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# The Reactions of Photogenerated Solvated Electrons in Methanolic Solutions of Potassium Iodide

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Hydrogen formation from UV-irradiated potassium iodide solutions was studied using $CH_3OH$ and $CH_3OD$ as the solvents and nitrous oxide and acids as the solvated-electron scavengers. The maximum quantum yield of the solvated electron in $CH_3OH$ was found to be 0.6 both in nitrous oxide and in acid solutions. It was concluded that the solvated electron produces hydrogen in pure methanol through Reaction (1), $e^-_{solv} \rightarrow H + CH_3O^-$, with a quantum yield of 0.35 at 25°. The rate constant of this reaction is $5.4 \times 10^5$ sec$^{-1}$, corresponding to a half-life of 1.3 $\mu$sec. From the results obtained with acid solutions, it was also concluded that nitrous oxide reacts with a solvated electron to produce one molecule of nitrogen in neutral methanol.

Solvated electrons are produced in aqueous solutions and many other polar liquids by the irradiation of ionizing radiations. The reactions of these solvated electrons, particularly of hydrated electrons, have been extensively studied by many investigators.[1] Solvated electrons have also been known to be produced by the UV irradiation of aqueous and alcoholic solutions of several inorganic[2] and organic compounds,[3] and, by the flash-photolysis technique, they have been shown to give an absorption spectra identical with those produced by ionizing radiations.[4-7]

Jortner *et al.*[8] studied the photochemical formation of solvated electrons using an electron scavenger in 0.15 M iodide solutions in methanol, ethanol, and isopropanol, and reported the quantum yields of 0.6—0.7 for the solvated electrons in these alcohols. Whereas they failed to observe the hydrogen formation from these solutions, Dainton *et al.*[9] observed it from an

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[1] See a recent review by E. J. Hart and M. Anbar, "The Hydrated Electron," Wiley-Interscience, New York (1970).

[2] G. Stein, *Adv. Chem. Ser.*, **50**, 230 (1965).

[3] L. I. Grossweiner and H. Joschek, *ibid.*, **50**, 279 (1965).

[4] M. S. Matheson, W. A. Mulac, and J. Rabani, *J. Phys. Chem.*, **67**, 2613 (1963).

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[6] L. I. Grossweiner, E. F. Zwicker, and G. W. Swenson, *Science*, **141**, 1180 (1963).

[7] G. Dobson and L. I. Grossweiner, *Radiat. Res.*, **23**, 290 (1964).

[8] J. Jortner, M. Ottolenghi, and G. Stein, *J. Phys. Chem.*, **67**, 1271 (1963).

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

UV-irradiated methanolic solution of lithium ferrocyanide.

In the $\gamma$-radiolysis of methanol, on the other hand, free solvated electrons are produced with $G=2.0$ and are believed to be a precursor of the product hydrogen.[10] Two possible pathways for the hydrogen formation from solvated electrons in radiation-irradiated methanol have been supposed:

$$e^-_{\text{solv}} \rightarrow H + CH_3O^- \qquad (1)$$

$$CH_3OH_2^+ + e^-_{\text{solv}} \rightarrow H + CH_3OH \qquad (2)$$

The pulse radiolysis studies showed that the decay of solvated electrons in alcohols is represented by the first-order kinetics,[11,12] indicating that they react principally with alcohol molecules. The rate constant of this decay reaction has been determined not only by the pulse-radiolysis technique, but also by steady-irradiation experiments.[13–15] However, there seem to be disagreements among these values larger than can be accounted for by experimental errors.

In contrast to the earlier result,[8] we observed the formation of hydrogen from UV-irradiated methanolic solutions of potassium iodide, and chose this system as an appropriate one for investigating the reaction of a solvated electron with a methanol molecule free from the interference of the competing reaction (Reaction (2)). This paper will report on the results of Reaction (1) as well as on the reaction of the solvated electron with nitrous oxide.

