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The Effect of the Temperature on the Formation of Solvated Electrons and Hydrogen in the Photolysis of a Methanolic Solution of Potassium Iodide

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In a previous paper[1] we reported the photochemical formation of the solvated electron and its reactions in methanolic solutions of potassium iodide. The solvated electrons in methanol decompose with a rate constant of $5.4\times10^5\ \text{sec}^{-1}$ to form hydrogen. Hydrogen is also produced from UV-irradiated CH_3OD solutions; its isotopic composition was found to be nearly 100% HD. It was concluded, therfore, that the reaction:

$$e^-_{\text{solv}} \longrightarrow H + CH_3O^- \tag{1}$$

does occur in methanolic solutions, followed by:

$$H + CH_3OH \longrightarrow H_2 + CH_2OH \tag{2}$$

Reaction (1) had been assumed to occur in the radiolysis of methanol;[2-4] our previous result gave a sound basis to this assumption.

The temperature dependence of the rate constant of Reaction (1) has been determined with the radiolytic system by somewhat indirect procedures.[3] In this study, we determined the quantum yields of hydrogen from UV-irradiated methanolic solutions of potassium iodide at temperatures between −15 and 85°C, as well as those of the solvated electrons scavengeable by nitrous oxide. Both quantum yields were found to fit the Arrhenius equation, the energies of activation being obtained.

Experimental

The chemicals and procedures were essentially the same as those previously reported.[1] UV-irradiations at temperatures lower and higher than room temperature were carried out by placing irradiation ampoules in a Dewar vessel equipped with quartz windows. For experiments above 0°C, the ampoule was immersed in water thermostated at the desired temperatures. For experiments below 0°C, dry nitrogen gas which had been cooled with liquid nitrogen to the desired temperatures was blown into the Dewar vessel through copper tubing.

The concentrations of N_2O in methanolic solutions at various temperatures were calculated by using Bunsen absorption coefficients estimated by extrapolating the existing data in pure methanol.[5] All the solutions contained 0.1 M KI and were irradiated with UV light centered at 254 nm, as previously.[1]

Results and Discussion

Table 1 lists the quantum yields of N_2 from 0.1 M KI solutions containing N_2O and those of H_2 in the absence of N_2O at various temperatures.

Table 1. Temperature dependence of $\Phi(N_2)$ and $\Phi(H_2)$

Temp °C	$\Phi(N_2)$[a]	$\Phi(H_2)$[b]
−15	0.46±0.01 (6—9)	0.13±0.01
3	0.51±0.01 (5—6)	0.22±0.01
25	0.58±0.01 (1—5)	0.35±0.01
60	0.69±0.02 (3—4)	0.57±0.02
85	0.78±0.01 (3—4)	0.69±0.01

a) The quantum yields at N_2O concentrations in 10^{-2} M given in parentheses

b) The quantum yields for 0.1 M KI solutions not containing N_2O

As has been reported previously,[1] with an increase in the concentration of N_2O, $\Phi(H_2)$ decreases rapidly to null at about 5×10^{-4} M N_2O and $\Phi(N_2)$ reaches a plateau value of 0.59 above 1.2×10^{-2} M at 25°C. The same plateau value as for $\Phi(N_2)$ was obtained for $\Phi(H_2)$ with acid solutions. (Hydrogen ions react with e^-_{solv} to produce H atoms.) We have, therefore, concluded that N_2 is produced solely by the reaction of N_2O with e^-_{solv} in a stoichiometric ratio of $N_2/e^-_{\text{solv}}=1$. Furthermore, $\Phi(N_2)$ was observed to keep its plateau value of 0.59 over the N_2O concentration range studied ($(1—5)\times10^{-2}$ M).

These results may indicate that N_2O scavenges, in these concentration ranges, all the e^-_{solv} produced by the reaction:

$$I^{-*}_{\text{solv}} \longrightarrow I_{\text{solv}} + e^-_{\text{solv}} \tag{3}$$

competing with the deactivation process:

$$I^{-*}_{\text{solv}} \longrightarrow I^-_{\text{solv}} + \text{energy} \tag{4}$$

The quantum yields of N_2 in Table 1 were obtained at N_2O concentrations of $(1—9)\times10^{-2}$ M; therefore, these values may be regarded as the limiting quantum yields of e^-_{solv} produced by Reaction (3).

