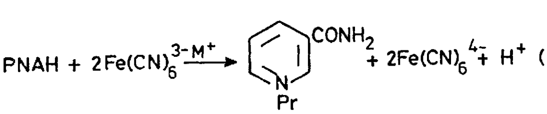
Alkali-metal Ion Acceleration of the Electron-transfer Reaction between *N*-Propyl-1,4-dihydronicotinamide and Ferricyanide Ion

By TADASHI OKAMOTO,* ATSUYOSHI OHNO, and SHINZABURO OKA
(*Institute for Chemical Research, Kyoto University, Gokasho, Uji,* 611 *Japan*)

Summary Alkali-metal ions caused an acceleration of the reaction between *N*-propyl-1,4-dihydronicotinamide and $Fe(CN)_6^{3-}$ in the decreasing order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+ =$ *ca.* Et_4N^+, which suggests the acceleration of the electron-transfer process by polarizable alkali-metal ions.

SALT effects are observed over a wide range of chemistry,[1] but specific acceleration by alkali-metal ions is not a general phenomenon. Electron-transfer reactions between negative ions are known to be accelerated in the presence of alkali-metal ions by reducing the repulsive force of the approaching two negative charges.[2] We now report a similar acceleration by alkali-metal ions for a reaction of a neutral molecule with a negative ion, the electron-transfer reaction (1) between *N*-propyl-1,4-dihydronicotinamide (PNAH) and ferricyanide ion,[3] in which the repulsive force of the reactants would not be so significant.



(1)

The rates were followed spectrophotometrically as described before.[3] The effect of the added alkali metal salts was determined with the following concentrations of each component; $K_3Fe(CN)_6$ $5{\cdot}0 \times 10^{-4}$ M, K_2CO_3 $2{\cdot}5 \times 10^{-3}$ M, PNAH $2{\cdot}5 \times 10^{-5}$ M, and salt $1{\cdot}5 \times 10^{-2}$ to 10^{-3} M. Good pseudo-first order correlation was observed throughout the salt concentrations examined. There was a linear dependence of the apparent second-order rate constant k_2 ($k_{obs}/[Fe(CN)_6^{3-}]$) on the concentration of added salt (Figures 1 and 2).

$$M^+ + Fe^{III} \overset{K_{M^+}}{\rightleftharpoons} [M^+ - - - Fe^{III}] \qquad (2)$$

$$[M^+ - - - Fe^{III}] + PNAH \xrightarrow{k_{M^+}} \text{products} \qquad (3)$$

$$Fe^{III} + PNAH \xrightarrow{k_0} \text{products} \qquad (4)$$

$$-\frac{d\,[PNAH]}{dt} = [PNAH]\,[Fe^{III}] \times \frac{k_0 + \Sigma k_{M^+}K_{M^+}[M^+]}{1 + \Sigma K_{M^+}[M^+]} \qquad (5)$$

TABLE. Influence of salts on the rate constant

Chloride	Li	Na	K	Rb	Cs	Et_4N
$10^{-2}k_{M+}K_{M+}$/l mol^{-1} s^{-1}	0	8·15	14·9	23·0	83·2	−2·85
k_0'/l mol^{-1} s^{-1}	31·0	29·6	(20·4)[a]	29·4	30·1	29·7
log K_W		−0·77	−0·42		−0·26	

[a] k_0

Good pseudo-first-order kinetics together with a levelling off of the rate at high concentrations of caesium chloride show that the equilibrium in equation (2) is fast compared with the rate-determining step. Since K_{M+} values for alkali-metal ions are <10 in water,[4] the term $\Sigma K_{M+}[M^+]$ can be neglected compared with unity in the denominator of (5), which leads, to a first approximation, to equation (6) for the apparent rate constant. The product of the