## Experimental

*Chemicals.* Reagent-grade methanol supplied by the Wako Pure Chemical Co. was purified by distillation from a dinitrophenylhydrazine-$H_2SO_4$ solution. Deuterated methanol, $CH_3OD$(>99 atom%D), was obtained from CIBA, Ltd., and was purified similarly by using a small spinning-band distillation apparatus. The isotopic purity of the distilled $CH_3OD$ was determined by NMR and was found to be usually ~99%.

The potassium iodide and hydrochloric and sulfuric acids were of a reagent grade from Wako and were used without further purification. Nitrous oxide and carbon dioxide, standard gases from the Takachiho Trading Co., were purified by distillation *in vacuo*.

*Sample Preparation.* A weighed amount of potassium iodide was degassed thoroughly in an irradiation ampoule before transferring degassed methanol into the ampoule by distillation on a vacuum line. When an acid solution was prepared, a small amount of acid was degassed beforehand and then added to the degassed methanolic solution through a break-seal. A such meticulous care was necessary to prevent the coloration due to iodine liberation in the solutions prepared.

Nitrous oxide and carbon dioxide were added to the solution volumetrically, their concentrations being calculated from the solubility data.[16]

*Irradiation.* The light source was an Ushio ULO-6DQ low-pressure mercury lamp, which was operated at 38V AC and 0.15 A with a voltage stabilizer. A 254-nm light was isolated by the use of an interference filter.[17] The methanolic solution of potassium iodide has a CT spectrum, with its peak at 220 nm extending to nearly 270 nm. The irradiation ampoule was a quartz cylinder, 2 cm in i.d. and 10 cm in length. All the photolyses were conducted at room temperature (~25°).

The light intensity and the quantum yields were determined by using a potassium ferrioxalate actinometer; the potassium ferrioxalate had been prepared according to the method described by Calvert and Pitts.[18] The concentration of the ferrous ions formed was determined by the *o*-phenanthroline method, and the quantum yield was taken to be $\Phi(Fe^{2+})=1.25$ at 254 nm.[18] The light intensity was in the range of $(2.7—8.3)\times 10^{-9}$ einstein $l^{-1}$ $sec^{-1}$.

*Analytical Procedures.* The hydrogen was determined by combustion on cuprous oxide using a micro gas-analyzer.[19] The amount of nitrogen produced from nitrous oxide solutions was determined from the residual gas volume after complete combustion, followed by absorption on magnesium perchlorate and Ascarite in the gas-analyzer. The formaldehyde was determined by the chromotropic-acid method.[19] The isotopic compositions of the hydrogen produced from $CH_3OD$ samples were determined by mass-spectrometric analysis.[20]

*Flash Photolysis.* The details of the flash-photolysis apparatus have been described previously.[21] Briefly, the photolysis flash consisted of two Ushio xenon lamps. The operating characteristics of the lamps were 100 joule of energy per flash and 10 μsec for flash duration to a 50% peak. The reaction vessel was a quartz cylinder, 10 mm in i.d. and 10 cm in length, with flat plates sealed on either end.

*Pulse Radiolysis.* The rate constant of the reaction between solvated electron and nitrous oxide in methanol was determined by the pulse-radiolysis technique using a 3 MV Van de Graaff accelerator; the details will be published elsewhere.[22]

## Results

*Iodide Solutions in $CH_3OH$.* Potassium iodide solutions (0.05—0.1 M) in $CH_3OH$ produce hydrogen as a gaseous product upon UV irradiation. In the absence of potassium iodide, the UV irradiation produces no detectable hydrogen. A typical result is shown in Fig. 1, from which the quantum yield for hydrogen formation can be calculated to be 0.35 at 25°.

Another stable product from methanol is formalde-

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

[11] I. A. Taub, D. A. Harter, M. C. Sauer, Jr., and L. M. Dorfman, *J. Chem. Phys.*, **41**, 979 (1964).

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

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[15] R. A. Basson and H. J. van der Linde, *J. Chem. Soc., A*, **1967**, 28.

[16] a) $N_2O$: A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," **2**, 4th Ed., American Chemical Society, Washington, D.C. (1965), p. 802. b) $CO_2$: *ibid.*, **1**, p. 479.