Thus, $\Phi(e^-_{\text{solv}})$ may be expressed by:

$$\Phi(e^-_{\text{solv}}) = \Phi(N_2) = \frac{k_3}{k_3+k_4} \tag{i}$$

Since the deactivation of I^{*-}_{solv} is a collisional process, k_4 may be expected to be proportional to $T^{1/2}$. On the other hand, k_3 should be regulated by the rate of rotational movements in methanol and should, therefore, be proportional to the fluidity. Since the temperature dependence of the viscosity is given by $\eta=A'\exp(B/RT)$, k_3 may be expressed by:

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[1] H. Seki and M. Imamura, This Bulletin, **44**, 1538 (1971).

[2] J. H. Baxendale and F. W. Mellows, *J. Amer. Chem. Soc.*, **83**, 4720 (1961).

[3] K. N. Jha and G. R. Freeman, *J. Chem. Phys.*, **48**, 5480 (1968).

[4] F. S. Dainton, G. A. Salmon, and P. Wardman, *Proc. Roy. Soc.* (London), *A*, **313**, 1 (1969).

[5] A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. 2, 4th Ed., American Chemical Society, Washington, D. C. (1965), p. 802.

$$k_3 = A_3\exp(-E_3/\boldsymbol{R}T) \qquad \text{(ii)}$$

where E_3 is expected to be equal to B.

From Eqs. (i) and (ii), it seems that the temperautre dependence of $\Phi(\mathrm{e}^-_{\mathrm{solv}})$ can be approximately expressed by Eq. (iii):

$$\ln\left(\frac{1}{\Phi(\mathrm{e}^-_{\mathrm{solv}})}-1\right)=\ln\frac{k_4}{A_3}+\frac{E_3}{\boldsymbol{R}T} \qquad \text{(iii)}$$

From the plot according to Eq. (iii) shown in Fig. 1, E_3=2.7 kcal/mol is obtained. This value is close to the constant, B, for methanol (2.3 kcal/mol) in the same temperature range as that used in this study. In aqueous solutions the corresponding value of 4.7±0.5 kcal/mol has been obtained (B=4.5 kcal/mol).6)

Previously we have not decided whether or not all the $\mathrm{e}^-_{\mathrm{solv}}$ scavengeable with N_2O (Φ=0.59) are free and participate in the H_2-formation process in the absence of N_2O. Figure 2 shows the homogeneous-kinetics plot of the data obtained at room temperature (25°C) according to this equation:

$$\frac{1}{\Phi(N_2)}=\frac{1}{\Phi(\mathrm{e}^-_{\mathrm{solv}})}\left(1+\frac{k_1+k_x[\mathrm{X}]}{k_{N_2O}[N_2O]}\right) \qquad \text{(iv)}$$

Here, X represents the reactive species (toward $\mathrm{e}^-_{\mathrm{solv}}$) not producing H atom (*i.e.*, I or I_2^- and/or impurity, if any). The straight line connecting points at low N_2O concentrations (10^{-4}M) can be extrapolated to $1/\Phi(N_2)=1.7$ or $\Phi(N_2)=0.59$, which is in agreement with the plateau value of $\Phi(N_2)$ obtained at (1—5)×10^{-2}M N_2O. These results indicate that all the $\mathrm{e}^-_{\mathrm{solv}}$ scavengeable with N_2O at concentrations of (1—5)×10^{-2}M are free and can produce H_2 in the absence of N_2O.7)

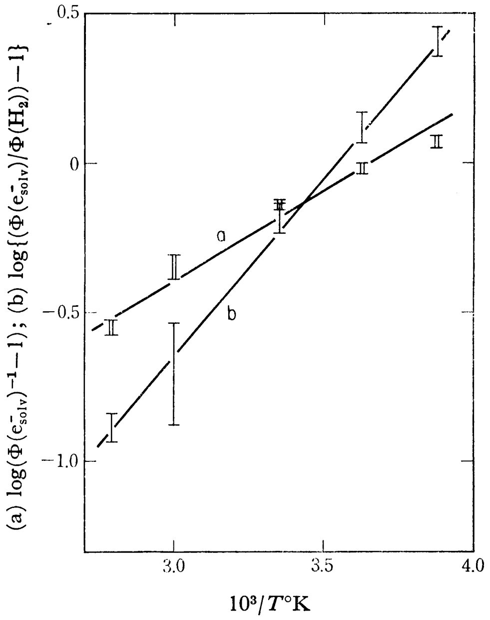

Fig. 1. Arrhenius plots for (a) $\Phi(\mathrm{e}^-_{\mathrm{solv}})$ and (b) $\Phi(H_2)$ according to Eqs. (iii) and (v).

