SOLVENT EFFECTS ON THE PHOTOCHEMISTRY OF THE IODIDE ION

BY JOSHUA JORTNER, MICHAEL OTTOLENGHI, AND GABRIEL STEIN

Department of Physical Chemistry, Hebrew University, Jerusalem, Israel

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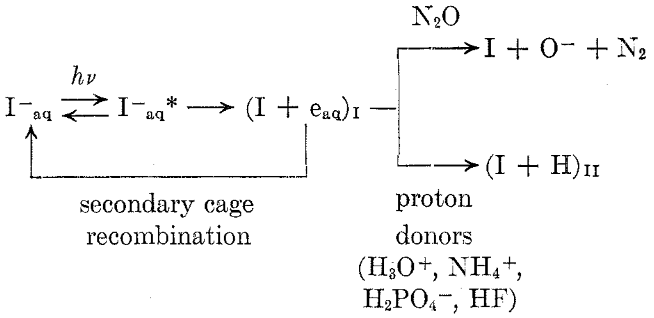
The photochemistry of the I^- ion in D_2O, ethanol, methanol, isopropyl alcohol, and methyl cyanide is investigated and the results compared to those previously obtained in H_2O solutions. It is shown that solvated electrons appear as a detectable intermediate in all these solvents and that the cross section for primary dissociation, Γ, is solvent dependent. The kinetic behavior in the case of D_2O is analogous to that previously proposed for H_2O solutions. The rate constant of the cage scavenging reaction $H + H^+$ in H_2O is found to be equal to that of $D + D^+$ in D_2O.

In a previous series of papers,[1-5] the photochemistry of the I^- ion in aqueous solutions was investigated. The use of specific scavengers enabled the identification of intermediates. The kinetic study of the dependence of the quantum yield of the final products on scavenger concentration indicated the operation of photochemical cage effects. The results may be represented by the general scheme



$$I^-_{aq} \underset{}{\overset{h\nu}{\rightleftarrows}} I^-_{aq}{}^* \longrightarrow (I + e_{aq})_I \begin{cases} \xrightarrow{N_2O} I + O^- + N_2 \\ \xrightarrow[\text{donors } (H_3O^+,\ NH_4^+,\ H_2PO_4^-,\ HF)]{\text{proton}} (I + H)_{II} \end{cases}$$

secondary cage recombination

$I_{aq}{}^{*-}$, the excited aqueous ion, is formed by excitation of an outer 5p electron of I^- to an s-type expanded orbital[6] in the polarization field of the oriented solvent medium.[6a,b] This excited state may dissociate thermally into an iodine atom and a solvated electron, e_{aq}, both in the same solvent cage—$(I + e_{aq})_I$. Alternatively it may decay back to the ground state. The competition between these processes determines the quantum yield, Γ, for the formation of the pair e_{aq} and I in the photochemical cage. At high scavenger concentrations a constant quantum yield of the final products, independent of scavenger concentration, was observed. This value, $\gamma_{max} = 0.290 \pm 0.05$ at 25° and 2537 Å. for all scavenger systems,[2-5] corresponds to total scavenging of solvated electrons from the cage $(I + e_{aq})_I$ and may thus be identified as the primary dissociation yield of the excited state, Γ.

Specific scavengers, *e.g.*, proton donors,[1,2,5] oxygen,[4] or nitrous oxide,[3] react with the solvated electron competing with cage recombination. The kinetics of the scavenging process could be well represented on the basis of the treatment proposed by Noyes,[7] adapted by us to more complex systems in which parallel and consecutive scavenging occur over a large range of scavenger concentrations.[2]

Both the kinetic analysis and the fact that $\gamma_{max} < 1$ indicated that the scavenging process does not involve a direct interaction of the scavenger with the spectroscopic excited state of the ion.

In the present paper we report our experiments in which solvents other than H_2O (*i.e.*, D_2O, alcohols, and CH_3CN) were used, in an attempt to establish whether the mechanisms, previously derived are of general validity, and in particular whether the solvated electron appears as a detectable intermediate in solvents other than H_2O.