$$k_{obs} = [Fe^{III}]\ (k_0 + \Sigma k_{M+}K_{M+}[M^+]) \qquad (6)$$

constants, $k_{M+}K_{M+}$, was calculated from the initial slope of the plot of k_2 *vs.* [K$^+$], and a value for k_0 of 20·4 l mol^{-1} s^{-1} was estimated by extrapolation from the intercept of the plot (Figure 1). For the salts other than K$^+$, the solutions contained two types of cation, K$^+$ and the added cation. The value of k_2 at zero concentration of added salt, k_0', for each ion is in a good accordance with the calculated value ($k_0 + k_{K^+}K_{K^+}[K^+] = 20·4 + 1·49 \times 10^3 \times 6·5 \times 10^{-3} = 30·1$) (Table). The slopes in Figure 2 do not correspond exactly to $k_{M+}K_{M+}$ strictly, since this term includes the effect of replacing K$^+$ by the added cation in the complex; this is most significant for strongly co-ordinating ions, so that the actual $k_{M+}K_{M+}$ value for Cs$^+$ would be larger than that estimated from Figure 2. This effect is expected to be small for Na$^+$. A small acceleration due to Li$^+$ could be masked by this effect of K$^+$. The observed accelerations could arise in part from ionic strength effects. However, all the salts were added over roughly similar concentration ranges, and so ionic strength differences between the salts are largely eliminated. Hence ionic strength effects do not contribute significantly to the accelerations.

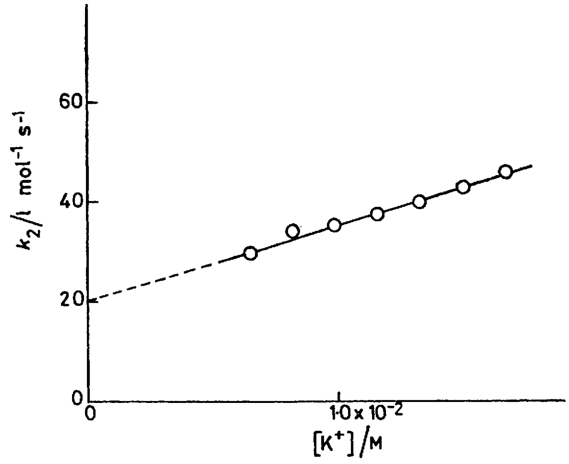


FIGURE 1. Dependence of k_2 on [K$^+$].

As already mentioned, repulsion would not have as significant an effect on the electron-transfer reaction between a neutral molecule and a negative ion as it would on the reaction between two negative ions. Therefore, neutralization of electrostatic repulsion would not contribute significantly to the acceleration observed here, which must, then, be related to the electron-transfer step itself.

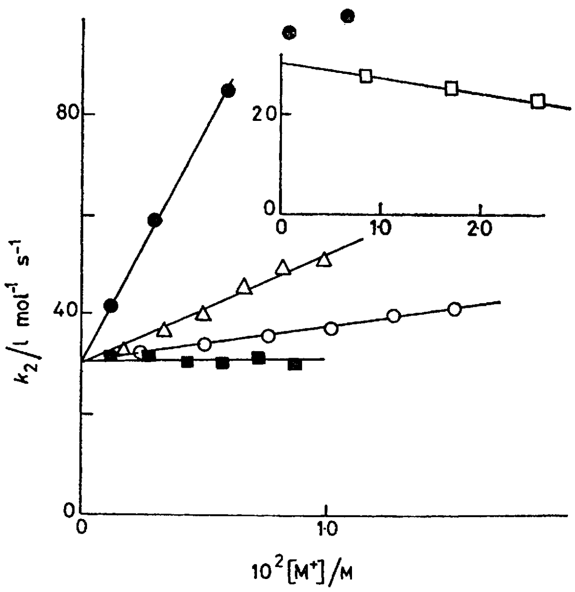


FIGURE 2. Dependence of k_2 on [M$^+$], ■ LiCl, ○ NaCl, △ RbCl, ● CsCl, and □ Et_4NCl.

In contrast to the results of Wahl *et al.*,[2a] a small negative salt effect was observed for tetraethylammonium ion. Since K_{M+} for this ion is not very different from that for K$^+$,[5] a smaller k_{M+} value for the Et_4NCl-catalysed reaction than that for the K$^+$-catalysed reaction must be responsible for the observed negative effect. There would be the normal neutralization effect for Et_4N^+, and the result could not be accounted for by the absence of neutralization of the electrostatic effect. Steric repulsion may be a factor, but the catalytic constants for alkali-metal ions suggest that caesium ion is far more effective as a catalyst than would be expected from its association constant, showing that steric repulsion is not the most important factor in the observed catalysis. A more plausible explanation for the present results is that alkali-metal ions catalyse the electron-transfer reaction not only by decreasing electrostatic repulsion but also by accelerating the electron-transfer step itself by a polarizable species which behaves as an electron conductor.[6]

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