[17] The interference filter obtained from Nippon Shinku Kogaku Co. had $\lambda_{max}=256$ nm with a half-width of 18 nm.

[18] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York (1966), p. 783.

[19] M. Imamura, S. U. Choi, and N. N. Lichtin, *J. Amer. Chem. Soc.*, **85**, 3565 (1963).

[20] Massspectrometric determination was carried out at Tokyo Metropolitan Isotope Center and at Tokyo Institute of Technology.

[21] A. Kira and K. Nishi, *Rep. Inst. Phys. Chem. Res.*, **44**, 56 (1968).

[22] A. Kira, S. Arai, and M. Imamura, *ibid.*, to be published.

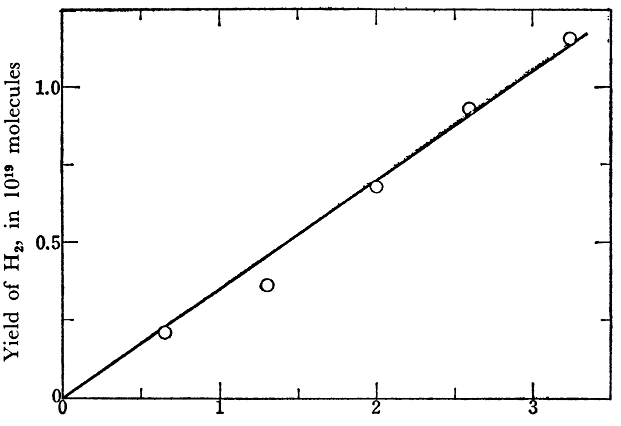

Fig. 1. Formation of hydrogen from UV-irradiated methanolic solution of potassium iodide. [KI]=0.1 M.
UV irradiation was carried out through an interference filter (see Ref. 17) at room temperature. $\Phi(H_2)$ is calculated to be 0.35.

hyde, which was determined after removing iodide from the irradiated solution by distillation *in vacuo*. The average quantum yield for formaldehyde is 0.3 at 25°, which is approximately the same as the value for $\Phi(H_2)$ from an iodide solution without a scavenger.

The quantum yields for hydrogen and formaldehyde were found to be independent of the iodide concentration within the range studied; most of the experiments were carried out at 0.1 M KI.

A flash photolysis study revealed the transient formation of $I_2^-$, which has absorption maxima at about 390 and 750 nm and which decays with a half-life of about 100 $\mu$sec at 420 nm; neither spectrum nor decay of the solvated electron could be observed because of the relatively long resolution time of the apparatus used. The absorption spectrum of $I_2^-$ in methanol resembles those observed in aqueous[5] and ethanolic solutions.[7]

*Effect of Electron Scavengers. $N_2O$.* Nitrous oxide has been known as an effective solvated-electron scavenger, and its solution in methanol, in the absence of iodide, has been confirmed not to produce nitrogen upon UV irradiation. However, when nitrous oxide was added to the iodide solution in methanol, it produced nitrogen and the hydrogen yield was reduced. The quantum yields of nitrogen as well as hydrogen are plotted in Fig. 2 as a function of the nitrous oxide concentration.

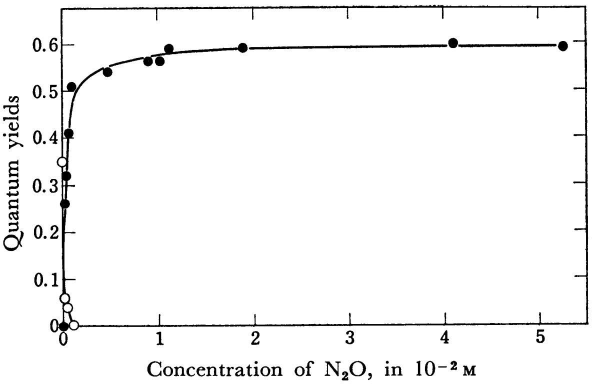

Fig. 2. Dependence of quantum yields for nitrogen and hydrogen on the concentration of nitrous oxide. [KI]=0.1 M.
●, $N_2$; ○, $H_2$

