can be neglected compared to 1.

As pointed out above, the solubility of oxygen does not increase even when the alkalinity of the solution is raised to 2 N in NaOH.[7] This means that $[O_2OH^-]$ is far less than $[O_2]$. Since $[O_2OH^-]$ is much less than $[O_2]$ at pH 14.3, *i.e.*, in 2 N NaOH solution, the value of $K_{O_2OH^-}$ should be far less than $10^{-0.3}$. It is also seen that, at pH's below 7.5, $K_{O_2OH^-}[OH^-]$ in eq 8 is negligible compared to 1, and $[O_2]_{total}$ can be replaced by $[O_2]$. In this way, eq 8 is simplified to

$$-\frac{d[Fe(II)]}{dt} = 4kK_{FeOH^+}K_{O_2OH^-}[Fe(II)][O_2][OH^-]^2 \qquad (9)$$

By comparing eq 1 with 9, we can put

$$k_0 = 4kK_{FeOH^+}K_{O_2OH^-} = 5.7 \times 10^{13} \qquad (10)$$

The value of k must be smaller than the rate constant 1.4×10^{11} for the reaction between H^+ and OH^-. Therefore, the smallest possible value of $K_{O_2OH^-}$ is $10^{-2.5}$. Thus, if the proposed mechanism is valid, the value of $K_{O_2OH^-}$ should lie in the range

$$10^{-2.5} < K_{O_2OH^-} < 10^{-0.3} \qquad (11)$$

from which it will be seen that the value of the specific rate constant k lies in the range

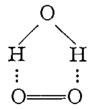
$$4.6 \times 10^9 < k < 1.4 \times 10^{11} \qquad (12)$$

Such a large value of k suggests that the reaction between $FeOH^+$ and O_2OH^- is most likely diffusion controlled and predicts the activation energy to be very small. Stumm and Lee[2] estimated an apparent activation energy to be 23 kcal/mol from the temperature dependence of the overall rate constant k_0 in eq 1. However, since k_0 depends on k, K_{FeOH^+}, and $K_{O_2OH^+}$ as will be seen in eq 10 the apparent activation energy is the sum of three terms

$$E_{app} = E_a + \Delta H°_{FeOH^+} + \Delta H°_{O_2OH^-}$$

where E_a is the activation energy of the reaction between $FeOH^+$ and O_2OH^- and $\Delta H°_{FeOH^+}$ and $\Delta H°_{O_2OH^-}$ are the enthalpies of the formation reaction of $FeOH^+$ and O_2OH^-, respectively.

Heidt and Johnson[9] obtained some evidence that the oxygen molecules dissolved in water are hydrated to form $OH_2 \cdots O{=}O \cdots H_2O$ and/or



Then it is reasonable to assume that the water molecules coordinated to oxygen can dissociate in the same sense as in the hydrolysis of metal ions. The forms of oxygen ions O_2OH^- and $O_3{}^{2-}$ will be equivalent to the first-step and the second-step dissociated forms of hydrated oxygen molecule described above.

The values of $\Delta H°_{FeOH^+}$ and $\Delta H°_{O_2OH^-}$ will be about 10 kcal/mol because the enthalpies of the dissociation reactions of these hydrated species are expected to be about the same as that of the neutralization of weak acid with base. Hence the value of E_a is 3 kcal/mol, consistent with the above assumption that the rate-determining process is controlled by the diffusion of $FeOH^+$ and O_2OH^-.

---

[8] B. O. A. Hedström, *Arkiv Kemi*, **5**, 457 (1953).

[9] J. Heidt and A. M. Johnson, *J. Am. Chem. Soc.*, **79**, 5587 (1957).

CONTRIBUTION FROM THE DOW CHEMICAL COMPANY,
ROCKY FLATS DIVISION, GOLDEN, COLORADO 80401

Plutonium Species in Propane-1,2-diol Carbonate Solution. Preparation of a Multivalent Plutonium Compound

BY J. M. CLEVELAND, G. H. BRYAN, AND W. G. EGGERMAN

Received August 14, 1969

Aside from brief spectrophotometric studies in dimethylformamide, dimethyl sulfoxide, and ethanol[1] and a more thorough study in anhydrous acetic acid,[2] the chemistry of plutonium in nonaqueous solvents has been neglected, despite the potential advantages resulting from the absence of strong solvent coordination and hydrolysis. This paper describes an investigation using propane-1,2-diol carbonate (PDC), whose high dielectric constant of 69,[3] convenient liquid range, and chemical stability make it a promising choice for a nonaqueous solvent. The plutonium–chloride system was selected for study because of the ready

---

[1] A. Ekstrom, M. S. Farrell, and J. J. Lawrence, *J. Inorg. Nucl. Chem.*, **30**, 660 (1968).

[2] M. Alie, Q. C. Johnson, H. D. Cowan, and J. F. Lemons, *ibid.*, **29**, 2327 (1967).

[3] "Propylene Carbonate," Technical Bulletin, Jefferson Chemical Co., Houston, Texas, 1956.