Spectroscopic studies[8] indicate that the ultraviolet absorption spectra of I^- in the solvents employed by us involves charge transfer bands. We are therefore dealing with the same type of excited state as that previously described for I^- in H_2O. As to previous photochemical studies, Edgecombe and Norrish[9] have used flash photolysis techniques for an investigation of the intermediates in ultraviolet irradiated solutions of I^-. Their results indicate that the species I_2^- is not restricted to aqueous solutions, thus demonstrating that I atoms are also formed, in a primary photochemical stage, in solvents such as alcohols and methyl cyanide.

Experimental

Irradiations were carried out at 25° and 2537 Å. as described previously.[1,2]

Materials.—D_2O was purified as described previously.[2] Methanol and ethanol, BDH Analar, were dried by refluxing over Mg metal in the presence of I_2 and then redistilled twice. Isopropyl alcohol, BDH laboratory reagent grade, was freed of peroxides by refluxing over $SnCl_2$, redistilled twice, and dried over $CaSO_4$. Methyl cyanide was obtained in spectroscopic grade from Eastman Kodak Co. and used without further purification.

Actinometry.—In all solutions used the optical path was 3 cm. and conditions of total absorption were attained. Therefore, the actinometric data were as described previously[1,2]; the light intensity was $J = 1.5 \times 10^{-6}$ einstein l.$^{-1}$ sec.$^{-1}$.

Gas Analysis.—Nitrogen produced in N_2O containing solutions was determined by a McLeod and a Pirani gage after freezing the N_2O and solvent vapor in a liquid air trap.

Results

Solutions in D_2O.—It was found that the molar extinction coefficient of I_3^- in D_2O was equal to that measured under the same conditions in H_2O,[1] so that the same calibration could be used for the determination of the I_2 liberated. Evacuated solutions of 0.15 *M* KI were irradiated and the D^+ concentration was adjusted by adding concentrated H_2SO_4 diluted with D_2O. $[D^+]$ was calculated from the amount of H_2SO_4 added, using[10] $K_{DSO_4^-} = 8 \times 10^{-3}$ (while the corre-

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[1] J. Jortner, R. Levine, M. Ottolenghi, and G. Stein, *J. Phys. Chem.* **65**, 1232 (1961).

[2] J. Jortner, M. Ottolenghi, and G. Stein, *ibid.*, **66**, 2029 (1962).

[3] J. Jortner, M. Ottolenghi, and G. Stein, *ibid.*, **66**, 2037 (1962).

[4] J. Jortner, M. Ottolenghi, and G. Stein, *ibid.*, **66**, 2042 (1962).

[5] J. Jortner, M. Ottolenghi, J. Rabani, and G. Stein, *J. Chem. Phys.*, in press.

[6] (a) R. Platzman and J. Franck, "Farkas Memorial Volume," Jerusalem, 1952, p. 21; (b) G. Stein and A. Treinin, *Trans. Faraday Soc.*, **55**, 1087 (1959).

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

[8] (a) I. Burak and A. Treinin, to be published; (b) M. Smith and M. C. R. Symons, *Discussions Faraday Soc.*, **24**, 206 (1957).

[9] F. H. C. Edgecombe and R. G. W. Norrish, *Proc. Roy. Soc.* (London), **A253**, 154 (1959).

[10] E. C. Noonan and V. K. La Mer, *J. Phys. Chem.*, **43**, 247 (1939).

