The *NN'*-Ethylenebis(salicylaldiminato)vanadium(III)–Oxygen Reaction in Pyridine: Evidence for a Vanadium(III)–Oxygen Adduct

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Summary The kinetics of the reaction between *NN'*-ethylenebis(salicylaldiminato)vanadium(III), V(salen)$^+$, and oxygen in pyridine indicate that a V(salen)$^+$–oxygen adduct is formed.

THIS communication describes the reaction between oxygen and *NN'*-ethylenebis(salicylaldiminato)vanadium(III), V(salen)$^+$, in pyridine. Evidence is presented for the existence of a V(salen)$^+$–oxygen complex as an intermediate in the reaction. This is the first vanadium(III)–oxygen adduct that has been characterized, and has important implications concerning the role of vanadium complexes in the blood of ascidians and the wide range of rate constants observed for vanadium(III)–oxygen reactions.

An equimolar mixture of salicylaldehyde ethylenediamine and anhydrous vanadium(III) chloride (Fluka, A. G., purum) in pyridine was heated and nitrogen (min. 99·99%) was bubbled through the mixture for 5—6 h. A brown solid was precipitated. When dried under nitrogen at room temperature, the solid retained an odour of pyridine. This precipitate was evacuated to 0·05 mm of Hg pressure at room temperature for 5 h. The analysis showed the compound to be $V(C_{16}H_{14}O_2N_2)Cl,C_5H_5N$. The spectrum of this complex in pyridine has maxima at 360 and 580 nm and a shoulder at 450 nm, and conductance measurements show it to be a 1 : 1 electrolyte in pyridine at the concentrations used. The corresponding vanadium(IV) complex $VO(C_{16}H_{14}O_2N_2),C_5H_5N \equiv VO(salen),C_5H_5N$ was prepared by a standard technique,[1] and has absorbance maxima at 370 and 590 nm. Spectra taken during the course of the V(salen)$^+$–oxygen reaction show two isosbestic points at 355 and 390 nm. The spectrum of the final vanadium complex corresponds to that of VO(salen), so that oxygen oxidizes the vanadium(III) complex to the vanadium(IV) complex. It should be noted that there is sufficient water in the solution to allow for the association of a water molecule with a vanadium(IV) and its subsequent hydrolysis. Experiments using an oxygen analyser indicate that four

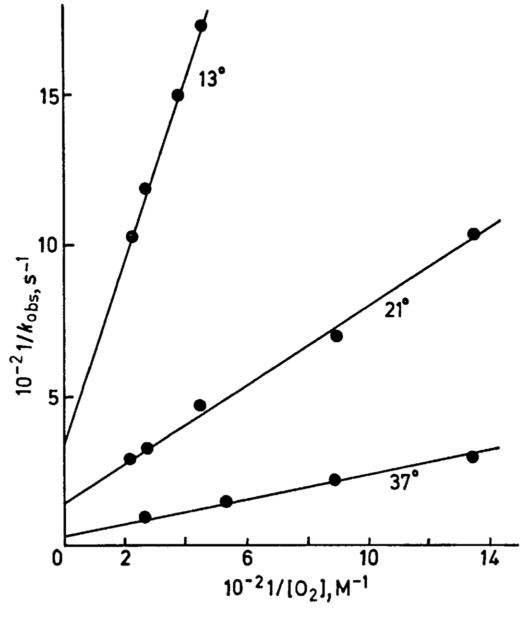

FIGURE. *Plot of* $1/k_{obs}$ (s^{-1}) *against* (M^{-1}) *at* 13, 21, *and* 37°. *Oxygen concentrations from W. F. Link, "Solubilities: Inorganic and Metal-Organic Compounds," Vol.* II, *4th edn., Amer. Chem. Soc., Washington, D.C.,* 1965, *p.* 1235.

moles of V(salen)$^+$ complex are consumed for every mole of oxygen present.