The quantum yield of nitrogen reaches a plateau value of 0.59 above $1.2\times10^{-2}$ M $N_2O$, independent of the iodide concentration within the range investigated. This limiting yield is in good agreement with the value obtained by Jortner *et al.* (0.6).[8] With an increase in the concentration of nitrous oxide, the yield of hydrogen decreases rapidly, no hydrogen being detected at nitrous oxide concentrations as low as $5\times10^{-4}$ M. In the presence of nitrous oxide, a small amount of $I_3^-$ was found to be produced; this was not detected in the absence of nitrous oxide.

*$CO_2$.* Carbon dioxide, a solvated-electron scavenger, reduces $\Phi(H_2)$, no hydrogen being detected at concentrations as low as $10^{-3}$ M.

*$H^+$.* Hydrochloric or sulfuric acid was also added as a solvated-electron scavenger. As is shown in Fig. 3, the quantum yield for hydrogen increases with an increase in the concentration of acid, the plateau value being 0.57 for each acid. The plateau value of the quantum yield is in agreement with the plateau value of $\Phi(N_2)$ in nitrous oxide solutions.

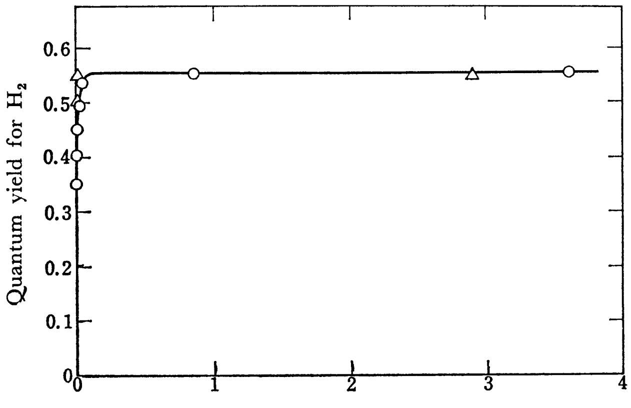

Fig. 3. Dependence of the quantum yield for hydrogen on the concentration of acids. [KI]=0.1 M.
○, $H_2SO_4$; △, HCl

*Iodide Solutions in $CH_3OD$.* Hydrogen was found to be produced by the UV irradiation also from iodide solutions in $CH_3OD$. The quantum yield for hydrogen, however, is considerably lower than that in $CH_3OH$, about 1/20 for the 0.1 M KI solution. The isotopic composition of hydrogen produced from 0.1 M KI solutions in $CH_3OD$ was determined to be $H_2 : HD : D_2 = 16 : 84 : 0$. As the purified $CH_3OD$ contained ~1% $CH_3OH$, the observed isotopic compositions of hydrogen were subjected to corrections for the low rate of hydrogen production and the isotopic purity of the solvent. The result is that the fractions of HD should be very close to 100% if the 100% $CH_3OD$ is used as a solvent. In the presence of nitrous oxide, however, the plateau value of $\Phi(N_2)$ (0.72) is substantially higher than that in $CH_3OH$ (0.59). Similar results have also been reported with $H_2O$ and $D_2O$ by Jortner *et al.*[8)]

Although the quantum yield for hydrogen is very low in the 0.1 M KI solution in $CH_3OD$, it showed a steady increase with a decrease in the concentration of iodide, and, simultaneously, the fraction of $H_2$ in the product hydrogen was found to increase. However, the limiting quantum yield for nitrogen from $CH_3OD$ solutions containing nitrous oxide is independent of the iodide concentration, as in the $CH_3OH$ solutions. This apparently interesting phenomenon is being subjected to further study.