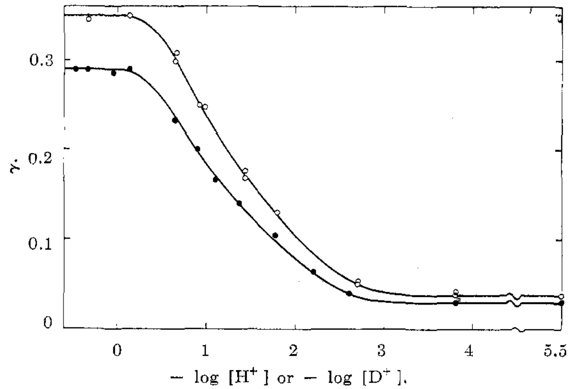

Fig. 1.—Solutions of I^- (0.15 M) in D_2O, ○. Dependence of $\gamma(I_2)$ on pD (= $-\log [D^+]$). For comparison results[1] in H_2O are shown, ●.

sponding value for H_2O is $K_{HSO_4^-} = 2 \times 10^{-2}$). $\gamma(I_2)$, the quantum yield for iodine formation, was determined in the range $10^{-6}\ M < [D^+] < 2\ M$. The values derived from the initial slopes of $[I_2]$ *vs.* the irradiation time, t, are shown in Fig. 1 and compared with those obtained in H_2O solutions.[1]

As in the case of H_2O solutions[1,2] the pH dependence of $\gamma(I_2)$ in this pH region should be attributed to the competition

$$(I + D)_{II} \longrightarrow I^- + D^+ \text{ (cage recombination)} \qquad (1)$$

$$(I + D)_{II} + D^+ \longrightarrow \text{radicals in bulk of soln.} \qquad \text{(cage scavenging}^{11}\text{)} \qquad (2)$$

The value of $\Gamma = \gamma_{max}(I_2)$, the maximum quantum yield reached when total scavenging occurs from both cages $(I + e_{aq})_I$ and $(I + D)_{II}$, is 0.35 in D_2O compared with 0.29 in H_2O. The value $\Gamma = 0.35$ in D_2O obtained from $\gamma_{max}(I_2)$ in acid solutions (pD < 0.9) agrees with that obtained previously[2] in D_2O for γ_{max}(HD) when methanol or isopropyl alcohol, instead of D^+, was used as the D atom scavenger at pD 2.9.

When dealing with acid H_2O solutions at pH < 2.5 it was shown[1,2] that at the initial stages of the reaction, when very small amounts of I_2 are present, each H atom scavenged by H^+ is converted ultimately into H_2^+ which is capable of oxidizing another I^- ion according to

$$I^- + H_2^+ \longrightarrow I + H_2 \qquad (3)$$

followed by

$$I + I \longrightarrow I_2 \qquad (4)$$

However, when $[I_2]$ becomes considerable, the back reactions: $I_2 + H_2^+ \rightarrow I_2^- + 2H^+$ and $I_2 + H \rightarrow I_2^- + H^+$ should also be taken into account. These reactions cause a lowering of $\gamma(I_2)$ and $\gamma(H_2)$ and are therefore responsible for the deviations of the plots of $[I_2]$ *vs.* t from linearity. In such a case it was shown that the dependence of $[I_2]$ (or $[H_2]$) on t is given by[1]

$$\frac{t}{[I_2]} = \frac{1}{\gamma_i J} + \frac{k_r[I_2]}{k_{ox}2J\gamma_i[I^-]} \qquad (5)$$

where t is the duration of irradiation, $[I_2]$ and $[I^-]$ the concentrations of iodine and iodide ion at time t, γ_i is the initial quantum yield of I_2, k_r and k_{ox} are complex rate constants depending on $[H^+]$. To investigate whether the mechanism derived in the case of H_2O solutions holds for D_2O as a solvent, $t/[I_2]$ is plotted as a function of $[I_2]$. Straight lines are obtained (Fig. 2) in agreement with equation 5. Thus in accordance with the considerations previously given,[1,2] the mechanism including competition in the bulk between I_2 and I^- for H_2^+ is pertinent. The values of $A = k_r/k_{ox} = 2 \times [I^-] \times$ slope/intercept are given in Table I together with the corresponding values in H_2O,[1] showing that there is no significant change in the value of this ratio while passing from H_2O to D_2O. From the intercepts of Fig. 2 the initial $\gamma(I_2)$ values could be obtained. These are compared in Table II with the experimental values of Fig. 1.

