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LETTER

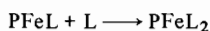
Activation Volumes for the Axial Ligations of Hemin in *N,N*-Dimethylformamide

HITOSHI OTAKE, ATSUSHI MIYATA
and HIROSHI TOMIYASU*

Research Laboratory for Nuclear Reactors, Tokyo Institute
of Technology, O-okayama, Meguro-ku, Tokyo 152 (Japan)

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In spite of the many kinetic studies on reactions at the axial positions of ferric porphyrins [1–6], the mechanism has not been established in detail. The most common mechanism appears to be stepwise reactions, typical examples of which, given by Pasternack *et al.* [1] for reactions between high-spin five-coordinate ferric porphyrins and strong-field ligands, are shown below (Scheme 1)



Scheme 1.

where PFe = ferric porphyrins, S = coordinating solvents such as dimethyl sulfoxide (Me_2SO) and L = strong-field ligands such as imidazole and the cyanide ion.

The present paper presents activation volumes for reactions at the axial positions of hemin (ferric protoporphyrin IX) with cyanide (CN^-) and imidazole (Im) in *N,N*-dimethylformamide (DMF) and the reaction mechanism is discussed on the basis of activation parameters.

Experimental

Kinetic experiments were carried out by use of Union-Giken RA-401 and Hikarikoatsu FIT-3 stopped-flow spectrophotometers under normal and high pressures, respectively. DMF (Wako Pure Chemical Ind.) was dried over 3A molecular sieve and

distilled before use. All other chemicals were reagent grade (Wako).

Results and Discussion

The stopped-flow spectra obtained at normal pressure for the reaction between hemin and CN^- in DMF gave two distinct traces with different time scales under pseudo-first-order conditions [hemin] \ll [CN^-]: the first reaction was very fast, the time scale being nearly the limit of the stopped-flow measurements, and the observed rate constant was proportional to [CN^-], giving the second-order rate constant $k_1 = 8.82 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (1 M = 1 mol kg^{-1}) at 25 °C; the relatively slow second reaction (called hereafter the k_2 path) was attributed to the formation of the final complex PFeL_2 from PFeL . In the reaction with imidazole, only a single trace was observed, the time scale being about the same as that of the k_2 path for the reaction with CN^- . Based on the stepwise reaction mechanism (Scheme 1), this trace can be assigned to the k_2 path (the second step) and the first step is assumed to be too fast to be measured. Since the first step in Scheme 1 was very fast for stopped-flow measurements even for the reaction with CN^- , the effect of pressure on the rate was investigated only for the k_2 path.

In Figs. 1 and 2, the observed first-order rate constants k_{obs} are plotted as functions of ligand concentrations, [CN^-] and [Im], at various pressures. It can be seen in these Figures that k_{obs} is linear, passing through the origin within experimental error at constant pressures, the slopes yielding the second-order rate constant k_2 . Figure 3 shows plots of $\ln k_2$ versus pressure. From the linear relationship of the plots in Fig. 3, the activation volumes were determined to be -11.4 ± 2.3 and $-7.6 \pm 1.3 \text{ cm}^3 \text{ mol}^{-1}$ for the ligations of CN^- and Im, respectively.

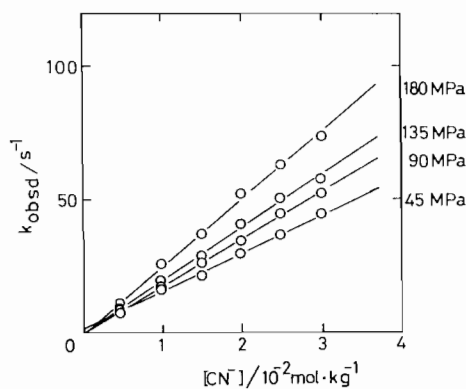


Fig. 1. Plots of k_{obs} vs. the concentration of CN^- at various pressures; [PFe] = $1.1 \times 10^{-4} \text{ M}$ at 20 °C.

*Author to whom correspondence should be addressed.