*Rate Constant of the $e^-_{solv}+N_2O$ Reaction in Methanol.* The rate constant of the reaction between the solvated electron and nitrous oxide in methanol was determined by the pulse-radiolysis technique. The decay of the solvated electron obeys the second-order kinetics, and its rate constant was found to be $1.3\times10^{10}$ M$^{-1}$sec$^{-1}$, which is in fair agreement with the previous value ($1.3\times10^{10}$ M$^{-1}$sec$^{-1}$) obtained by us from the competition kinetics in the $\gamma$-radiolysis of methanol.[10)] This value also agrees with that of $(1.4\pm0.4)\times10^{10}$ M$^{-1}$sec$^{-1}$ obtained by Dainton *et al.* from competition kinetics using nitrous oxide and benzyl chloride in methanol.[9)]

## Discussion

Photochemical studies of aqueous solutions of potassium iodide have been carried out extensively, and the primary processes seem to be relatively well understood.[2)] Some difficulties in the interpretation of differences in the peak wavelengths of negatively-charged transients produced by the flash irradiation of several aqueous inorganic solutions[23)] have been eliminated by the results from novel flash-photolysis experiments carried out by Devonshire and Weiss.[5)] They succeeded in showing that the transient species produced from UV-irradiated aqueous solutions of several inorganic salts have absorption spectra identical with that of the hydrated electron obtained in the pulse radiolysis of aqueous systems.

Scavengers added to aqueous solutions react with hydrated electrons, not with the excited iodide ions,[24,25)] and may compete with the secondary diffusive recombination. Recent results by Czapski, Ogdan, and Ottolenghi,[25)] who investigated the photochemistry of aqueous solutions of iodide and bromide in the presence of high concentrations of nitrous oxide, have revealed that the "cage effect" takes place in the iodide system.

Similar results have been obtained for methanolic and ethanolic solutions of iodide,[6–8)] no elaborate discussions of the primary processes taking place in UV-irradiated iodide solutions being required at the present stage. The primary processes for iodide ions are assumed here to be:

$$I^-_{solv} + h\nu \rightarrow I^{-*}_{solv} \tag{3}$$

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

$$I^{-*}_{solv} \rightarrow (I_{solv} + e^-_{solv}) \begin{cases} \nearrow I_{solv} + e^-_{solv} & \text{(5a)} \\ \searrow I^-_{solv} & \text{(5b)} \end{cases}$$

The parentheses in the above scheme mean that $I_{solv}$ and $e^-_{solv}$ are formed in a pair; Reaction (5b) represents the secondary recombination process.

In the present study, in the absence of an electron scavenger, the UV irradiation produces hydrogen with $\Phi(H_2)=0.35$ at 25°. Hydrogen may reasonably be assumed to form from the solvated electrons produced by Reaction (5a). The solvated electron has an absorption spectrum extending to short wavelengths.[1)] We compared the quantum yield obtained by the use of an interference filter with that obtained by the use of a glass filter that transmits longer wavelengths, and found no significant difference in the $\Phi(H_2)$ between the two cases. This experiment may rule out the possibility of the participation of photo-excited solvated electrons in producing hydrogen, as has been suggested for rigid matrices at 77°K.[26)]

The results on the isotopic composition of hydrogen from the UV-irradiated $CH_3OD$ solutions indicate that hydrogen arises *via* Reaction (1), which results in the rupture of the hydroxyl hydrogen of methanol. Since the abstraction of the hydrogen atom by another hydrogen atom or by free radicals in liquid methanol takes place principally at the $\alpha$-position,[27,28)] the nearly 100% HD production after corrections for the isotopic purity of $CH_3OD$ used and for the lower yield of hydrogen in the $CH_3OD$ solution can be explained satisfactorily by assuming Reaction (1). It should be noted here that, in the nitrous oxide solutions in $CH_3OD$, the plateau value of $\Phi(N_2)$ is as high as 0.72, substantially higher than that in $CH_3OH$, indicating that most of the solvated electrons produced are recaptured, probably by iodine atoms, before forming hydrogen in $CH_3OD$.

