Kinetics of Reactions of the Hydrated Electron; Apparent Conflicts between Data from Pulse Radiolysis and Steady-state Experiments

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WHEN two solutes A and B can react with the hydrated electron, e_{aq}^{-}, to form stable products P_a and P_b *via* the intermediates A^- and B^- [equations (1) and (2)] the rate constant ratio k_1/k_2 can be

$$e_{aq}^{-} + A \rightarrow A^- \rightarrow P_a \quad (1)$$

$$e_{aq}^{-} + B \rightarrow B^- \rightarrow P_b \quad (2)$$

obtained *either* from measurements of k_1 and k_2 separately by pulse radiolysis *or* from measurement of $G(P_a)$ or $G(P_b)$ for solutions containing both A and B. In the latter case the effect of [B] on $G(P_a)$ is given by equations (3a) and (3b), where G_e is the yield of hydrated electrons. If however electron transfer (4) from A^- to B can

$$\{G(P_a)\}^{-1} = G_e^{-1}\{1 + k_2[B]/k_1[A]\} \quad (3a)$$

$$\{G_e - G(P_a)\}^{-1} = G_e^{-1}\{1 + k_1[A]/k_2[B]\} \quad (3b)$$

occur and τ_a is the reciprocal of the first-order rate

$$A^- + B \rightarrow A + B^- \rightarrow A + P_b \quad (4)$$

constant for formation of P_a from A^-, then equation (5) should be applicable.

$$\{G(P_a)\}^{-1} = G_e^{-1}\{1 + k_2[B]/k_1[A]\}\{1 + k_4\tau_a[B]\} \quad (5)$$

Correspondingly if reaction (6) occurs instead of reaction (4) the appropriate equation is (7).

$$A + B^- \rightarrow A^- + B \rightarrow P_a + B \quad (6)$$

Consequently three situations may be recognised

$$\{G_e - G(P_a)\}^{-1} = G_e^{-1}\{1 + k_1[A]/k_2[B]\}\{1 + k_6\tau_b[A]\} \quad (7)$$

TABLE

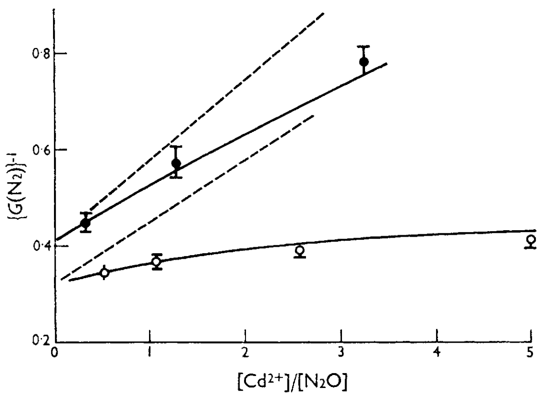
Rate constants for reactions of hyper-reduced ions with N_2O *and* H_2O_2.

Reaction	$10^{-8}k$ ($M^{-1}sec.^{-1}$) Ni+	Cd+	Co+
$M^+ + N_2O \rightarrow N_2 + MO^+$ or $M^{2+} + O^-$	0·51	0·01	7*
$M^+ + H_2O_2 \rightarrow H_2O + MO^+$ or $OH^- + OH + M^{2+}$	2·1	28	19

* This value from steady-state studies only

by plotting $\{G(P_a)\}^{-1}$ against [B]/[A]: (i) when reactions (4) and (6) do not occur a straight line is obtained from which a value of k_1/k_2 is calculated which accords with the pulse radiolysis data, (ii) when (4) occurs but (6) does not, positive deviation from the line appropriate to case (i) should be observed, and (iii) when (6) occurs but (4) does not, negative deviation should result.

Case (i) is the most frequent. Recently we have identified case (iii) for A = N_2O and B = Co^{2+}, Ni^{2+}, and Cd^{2+}, and the Figure illustrates typical results when B = Cd^{2+}. The true value of k_1/k_2 is obtained by plotting $\{G_e - G(N_2)\}^{-1}$ against $[Cd^{2+}]^{-1}$ when $[N_2O]$ is kept constant [*cf*, equation (7)]. Substitution of this value in equation (3a) leads to the broken lines in the Figure, whereas the actual values of $\{G(N_2)\}^{-1}$ when plotted against $[Cd^{2+}]/[N_2O]$ fall on slight curves lying well below these lines. The full lines correspond to $k_6(Cd^+ + N_2O) \times \tau(Cd^+ \rightarrow ?) = 150\ M^{-1}$.



Dependence of $\{G(N_2)\}^{-1}$ *on* $[N_2O]$ *and* $[Cd^{2+}]$ *for* γ-*irradiated aqueous solution containing* $CdSO_4$ *and* $[N_2O] = 10^{-2}$ M (O) *or* $1·5 \times 10^{-3}$ M (●) at $\mu = 0·40$. *Broken line corresponds to* $k_1/k_2 = 2·6$ *and* $k_6\tau_b = 0$; *full line to* $k_1/k_2 = 2·6$ *and* $k_6\tau_b = 150\ M^{-1}$.

In these experiments B^- = Co^+, Ni^+, or Cd^+ each of which has a characteristic absorption spectrum. Therefore k_6 may be measured directly by pulse radiolysis and the values we have obtained are shown in the Table. The products of reaction (6) other than nitrogen are unknown and may be CoO^+, NiO^+, and CdO^+ or $Co^{2+} + O^-$, $Ni^{2+} + O^-$, and $Cd^{2+} + O^-$, respectively.

A similar situation arises when H_2O_2 is used instead of N_2O to compete with Co^{2+}, Ni^{2+}, and Cd^{2+} for hydrated electrons, the reaction corresponding to (6) being (8). Values of k_8 are shown

$$H_2O_2 + B^- \rightarrow H_2O + BO^- \text{ or } OH^- + OH + B \quad (8)$$

in the Table from which it is seen that for A = N_2O the order of reactivity is $Co^+ > Ni^+ > Cd^+$ whereas for A = H_2O_2 it is $Cd^+ > Co^+ > Ni^+$.

Case (ii) will be discussed in a separate communication.

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[1] J. H. Baxendale, E. M. Fielden, and J. P. Keene, *Proc. Roy. Soc.*, 1965, *A*, **286**, 320.