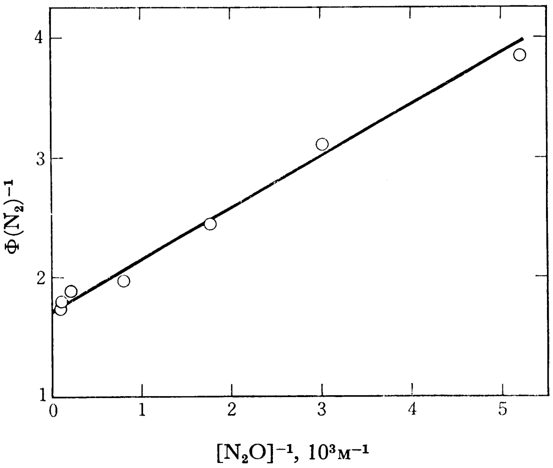

Fig. 2. A homogeneous-kinetics plot of $\Phi(N_2)$ for KI solutions containing N_2O at 25°C according to Eq. (iv).

Since H_2 is produced solely by Reactions (1) and (2), and since the rate of the latter reaction is about 100 times faster than the former, $\Phi(H_2)$ at each temperature is expressed by:

$$\Phi(H_2)=\Phi(\mathrm{e}^-_{\mathrm{solv}})\times\frac{A_1\exp(-E_1/\boldsymbol{R}T)}{A_1\exp(-E_1/\boldsymbol{R}T)+A_x\exp(-E_x/\boldsymbol{R}T)[\mathrm{X}]}$$

or:

$$\ln\left(\frac{\Phi(\mathrm{e}^-_{\mathrm{solv}})}{\Phi(H_2)}-1\right)=\ln\frac{A_x}{A_1}[\mathrm{X}]+\frac{E_1-E_x}{\boldsymbol{R}T} \qquad \text{(v)}$$

The plot according to Eq. (v) is shown in Fig. 1, from which E_1-E_x=5.4 kcal/mol. As has been stated above, X is a general expression for reactive species toward $\mathrm{e}^-_{\mathrm{solv}}$; therefore, its rate constant, k_x, may be regarded as very close to a diffusion-controlled one. If we take $E_x\simeq2.8$ kcal/mol,3) $E_1\simeq8$ kcal/mol is obtained. The entropy of activation, $\Delta S^{\neq}$, can be estimated from the values of $k_1$1) and E_1 to be −6 cal/deg·mol.

The value of E_1 estimated by Jha and Freeman3) is 3.7 kcal/mol, lower than the present one. They estimated E_1 from the temperature dependence of the rate-constant ratio, $k(\mathrm{e}^-_{\mathrm{solv}}+N_2O)/k_1$, obtained from plots of $1/G(N_2)$ *vs.* $1/[N_2O]$ at −97, 25, and 150°C. There is, however, an ambiguity about the N_2O concentration at 150°C that was estimated by a long extrapolation of the Bunsen coefficient. Furthermore, their value of the rate-constant ratio of 1.1×10^4M^{-1} at 25°C is too low. This value can be expected to be (2—3)×10^4M^{-1} on the basis of the reasonable values of $k(\mathrm{e}^-_{\mathrm{solv}}+N_2O)=1.3\times10^{10}$M^{-1} sec^{-1} 1,4,8) and k_1=(4—6)×10^5 sec^{-1};1,3,9) in fact, we have ourselves obtained 2.4×10^4M^{-1} for $k(\mathrm{e}^-_{\mathrm{solv}}+N_2O)/k_1$ in a previous paper.1) The present disagreement in E_1 may be in part due to such reasons, though no quantiative accounts are available at this moment.

It does not seem that the value of E_1 is necessarily equal to that of the dielectric relaxation, as was suggested by Jha and Freeman.3) Since E_1 should be used not only to rearrange the solvent structure but also to form an activated state producing CH_3O^- and H, E_1 may be expected to be higher than the activation energy of the dielectric relaxation.

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6) F. S. Dainton and S. R. Logan, *Proc. Roy. Soc.* (London), *A*, **287**, 281 (1965).

7) This conclusion does not necessarily rule out the effect of the solvent cage in which geminate recombination may take place since the concentration of N_2O employed was not high enough.

8) H. Seki and M. Imamura, *J. Phys. Chem.*, **71**, 870 (1967).

9) F. S. Dainton, J. P. Keene, T. J. Kemp, G. A. Salmon, and J. Teplý, *Proc. Chem. Soc.*, **1964**, 265.