The fact that, despite the higher $\Phi(N_2)$ in $CH_3OD$ than in $CH_3OH$, the quantum yield for hydrogen is lower in $CH_3OD$ than in $CH_3OH$, may be explained in terms of the isotope effect on the O–H (O–D) bond rupture. A similar isotope effect has been observed in the reactions of hydrated electron with $H_2O$[29)] and $D_2O$:[30)] $k(e^-_{aq}+H_2O)=16$ M$^{-1}$ sec$^{-1}$ and $k(e^-_{aq}+D_2O)=1.25$ M$^{-1}$ sec$^{-1}$.

As a necessary consequence of the formation of solvated electrons, iodine atoms are produced (Reaction 5a), followed by the transient formation of $I_2^-$. Iodine atoms or $I_2^-$ are expected to oxidize $CH_2OH$ radicals produced by the $H+CH_3OH\rightarrow H_2+CH_2OH$ reaction to give formaldehyde:

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[23)] J. J. Weiss in "The Chemistry of Ionization and Excitation," G. R. A. Johnson and G. Scholes, Ed., Taylor & Francis, Ltd., London (1967), p. 17.

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

[25)] G. Czapski, J. Ogdan, and M. Ottolenghi, *Chem. Phys. Lett.*, **3**, 383 (1969).

[26)] T. Shida and W. H. Hamill, *J. Amer. Chem. Soc.*, **88**, 3689 (1966).

[27)] J. H. Baxendale and G. Hughes, *Z. Physik. Chem.*, **14**, 323 (1958).

[28)] R. Nagai and M. Imamura, unpublished results.

[29)] E. J. Hart, S. Gordon, and E. M. Fielden, *J. Phys. Chem.*, **70**, 150 (1966).

[30)] E. J. Hart and E. M. Fielden, *ibid.*, **72**, 577 (1968).

$$\mathrm{I(or\ I_2^-) + CH_2OH \rightarrow CH_2O + I^-(2I^-) + H^+} \qquad (6)$$

Some of the iodine atoms capture solvated electrons to form iodide ions. This reaction sequence is supported quantitatively by the experimental fact that the quantum yield for formaldehyde, $\Phi(\mathrm{CH_2O})$, is approximately the same as $\Phi(\mathrm{H_2})$. The second-order decay of the transiently-formed $\mathrm{I_2^-}$ and the non-formation of $\mathrm{I_3^-}$ as a stable product also support the above argument. Dobson and Grossweiner[7)] have assumed similar reactions of I or $\mathrm{I_2^-}$ as well as the decay of solvated electrons in ethanolic solutions.

Upon the addition of nitrous oxide, solvated electrons are efficiently scavenged and nitrogen is formed:

$$\mathrm{e^-_{solv} + N_2O \rightarrow N_2 + O^-} \qquad (7)$$

As may be seen from Fig. 2, at the nitrous oxide concentration of $1\times10^{-2}$ M, $\Phi(\mathrm{N_2})$ reaches a plateau value of 0.59, higher than $\Phi(\mathrm{H_2})$ in the absence of electron scavengers, and $\Phi(\mathrm{H_2})$ diminishes to zero at concentrations as low as $5\times10^{-4}$ M $\mathrm{N_2O}$. These facts indicate that hydrogen is not produced by the reaction between the photo-excited iodide ion and methanol, and that, in the concentration range studied, nitrous oxide competes not only with hydrogen formation and the reaction with iodine, but also with the secondary recombination for solvated electrons. Other modes of nitrogen formation by the $\mathrm{N_2O+O^-\rightarrow N_2+O_2^-}$ reaction, sometimes assumed in the radiolysis of organic systems and by the reaction with the photo-excited iodide ion can be ruled out by the results with acid solutions, as will be mentioned below. It was shown previously[10)] that reactions of nitrous oxide with H atoms or $\mathrm{CH_2OH}$ radicals do not give rise to nitrogen formation.

Carbon dioxide also scavenges the solvated electron efficiently. At the concentration of $10^{-3}$ M, the formation of neither hydrogen nor formaldehyde could be detected; a lack of information on the reaction of $\mathrm{CO_2^-}$ limits any realistic evaluation of the observation that formaldehyde is not formed.