The pD dependence of the initial quantum yields should be interpreted in terms of a consecutive scavenging by the D^+ ion[1,2]

$$(I + e_{aq})_I \xrightarrow{D^+} (I + D)_{II} \xrightarrow{D^+} \text{radicals in bulk}$$

Remembering that in the region pD < 2 the scavenging of e_{aq} from $(I + e_{aq})_I$ is complete,[2] the dependence of $\gamma(I_2)$ on $[D^+]$ will be given by Noyes' scavenging equation[7]

$$\gamma = \gamma_r + 2a_{II}\Gamma_{II}\sqrt{\pi k_{D+D^+}[D^+]} \qquad (6)$$

which is valid at small $[D^+]$ values. γ_r is the "residual yield" of radicals escaping cage recombination in the absence of external scavengers, Γ_{II} is the cross section for formation of the cage $(I + D)_{II}$ and a_{II} a constant related to microscopic parameters[12] of the radicals in the cage $(I + D)_{II}$. The theoretical significance of γ_r, Γ_{II}, and a_{II} in such a consecutive scavenging system was previously discussed.[2] Figure 3 shows the extrapolated values of $\gamma(I_2)$ as a function of $\sqrt{(D^+)}$. A straight line is obtained, confirming the operation of the mechanism involving scavenging from the photochemical cage.[1,2] The intercept in Fig. 3 gives $\gamma_r = 0.13$ in D_2O compared[1] with $\gamma_r = 0.09$ for H_2O. From the slope of Fig. 3, $\Gamma_{II}2a_{II}\sqrt{\pi k_{D+D^+}} = 0.4$ l.$^{1/2}$ mole$^{-1/2}$. Setting[2] $\Gamma_{II} = \Gamma = 0.35$, $2a_{II}\sqrt{\pi k_{D+D^+}} = 1.14$ l.$^{1/2}$ mole$^{-1/2}$. Setting $\Gamma_{II} = \Gamma - \gamma_r = 0.22$ this parameter will be 1.8 l.$^{1/2}$ mole$^{-1/2}$. These results are compared in Table III with the corresponding ones in H_2O solutions.[1] Thus the main difference between solutions of I^- in H_2O and D_2O lies in the value of Γ. The subsequent steps in the mechanism are equal in both cases, and support the kinetic analysis given for H_2O.[12]

Table I

The Dependence of the Ratio k_r/k_{ox} on pD and pH in D_2O and H_2O Solutions, Respectively

D_2O Soln.		H_2O Soln.[1]	
pD	$\frac{k_r}{k_{ox}} \times 10^{-4}$	pH	$\frac{k_r}{k_{ox}} \times 10^{-4}$
0.65	0.65	0.65	0.58
0.95	1.2	0.90	0.71
1.44	3.2	1.10	1.46
1.82	5.9	1.36	2.25
...	...	1.78	5.20

An examination of Table III shows that no significant difference exists between the ratio $\gamma_r^{extrapol}/\Gamma$ in the two solvents (0.37 in D_2O compared to 0.32 in H_2O).

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(11) The exact nature of this process, involving either a direct formation of D_2^+ or a charge transfer from D to D^+, was previously discussed.[2]

(12) R. M. Noyes, *J. Am. Chem. Soc.*, **78**, 5486 (1956).

TABLE II

INITIAL QUANTUM YIELDS IN THE PHOTOCHEMISTRY OF I^- ($[I^-] = 0.15\ M$) IN D_2O

	$\gamma_i(I_2)$	
pD	Exptl. value	From intercepts of Fig. 2
0.65	0.300	0.314
0.95	.244	.278
1.44	.175	.220
1.82	.130	.190

