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Activation Volume for the Reaction of Nitrilotriacetatodioxovanadate(V) with Hydrogen Peroxide as studied by a High-Pressure Stopped-Flow Technique

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We have studied reactions of hydrogen peroxide with some aminopolycarboxylatovanadate(V) complexes in aqueous solution [1, 2]. The large negative entropy of activation for the peroxo complex formation is ascribed to a highly oriented transition state and provides strong evidence for an associative mode of activation [2].

We attempted to study the reaction with a high-pressure stopped-flow apparatus which has only recently been used in this laboratory [3]. All materials in contact with the reaction solution are made of platinum and Diflon (fluorocarbon polymer). Mixing efficiency, dead time and pressure constancy of the apparatus are all satisfactory for following reactions with a half life longer than 0.5 s. The pressure in the reaction solution was monitored with a manganin resistance pressure gauge. After mixing a vanadium(V)–NTA complex (nitrilotriacetatodioxovanadate(V): $VO_2(nta)^{2-}$) solution with a hydrogen peroxide solution under various pressures up to 1200 kg cm^{-2}, the reaction was followed spectrophotometrically at 432 nm, a wavelength of maximum absorption of the peroxo complex. The half life time of the reaction under our experimental conditions is larger than several seconds.

Over the pH range 2.2–4.2 at atmospheric pressure, the rate law for the formation of the peroxo complex is given by the following [2]:

$$\frac{d[VO(O_2)(nta)^{2-}]}{dt} = \{k_1 + k_2[H^+]\}[VO_2(nta)^{2-}][H_2O_2] \qquad (1)$$

where $k_1 = 7.41$ mol^{-1} dm^3 s^{-1} and $k_2 = 1.86 \times 10^4$ mol^{-2} dm^6 s^{-1} at 25 °C and I = 1.00 mol dm^{-3}. The reaction was followed over a wider range of pH 2–6.5, MES (2-(N-morpholino)ethanesulfonic acid) being used as pH buffer. The second-order rate constants thus obtained are in excellent agreement with the above values. At pH higher than 5.5 the k_2 path in eqn. 1 being negligible, the rate is independent of hydrogen ion concentration. Thus values of k_1 at $[H^+] = 2.67 \times 10^{-6}$ mol kg^{-1}, 1.48×10^{-6} mol kg^{-1} and 1.41×10^{-6} mol kg^{-1} were determined at pressures up to 1200 kg cm^{-2} at 25 °C. The plot of $\ln k_1$ against pressure is shown in Fig. 1.

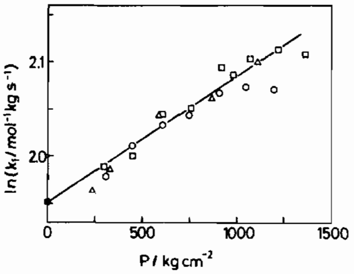

Fig. 1. Pressure dependence of $\ln k_1$. Conditions: 25 °C, I = 1.08 ($NaClO_4$), $C_{MES} = 1.05 \times 10^{-2}$. ○, $C_V = 3.68 \times 10^{-4}$, $C_{NTA} = 4.63 \times 10^{-4}$, $C_{H_2O_2} = 1.84 \times 10^{-2}$, $[H^+] = 2.67 \times 10^{-6}$; △, $C_V = 1.87 \times 10^{-4}$, $C_{NTA} = 2.35 \times 10^{-4}$, $C_{H_2O_2} = 9.65 \times 10^{-3}$, $[H^+] = 1.48 \times 10^{-6}$; □, $C_V = 2.10 \times 10^{-4}$, $C_{NTA} = 3.47 \times 10^{-4}$, $C_{H_2O_2} = 1.22 \times 10^{-2}$, $[H^+] = 1.41 \times 10^{-6}$. C_X refers to the total concentration of X in mol kg^{-1}. Each point is the average of two or more determinations.

According to the transition state theory the change in rate constant with pressure is given by

$$(\partial \ln k_1/\partial P)_T = -\Delta V^{\ddagger}/RT \qquad (2)$$

The data were fitted to an equation linear in pressure by fixing the value at the atmospheric pressure. The activation volume $\Delta V^{\ddagger}$ was determined to be -3.3 ± 0.6 cm^3 mol^{-1}. The measured volume of activation $\Delta V^{\ddagger}$ can be expressed as the sum of an intrinsic part $\Delta V^{\ddagger}_{int}$ and an electrostrictive part $\Delta V^{\ddagger}_{el}$ [4]. $\Delta V^{\ddagger}_{int}$ will be positive or negative according to the importance of bond-breaking or bond-making, respectively, in the activation process. There seems to be no or little contribution of solvational changes in our case with no change of charge in the transition state and thus $\Delta V^{\ddagger}_{el} \simeq 0$ cm^3 mol^{-1}. The negative activation volume is consistent with an associative mechanism in which H_2O_2 is entering into the inner coordination sphere of the metal ion in the activation process. Further investigations with other complexes at high pressure are in progress and will give more insight into the H_2O_2 entry reaction.

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