The addition of acid increases $\Phi(\mathrm{H_2})$ to a plateau value that is equal to the plateau value of $\Phi(\mathrm{N_2})$ in the nitrous oxide solution (Fig. 3). This result can be explained in terms of the efficient reactivity of the hydrogen ion towards the solvated electron:

$$\mathrm{e^-_{solv} + CH_3OH_2^+ \rightarrow H + \mathit{n}CH_3OH} \qquad (8)$$

It also has an important implication for the reaction between nitrous oxide and solvated electrons. If, as has been mentioned above, nitrous oxide reacts also with $\mathrm{O^-}$ to form an additional nitrogen, the $\Phi(\mathrm{H_2})$ in the acid solution should be lower than $\Phi(\mathrm{N_2})$ in the nitrous oxide solution. The rate constants of Reactions (7) and (8) are both in the order of $10^{10}$ $\mathrm{M^{-1}\,sec^{-1}}$, and no hydrogen-producing pathways other than Reaction (8) can be supposed for acid solutions. Therefore, we can conclude from the present results that nitrous oxide reacts with one solvated electron to produce one molecule of nitrogen in neutral methanolic solutions. The possibility of producing nitrogen by the reaction between the photo-excited ioide ion and nitrous oxide can also be ruled out from this viewpoint.

The same conclusion regarding the reaction between the solvated electron and nitrous oxide has been obtained by Jha and Freeman[13)] from the radiolysis results with acid and nitrous oxide solutions in methanol and by Jortner *et al.*[8)] from the photochemical study of aqueous iodide solutions as well. This has been assumed in our previous study carried out to determine the solvated-electron yield in methanol by the use of nitrous oxide as a solvated-electron scavenger.[10)]

In the presence of nitrous oxide in low concentrations, the hydrogen formation will compete with the reactions of solvated electrons with nitrous oxide, iodine, and an impurity (if any), and hydrogen and nitrogen are produced simultaneously. Under these conditions, therefore, the ratio of $\Phi(\mathrm{N_2})$ to $\Phi(\mathrm{H_2})$ is expressed by:

$$\frac{\Phi(\mathrm{N_2})}{\Phi(\mathrm{H_2})} = \Phi(\mathrm{e^-_{solv}}) \times \frac{k_7[\mathrm{N_2O}]}{k_1 + k_7[\mathrm{N_2O}] + k_x[\mathrm{X}]} \Bigg/ \Phi(\mathrm{e^-_{solv}}) \times \frac{k_1}{k_1 + k_7[\mathrm{N_2O}] + k_x[\mathrm{X}]}$$
$$= k_7[\mathrm{N_2O}]/k_1$$

Here, $\Phi(\mathrm{e^-_{solv}})$ is the assumed quantum yield for the free solvated electron competing among the reactions mentioned above; its value is not determined experimentally, however. $k_x[\mathrm{X}]$ is the overall expression for the reaction rate of the reactants other than nitrous oxide. As the two quantum yields were determined simultaneously from the same solution, the above conventional expression may be pertinent.

Figure 4 shows the linear relationship between $\Phi(\mathrm{N_2})/\Phi(\mathrm{H_2})$ and $[\mathrm{N_2O}]$ in the concentration range of $(1\text{—}5)\times10^{-4}$ M. According to the above equation,