This implies that the cage parameter β_{II}', related to γ_r and Γ_{II} by the equation[1] $\gamma_r = \Gamma_{II}(1 - \beta_{II}')$, has not changed markedly. Theoretical equations relating a and β' with microscopic parameters of diffusion have been developed by R. M. Noyes.[12] According to this study β' is related to ρ, the encounter diameter of the caged radicals, and to σ, the root mean square displacement distance for relative diffusive motion of the radicals. As the values of ρ in D_2O cannot differ from those in H_2O, σ should also be equal in the two solvents. The parameter a is related[12] to ρ, σ, and D, the diffusion coefficient of relative motion of the radicals. However only $\sqrt{D}$ appears in the expression for a so that, after taking into consideration the relatively small effect of the change in viscosity of D_2O compared to H_2O, we may conclude that a_{II} is also similar in the two solvents. These considerations imply (see Table III for the values of $2a_{II}\sqrt{\pi k}$) that the rate constant ratio $(k_{H^+ + H})_{H_2O}/(k_{D^+ + D})_{D_2O}$ is near to unity.

TABLE III

COMPARISON OF PHOTOCHEMICAL SCAVENGING DATA AND CAGE PARAMETERS FOR I^- IN H_2O[1,2] AND D_2O AT 2537 Å. AND 25°

(See ref. 1 for the back bulk reactions explaining the difference between the experimental value and the extrapolated value of γ_r)

Parameter	H_2O	D_2O
Γ	0.29	0.35
γ_r (experimental value)	0.030	0.045
γ_r (from extrapolation of eq. 6)	0.092	0.130
$2a_{II}\sqrt{\pi k_{H^+ + H}}$ and $2a_{II}\sqrt{\pi k_{D^+ + D}}$	1.57	1.8

The reaction $H + H_{aq}^+$ could involve the formation of H_2^+. If so, the absence of an isotope effect shows that H_2^+ is not formed by a proton transfer from H_3O^+ to an H atom, a process which would involve an O–H bond rupture. The results could also be consistent with charge transfer from H to H_{aq}^+. Some charge transfer processes indeed show an isotope effect, due to different interatomic distances within the primary hydration layer in the activated complex prior to the electron transfer, but others do not and the existence of such an effect depends markedly on the nature of the transition state.[13] The charge transfer mechanism is however excluded by the results in γ-irradiated solutions where no isotope exchange reaction of H atoms occurs in acid D_2O solutions[14] (see also ref. 2). A possible mechanism, consistent with both the absence of an isotope effect in the scavenging reaction now described and lack of isotope exchange of H atoms in γ-irradiated D_2O, may involve the formation of an H_2^+ complex in which H atoms are not equivalent, *e.g.*, $\{H\text{–}H\text{–}O{<}^{H}_{H}\}^+$ The velocity constant[1,2] of the reaction $H + H_{aq}^+$ is $< 10^5$ liter mole^{-1} sec.$^{-1}$; it does not therefore belong to that category of very fast diffusion controlled reactions which do not show isotope effects for this reason.

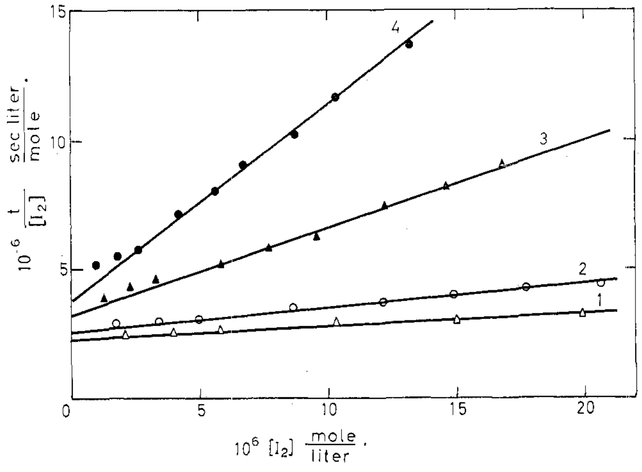

Fig. 2.—Determination of initial quantum yields in D_2O solutions of I^- by method of extrapolation: (1) pD = 0.65; (2) pD = 0.95; (3) pD = 1.44; (4) pD = 1.82.