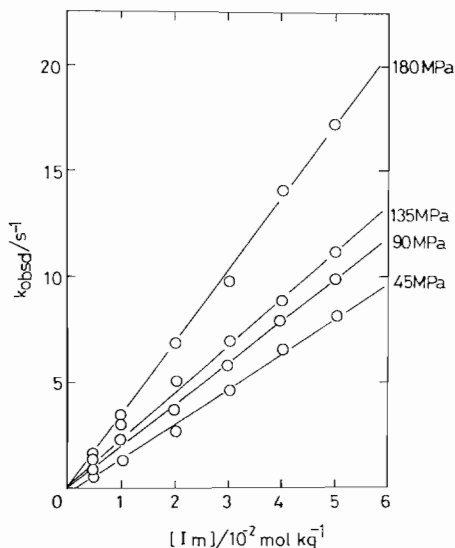


Fig. 2. Plots of k_{obs} vs. the concentration of Im at various pressures; $[\text{PFe}] = 1.1 \times 10^{-4} \text{ M}$ at 20°C .

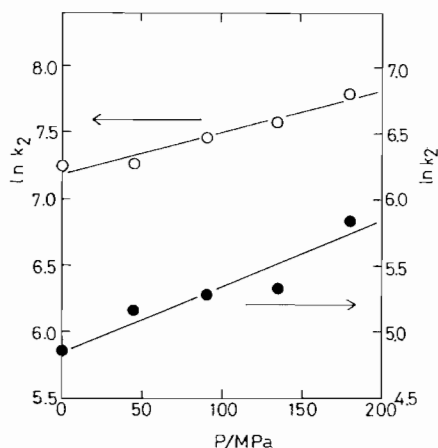


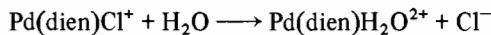
Fig. 3. Plots of $\ln k_2$ vs. pressure for the reactions with CN^- (●) and Im (○).

In general, reactions with such negative activation volumes are consistent with the associative nature of reaction mechanisms [7].

In the second step in Scheme 1, the entering ligand might approach associatively the iron atom from the distal site of the PFe-L bond, because the spin-state of a monoligand complex such as PFeL is generally believed to be high spin [3, 8, 9] and the sixth position is either vacant or weakly coordinated. Consequently, this mechanism leads to negative activation volumes. The effect of charge, e.g. charge formation or charge neutralization at activated complexes, should be taken into consideration in the observed values of the activation volumes

[7]. However, in the present reactions between $[\text{PFeCN}]$ and CN^- , and $[\text{PFeIm}]^+$ and Im, the electrostatic effect on the activation volumes would be small, because the formation of activated complexes results in neither charge formation nor charge neutralization.

The present results can be compared with those of a similar reaction: solvolysis in a square-planar complex $\text{Pd}(\text{dien})\text{Cl}^+$ (dien = diethylenetriamine) [10]



This reaction is considered to proceed via an associative mechanism and the activation volume is reported to be $-12.2 \sim -10.0 \text{ cm}^3 \text{ mol}^{-1}$ depending upon the substituting ligands, i.e. water is further substituted to form the final products. These values are close to a limiting activation volume of about $-13 \text{ cm}^3 \text{ mol}^{-1}$ for water exchange [7]. In the present reaction, since partial molar volumes of CN^- and Im are larger than that of water (i.e. the partial molar volume of CN^- is $32.5 \text{ cm}^3 \text{ mol}^{-1}$ [11] and that of Im is expected to be much larger), the absolute value of the limiting activation volume should be larger than $13 \text{ cm}^3 \text{ mol}^{-1}$. In conclusion, an associative interchange mechanism rather than a limiting associative mechanism appears to be operative for ligations of hemin.

From the temperature dependence of k_2 from 10 to 25°C at normal pressure, the activation enthalpy and entropy were determined as: $35.9 \pm 3.5 \text{ kJ mol}^{-1}$ and $-67.2 \pm 10.9 \text{ J K}^{-1} \text{ mol}^{-1}$, and $23.3 \pm 1.7 \text{ kJ mol}^{-1}$ and $-112 \pm 6.0 \text{ J K}^{-1} \text{ mol}^{-1}$ for the reaction with CN^- and Im, respectively. The large negative values of the activation entropy support the associative nature of the reaction mechanism.

Morishima *et al.* [12] have shown in their NMR studies that when five-coordinated chlorides of ferric porphyrins $[\text{PFeCl}]$ are dissolved in weak field coordinating solvents such as Me_2SO and alcohols, six-coordinate high-spin complexes $[\text{PFeS}_2]\text{Cl}$ are formed. Based on this result together with the estimated donating ability of DMF (i.e. the donor number [13] of DMF is 26.6 as compared with 29.8 and 20 for Me_2SO and ethanol, respectively), hemin is expected to exist in the form $[\text{PFeS}_2]\text{Cl}$ in DMF. This six-coordinate structure of high-spin hemin might support the proposed associative interchange mechanism.

Acknowledgement

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