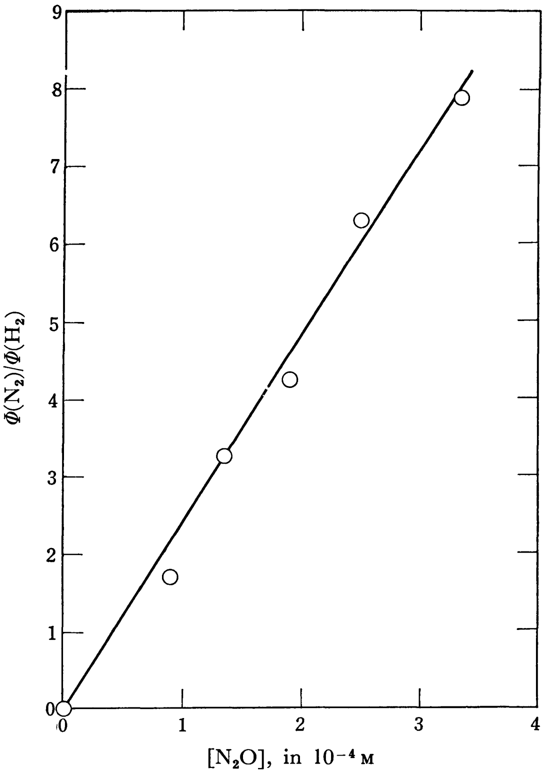

Fig. 4. A plot of $\Phi(\mathrm{N_2})/\Phi(\mathrm{H_2})$ *vs.* $[\mathrm{N_2O}]$ for UV-irradiated solutions of low nitrous oxide concentrations. $[\mathrm{KI}]=0.1$ M.

the slope of the straight line gives $k_7/k_1=2.4\times10^4$ M$^{-1}$. Taking $k_7=1.3\times10^{10}$ M$^{-1}$ sec$^{-1}$, one can obtain a first-order rate constant of $k_1=5.4\times10^5$ sec$^{-1}$, which corresponds to a half-life of 1.3 $\mu$sec.

The present $k_1$-value of $5.4\times10^5$ sec$^{-1}$ seems close to some literature values obtained directly by the pulse-radiolysis technique, $3.7\times10^5$ sec$^{-1}$ (20°),[12] or indirectly by the competition kinetics, $4.6\times10^5$ sec$^{-1}$ (25°),[13] with due consideration taken of the experimental errors involved in the preparation of samples of low nitrous oxide concentrations in this study; a much higher half-life of 7.5 $\mu$sec, corresponding to the lower rate constant of $0.9\times10^5$ sec$^{-1}$, has also been reported from a competition-kinetics study.[15]

Finally, it is interesting to compare the rate constant for Reaction (1) with that for the reaction of the hydrated electron with methanol in aqueous solutions. The rate constant for the latter reaction has recently been obtained by Hickel and Schmidt with photogenerated hydrated electrons in a hydrogen-saturated solution of sodium hydroxide as $k(e_{aq}^- + CH_3OH) \leq 400$ M$^{-1}$ sec$^{-1}$.[31] Although this reaction is essentially different from Reaction (1) that is the decomposition of the solvated electron, the comparison of these rate constants may have some relevance to the structure and reactivity of solvated electrons; no discussion can be made here, however.

*Conclusion.* The photochemical formation of solvated electrons from aqueous or alcoholic solutions of potassium iodide is not a novel subject. However, this system has been shown, according to circumstances, to be convenient for studying the reactions of solvated electrons, which all play an important role in the radiation chemistry of polar liquids.

In this study, it was concluded that the solvated electron forms hydrogen in methanol through Reaction (1), in which the hydroxyl hydrogen is dissociated. The rate constant of this reaction was determined explicitly. We have assumed that hydrogen is formed in neutral solutions from solvated electrons, escaping the primary and secondary recombinations (geminate recombination),[32] and that the scavengers used compete with the hydrogen-formation process in the lower concentration range and can compete with the secondary recombination in the higher concentration range. Although it is not essential for the present study whether or not nitrous oxide competes with the secondary recombination at higher concentrations, the linear dependency of $\Phi(N_2)$ on the square root of the nitrous oxide concentration[25,32] observed at these concentrations may support the above assumption.

It has also been shown that the reaction of the solvated electron with nitrous oxide yields one molecule of nitrogen in neutral methanolic solutions.

The authors wish to acknowledge the assistance of Mr. Hiro Ishida in a part of this study of acid solutions. They also wish to express their thanks to Dr. Shigeyoshi Arai and Dr. Akira Kira for their helpful suggestions in carrying out the flash-photolysis and the pulse-radiolysis experiments.

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[31] B. Hickel and K. H. Schmidt, *ibid.*, **74**, 2470 (1970).

[32] R. M. Noyes, *J. Amer. Chem. Soc.*, **77**, 2042 (1955).