THE EFFECT OF NITROUS OXIDE AND THE NATURE OF INTERMEDIATES IN THE PHOTOCHEMISTRY OF THE IODIDE ION IN AQUEOUS SOLUTION

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The nature of the intermediates formed from the excited state of the I^- ion was considered. The scavenging mechanism by N_2O was investigated. Nitrous oxide was found to act as a specific scavenger for electrons. Semiquantitative treatment of the scavenging mechanisms is carried out. Chemical evidence for the transient formation of electrons in the photochemical system is presented. The mechanism of radical formation by the dissociation of the excited state is discussed.

Introduction

In the preceding paper[1] we investigated the photochemistry of KI solutions over a wide pH region in the presence of specific scavengers. The experimental results could be adequately interpreted in terms of a consecutive scavenging model. H^+ ions act as scavengers for electrons formed from the dissociation of the excited state. They yield H atoms which can be scavenged by H^+ ion or by organic solutes, *e.g.*, aliphatic alcohols.

In the present work we investigated the nature of the intermediates formed from the excited state. Nitrous oxide was used by Dainton, *et al.*,[2,3] in a recent radiation chemical[2] and photochemical investigation[3] in an attempt to discriminate between various forms of H atoms. The experimental results were interpreted by these authors[3] by assuming that nitrous oxide is inert to H_2^+ but reacts rapidly with H atoms. These conclusions are at variance with a recent kinetic analysis of the reactivity of H atoms in aqueous N_2O solutions,[4] which suggests that N_2O actually acts as a specific scavenger for solvated electrons. A further investigation of this problem appeared desirable.

The experimental results presented in the present and the preceding work make possible a further insight into the mechanism of the utilization of the optical excitation energy in a chemical radical formation process.

Experimental

The photochemical experiments at 2537 Å. were performed as described in previous work.[1,5] All experiments were carried out at 25°.

Procedure.—N_2O-containing solutions were prepared by evacuation of the neutral KI solution and the separate container containing sulfuric acid as previously described. The branch containing the reaction vessel and the acid container were isolated from the vacuum system. The N_2O gas used was a Matheson product. The gas was purified from traces of O_2 by freezing several times in a liquid air trap and pumping the uncondensable gases. Finally the liquid air trap was removed and the pressure of the gas was measured by a mercury manometer or a McLeod gage. Then the photochemical branch was connected to the vacuum line containing the purified N_2O.

An equilibration during 2–3 hours was carried out, the solutions in the reaction cell and the acid container being strongly stirred by Teflon coated magnetic stirrers. The partial pressure of the N_2O, P_{N_2O}, was calculated from the volume ratio of the isolated branch and the vacuum line. The acid was added to the reaction cell before irradiation.

The pressure of the gas evolved from irradiated solution was determined by a McLeod gage. The water vapor in the system was condensed in a CO_2–acetone trap and the N_2O in a liquid nitrogen trap. The composition of the gas was determined by simultaneous measurement of the pressure by Pirani and McLeod gages. The composition of the gas was determined by calibrating the Pirani gage with N_2–H_2 mixture. N_2O concentration was calculated from available solubility data.[6]

Results

Photochemistry of Aqueous Neutral KI Solutions in the Presence of N_2O.—In the present work a previous investigation[3] of the photochemistry of the iodide ion in the presence of N_2O was extended, in an attempt to use nitrous oxide for establishing the nature of the species produced, and for a further test of the scavenging mechanism. The dependence of the quantum yield in neutral unbuffered solutions (pH 6) on I^- and N_2O concentration was investigated. The initial yields are presented in Table I and the complete curves in Fig. 1. The gas evolved from the irradiated neutral solutions was found to be pure N_2, at pH 6 and P_{N_2O} = 640 mm., $\gamma(N_2) = 0.29 \pm 0.01$. Thus $\gamma(N_2) = \gamma(I_2)$, confirming previous results.[3]

TABLE I

PHOTOCHEMISTRY OF I^- IN N_2O SOLUTIONS AT pH 6

Temp., 25°; light intensity $J = 1.5 \times 10^{-6}$ eins. l.$^{-1}$ sec.$^{-1}$

P_{N_2O}, mm.	C_{N_2O}, *M*	I^-, *M*	γ_i
644	2.0×10^{-2}	0.15	0.295 ± 0.005
500	1.58×10^{-2}	.15	$.293 \pm .005$
491	1.55×10^{-2}	.15	$.290 \pm .005$
427	1.35×10^{-2}	.15	$.294 \pm .005$
250	7.9×10^{-3}	.15	$.290 \pm .005$
147	4.65×10^{-3}	.15	$.290 \pm .005$
92	2.9×10^{-3}	.15	$.265 \pm .005$
45	1.42×10^{-3}	.15	$.235 \pm .005$
23	7.3×10^{-4}	.15	$.219 \pm .004$
4.6	1.45×10^{-4}	.15	$.161 \pm .003$
0.04	1.26×10^{-6}	.15	$.092 \pm .002$
525	1.65×10^{-2}	1×10^{-3}	$.28 \pm .03$[a]
525	1.65×10^{-2}	5×10^{-3}	$.286 \pm .005$
525	1.65×10^{-2}	1.5×10^{-2}	$.290 \pm .005$
525	1.65×10^{-2}	3.7×10^{-2}	$.290 \pm .005$

[a] γ corrected for incomplete light absorption.