If the mechanism for the reaction is

$$\mathrm{V(salen)^+ + O_2 \overset{K}{\rightleftharpoons} V(salen)O_2^+} \qquad (1)$$

$$\mathrm{V(salen)O_2^+ \xrightarrow{k_d} products} \qquad (2)$$

then in the presence of an excess of O_2 if reaction (1) equilibrates rapidly compared to (2),

$$-\frac{d[\mathrm{V(salen)^+}]}{dt} = \frac{k_d K[\mathrm{V(salen)^+}][\mathrm{O_2}].}{1 + K[\mathrm{O_2}]}$$

$$\text{Thus, } k_{obs} = \frac{k_d K[\mathrm{O_2}]}{1 + K[\mathrm{O_2}]} \text{ and } \frac{1}{k_{obs}} = \frac{1}{k_d} + \frac{1}{k_d\,K[\mathrm{O_2}]}$$

Plots of $1/k_{obs}$ against $1/[O_2]$ for the reaction in pyridine at 13, 21, and 37° when $[O_2]$ was at least in fivefold excess over the concentration of the complex are shown in the Figure. The kinetics were followed spectrophotometrically *at 450* nm, and first-order plots for the disappearance of V(salen)$^+$ were observed. From the intercepts of the plots in the Figure, values of k_d were determined. Values of k_d at various temperatures are $(2{\cdot}9 \pm 0{\cdot}3) \times 10^{-3}$ s^{-1}, 13°; $(6{\cdot}3 \pm 1{\cdot}2) \times 10^{-3}$, 21; and $(33 \pm 12) \times 10^{-3}$, 37. The value of k_d at 25° is $9{\cdot}8 \times 10^{-3}$ s^{-1}, and the activation parameters are $\Delta H^{\ddagger} = 17{\cdot}5 \pm 1{\cdot}6$ kcal/mole and $\Delta S^{\ddagger} = -9 \pm 5$ e.u.

The values of the equilibrium constants, K, evaluated from the slopes and intercepts are somewhat scattered, but the values lie between 100 and 250 M^{-1} at the three temperatures. It is clear from the data that the enthalpy for reaction (1) is not large.

It should be noted that the kinetic data do not distinguish between the suggested mechanism, reactions (1) and (2), and mechanisms in which (i) V(salen)O_2^+ is not a precursor to the products or (ii) a second bimolecular path leading to the products exists which does not involve V(salen)O_2^+ as a precursor to the products. The question of the nature of the immediate products of the reaction is left unresolved. As indicated previously VO(salen) is the final vanadium-containing product, but it can either be formed directly or by the formation of a vanadium(V) complex followed by its reaction with V(salen)$^+$ to yield VO(salen).[2-4]

The effects of added water and copper(II) on the reaction were investigated. Water has no effect on the rate constant for the reaction between 0·04 M (lowest water concentration) and 0·15 M. Above $[H_2O] = 0{\cdot}15$ M a decrease in the rate constant for the reaction is observed. The experiments reported here were done at $[H_2O] = 0{\cdot}06$ M.

Added copper(II), as anhydrous $CuCl_2$, increases the value of k_{obs}, but the increase in the observed rate constant between copper(II) concentrations of 5×10^{-6} M and 1×10^{-3} M is only 2·6 fold. The reaction studied here is not as sensitive to the presence of copper(II) as the vanadium(III)-oxygen reaction in acidic aqueous solution.[3]

From the value of the equilibrium constant for reaction (1), about 100—250 M^{-1}, and the concentrations used, up to 40% of the vanadium(III) could be in the form of a V(salen)$^+$-oxygen adduct in the initial stages of the reaction. Although the reaction obeys isosbestic behaviour on a less sensitive scale of the spectrophotometer (0—1·0 absorbance units), difference spectra [V(salen)$^+$-pyridine-nitrogen *vs* V(salen)$^+$-pyridine-oxygen)] on an expanded scale (0—0·1) shows a deviation from isosbestic behaviour at about 400 nm and the appearance of a deficiency in absorbance in the V(salen)$^+$-pyridine-oxygen solution in that wavelength region which is proportional to the excess oxygen concentration. Because of the speed of the reaction it has not been shown that the absorbance deficiency can be removed by the addition of nitrogen. However, it has been demonstrated by such experiments that a reversible oxygen adduct is formed in the VCl_3-pyridine-oxygen system.[5]

The reaction between V(salen)$^+$ and oxygen in ethanol and dioxan was investigated. At 25° in ethanol, a plot of k_{obs} (s^{-1}) against excess of $[O_2]$ was linear, so that no V(salen)$^+$-oxygen adduct could be distinguished kinetically. The bimolecular rate constant for the reaction was 2×10^{-1}M^{-1} s^{-1} at 25° in ethanol. In dioxan, no reaction took place at 35° over a period of 1 h. The slowness of this reaction and that of vanadium(III) in acid aqueous solution[3] may, in part, result from the inability of an oxygen adduct to be formed.

The observation of an oxygen adduct of V(salen)$^+$ reinforces the view that vanadium(III) complexes can act as oxygen carriers in ascidians.[6]

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