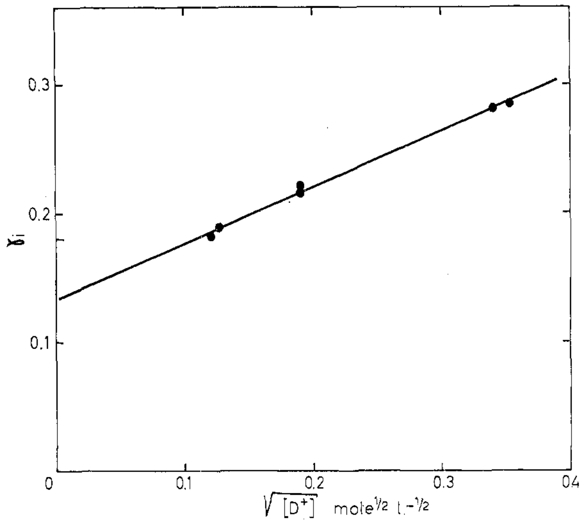

Fig. 3.—Initial quantum yield in D_2O solutions of I^- as a function of $\sqrt{[D^+]}$.

Primary Dissociation Yields in Some Non-aqueous Solvents.—The photochemistry of the I^- ion in methanol, ethanol, isopropyl alcohol, and methyl cyanide was investigated. N_2O was used as a radical scavenger.[3] Its solubility in methanol and ethanol is known[15] to be some 5 times greater than in H_2O. The I^- concentration was 0.15 M in methanol and 0.045 M in ethanol. In the case of isopropyl alcohol and methyl cyanide saturated solutions were used and $[I^-]$ was determined spectroscopically from measurements of the absorption of these solutions at wave lengths corresponding to $\epsilon = 5.5$. For I^- in methyl cyanide where $\epsilon = 5.5$ at 280 mμ,[8a] we found $[I^-] \cong 0.2\ M$. For $[I^-]$ in isopropyl alcohol only $h\nu_{max} \cong 130.5$ kcal. is known.[8b] However, for all solvents[8a] $h\nu_{max} - h\nu_{\epsilon = 5.5} \cong 18$ kcal., so that for I^- in isopropyl alcohol $h\nu_{\epsilon = 5.5} \cong 111.5$ kcal, and the value $[I^-] \cong 0.35\ M$ was found in this

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[13] R. A. Marcus, *J. Chem. Phys.*, **26**, 867 (1957).

[14] (a) T. W. Davis, S. Gordon, and E. J. Hart, *J. Am. Chem. Soc.*, **80**, 4487 (1958); (b) H. L. Friedman and A. H. Zeltman, *J. Chem. Phys.*, **28**, 878 (1958); (c) K. C. Kurien and M. Burton, Summary of Proceedings of the 4th Informal Conference on the Radiation Chemistry of Water, University of Notre Dame, Indiana, March 23–25, 1961.

[15] A. Siedell, "Solubility of Inorganic and Organic Compounds," D. Van Nostrand Co., Suppl. to 3rd Edition, 1952.

solvent. Measurements showed that at 2537 Å. total absorption could be assumed for all those solutions at 3 cm. path length. Table IV shows $\gamma(N_2)$, the quantum yield of N_2, at two N_2O pressures. The identity of the two sets of results shows that the quantum yield is independent of N_2O concentrations, hence $\gamma(N_2) = \Gamma$. Control tests were carried out for the evolution of H_2 in the absence of dissolved N_2O in the above solvents. No detectable amount of H_2 was found.