However, these results show that the quantum yield is independent of the I^- concentration over a wide region, indicating that the iodide ion does

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[1] J. Jortner, M. Ottolenghi, and G. Stein, *J. Phys. Chem.*, **66**, 2029 (1962).

[2] F. S. Dainton and D. B. Peterson, *Nature*, **186**, 878 (1960).

[3] F. S. Dainton and S. A. Sills, *ibid.*, **186**, 879 (1960).

[4] G. Czapski and J. Jortner, *ibid.*, **188**, 50 (1961).

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

[6] A. Seidell, "Solubilities of Inorganic and Organic Compounds," Supplement to the third edition, D. Van Nostrand, New York, N. Y., 1955.

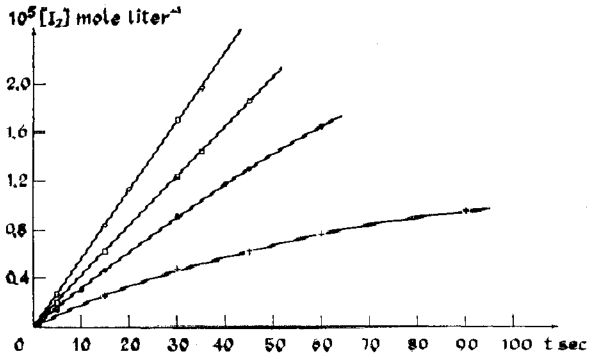

Fig. 1.—The dependence of I_2 production at constant light intensity on N_2O concentration; $J = 1.5 \times 10^{-6}$ einstein l.$^{-1}$ sec.$^{-1}$: ○, $N_2O = 1.6 \times 10^{-2}$ *M*; □, $N_2O = 7.3 \times 10^{-4}$ *M*; ●, $N_2O = 1.45 \times 10^{-4}$ *M*; +, $N_2O = 1.26 \times 10^{-6}$ *M*.

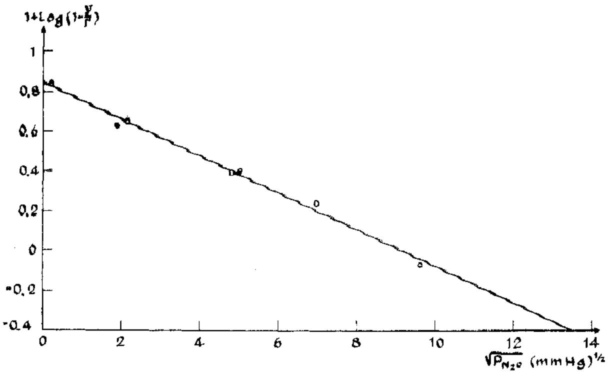

Fig. 2.—Scavenging plot for N_2O.

not take part in the primary radical formation process. This result is in variance with previous suggestions.[3]

At high N_2O concentration a limiting constant quantum yield independent of the scavenger concentration is obtained. This value $\Gamma = 0.293$ at 25° and 2537 Å. is identical with the limiting quantum yield obtained in other scavenger systems.[1,7]

As indicated by our previous results for the scavenging reaction in the presence of alcohols,[1] these specific scavengers for H atoms are not efficient in the neutral pH region (pH > 4). In this pH region H^+ ions are not present in sufficient concentration to serve as efficient scavengers for electrons, and thus H atoms are not produced. We thus conclude that the limiting yield obtained in the presence of N_2O in neutral solutions arises from the scavenging by N_2O of the precursors of H atoms, *i.e.*, electrons, formed from the dissociation of the excited state. The reaction mechanism in neutral N_2O solutions is presented in the form

$$(I + e)_I + N_2O \longrightarrow I + N_2 + O^- \quad (1)$$

For energetic reasons the back reaction between O^- and I is unfavorable in aqueous solution. The sum of the electron affinity of O and hydration energy of O^- (165 kcal.)[8] is higher than the corresponding sum for I (147 kcal).[8]

At pH below 10, O^- is effectively converted into an OH radical by

$$O^- + H_2O \longrightarrow OH + OH^- \quad (2a)$$

or

$$O^- + H^+ \longrightarrow OH \quad (2b)$$

The OH radicals thus formed act as an efficient oxidizing agent for I^- [9] by a diffusion controlled reaction

$$OH + I^- \longrightarrow I + OH^- \quad (3)$$

The equivalence of the quantum yields for nitrogen and iodine production is consistent with this mechanism.