TABLE IV

NITROGEN QUANTUM YIELDS IN THE PHOTOCHEMISTRY OF I^- IN ORGANIC SOLVENTS

	$\gamma(N_2)$	
Solution	P_{N_2O} = 500 mm.	P_{N_2O} = 280 mm.
0.15 *M* KI in methanol	0.60 ± 0.02	0.59 ± 0.02
0.045 *M* KI in ethanol	.66 ± .02	.65 ± .02
~0.2 *M* KI in isopropyl alcohol	.70 ± .02	.71 ± .02
~0.3 *M* KI in methyl cyanide	.75 ± .02	.75 ± .02

Discussion

The question arises whether the species reacting with N_2O in the various non-aqueous solvents may be unambiguously identified as the solvated electron, as in the cases of H_2O and D_2O. An alternative process may be[3] $H + N_2O \rightarrow N_2 + OH$, with H atoms which may be formed (in methanol and ethanol) *via* a dissociative electron capture by the solvent. This possibility is ruled out by the observation that no hydrogen gas is evolved when irradiating alcoholic solutions of I^- in the absence of N_2O. Hence H atoms are not formed in these solutions, where the solvent itself may act as an efficient scavenger for H atoms,[2,16] *via* dehydrogenation, leading to the evolution of H_2. In all cases the value $\gamma_{max} = \Gamma < 1$ indicates that N_2O does not interact directly with the spectroscopic excited state.

We may thus conclude that solvated electrons appear as reactive intermediates in the photochemistry of the iodide ion in all the solvents investigated in the present work, according to the scheme

$$I^-_{sol} \underset{}{\overset{h\nu}{\rightleftarrows}} I^{-*}_{sol} \longrightarrow (I + e_{sol}) \xrightarrow{N_2O} I + O^- + N_2 \quad (7)$$

The existence of solvated electrons, which have sufficiently long life time to react with chemical scavengers, in solutions of methanol and ethanol was recently confirmed by a radiation chemical study.[17]

The independence of the quantum yields, $\gamma(N_2)$, in Table IV, of $[N_2O]$ indicate that total electron scavenging by N_2O occurs in this concentration range. This supports the previous assumption that all solvents employed by us react relatively slowly with solvated electrons, thus $k_{e+N_2O}[N_2O] >> k_{e+solv}[solv.]$. As $[N_2O] = 10^{-2}\,M$ and $[solv.] \cong 20\,M$, we get $k_{e+N_2O}/k_{e+solv} >> 2 \times 10^3$.

Another conclusion which may be derived from these data is that the O^- ion (or the OH radical) produced according to eq. 7 reacts with the solvent (in the case of the alcohols probably by H atom abstraction) and does not contribute to the yield of gaseous products. A reaction between N_2O and the organic radicals formed by the reaction of OH or O^- with the solvent (CH_2OH and CH_3CHOH for methanol and ethanol, respectively) should be ruled out as it would lead to a chain reaction and consequently to too high N_2 yields. We confirmed this conclusion by measuring the N_2 yields in aqueous solutions saturated with N_2O and irradiated with 200 kv. X-rays. We found that the addition of 1 *M* ethanol did not change the value of G_{N_2} (the yield of N_2). In these solutions the same organic radicals as those appearing in our photochemical systems are produced by dehydrogenation of the alcohol by OH radicals. We may therefore rule out any reaction between the organic radicals and N_2O which can ultimately lead to the formation of N_2 or any other gaseous product.

The similar photochemical behavior of all these systems is consistent with the interpretation of their absorption spectra as due in all these solvents to electron transfer. In all cases a fraction Γ of these excited states is thermally converted to solvated electrons, capable of decomposing N_2O with the formation of N_2. The scavenging process by N_2O may thus serve as a photochemical criterion for the identification of charge transfer bands of anions in solution. The value of Γ is a result of the competition between deactivation of the spectroscopic excited state and its decomposition into the solvated electron in the photochemical cage. Changing the solvent changes the rates of both processes. The results reported so far do not enable us to decide their relative changes, as they probably depend simultaneously on a number of factors. To determine the nature of the two competing processes, which determine the value of Γ, it is desirable to study the effects of specific parameters, *e.g.*, temperature, wave length, and nature of dissolved ion. We hope to publish our results in this respect separately.

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(16) J. T. Allan and G. Scholes, *Nature*, **187**, 218 (1960).

(17) J. H. Baxendale and F. W. Mellows, *J. Am. Chem. Soc.*, **83**, 4720 (1961).