Dependence of $\gamma(I_2)$ on N_2O Concentration at pH 6.—In the concentration region below $C_{N_2O} = 3.14 \times 10^{-6}$ mole l.$^{-1}$ the quantum yield in N_2O solutions at pH 6 is found to be dependent on N_2O concentration (Table I). This effect is attributed to the competition between the scavenging reaction and secondary recombination of the iodine atom and the electron in the solvent cage. The experimental results were analyzed by application of the general scavenging equation[1]

$$\ln\left(1 - \frac{\gamma}{\Gamma}\right) = \ln\left(1 - \frac{\gamma_r}{\Gamma}\right) - \frac{2a_I}{\beta_I'}\sqrt{\pi k_{(N_2O + e)}[N_2O]} \quad (4)$$

Figure 2 shows that the experimental results are consistent with eq. 4 over the whole concentration region. These results for electron scavenging by N_2O are compared in Table II with our previous results[1] for electron scavenging by H^+. The agreement between the values of $\gamma_r{}^I$ in both cases shows the consistency of the treatment for two different scavengers. Assuming that the two scavenging processes involve the same radical pair, the results of Table II give the rate constant ratio for scavenging by H^+ and N_2O $k_{H^+ + e}/k_{N_2O + e} = 5$.

Table II

Kinetic Data for Electron Scavenging

Scavenger system	$\frac{2a_I}{\beta_I'}\sqrt{\pi k_S}$ mole$^{-1/2}$ l.$^{1/2}$	β_I'	$\gamma_r{}^I$
H^+, 1 *M* alcohol soln.	85	0.725	0.08 ± 0.005
N_2O, pH 6	38	0.759	0.07 ± 0.005

Effect of Light Intensity in the Presence of N_2O.—The dependence of $\gamma(I_2)$ on light intensity in neutral solutions containing N_2O is important for establishing the reaction mechanism, making possible the discrimination between ordinary bulk kinetics and diffusion controlled cage scavenging. The results presented in Table III indicate that

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[7] The limiting quantum yield in neutral solutions reported in ref. 3 is 0.16. In ref. 3 the wave lengths range was 2000–2600 Å. (light source and the temperature not specified). We have found a quite substantial temperature effect on the limiting quantum yield. At 10° we find $\Gamma = 0.20$.

[8] Heats of solution are taken from Latimer, Pitzer, and Slansky, *J. Chem. Phys.*, **7**, 108 (1939), the heat of solution of O^- taken to be equal to that of OH^-. Electron affinities from H. O. Pritchard, *Chem. Rev.*, **52**, 529 (1953).

[9] C. B. Senvar and E. J. Hart, *Proc. 2nd Int. Conf. Peaceful Uses At. Energy*, **29**, 19 (1958).

$\gamma_i(I_2)$ is independent of light intensity over a rather wide range.

TABLE III

DEPENDENCE OF $\gamma_i(I_2)$ ON LIGHT INTENSITY AT pH 6
$[I^-] = 0.15\ M$

J, einstein l.$^{-1}$ sec.$^{-1}$	$\gamma_i(I_2)$ $[N_2O] = 1.7 \times 10^{-2}$ M	$\gamma_i(I_2)$ $[N_2O] = 1.42 \times 10^{-3}$ M
15.0×10^{-7}	0.292	0.240
12.35×10^{-7}	.298	.235
6.05×10^{-7}	.294	.236
1.78×10^{-7}	.288	.230
Mean value	.293 ± 0.005	.235 ± 0.005

Any bulk mechanism will assign the reduction of the quantum yield below the limiting yield Γ to the competition between the recombination reaction of I atoms and the reducing radical in the bulk and the scavenging of the radical by N_2O. This will lead to the dependence of γ on light intensity in the N_2O concentration region where $\gamma < 0.29$. The experimental results at $N_2O = 1.4 \times 10^{-3}$ mole l.$^{-1}$ are in variance with this conclusion, yielding a strong support to the assumption that the decrease of $\gamma(I_2)$ with decreasing N_2O concentration is due to recombination in the cage.

The pH Dependence in N_2O Solution.—The pH dependence for I_2 formation in N_2O solution at $C_{N_2O} = 0.01\ M$ is presented in Fig. 3. This pH dependence is qualitatively similar to that previously observed.[3] In the present case initial yields are presented. When the pH is decreased below 3 a lowering of the quantum yield is observed, rising again to the limiting yield at high acid concentration. This behavior is in complete agreement with the general mechanism involving H atom formation by electron scavenging by H^+. In the pH region below 3 both H^+ and N_2O act as efficient scavengers for the cage $(I + e)_I$. Thus in the low pH region parallel scavenging occurs by both scavengers.

The general reaction mechanism in N_2O solutions will be presented in the form

$$(I + e)_I + N_2O \longrightarrow I + OH + N_2 \qquad k_{N_2O + e} \quad (1)$$

$$(I + e)_I \longrightarrow I + e \qquad \gamma_r^{I} \quad (5)$$

$$(I + e)_I + H^+ \longrightarrow (I + H)_{II} \qquad k_{H^+ + e} \quad (6)$$

$$(I + H)_{II} + H^+ \longrightarrow I + H^+ + H \qquad k_{H^+ + H} \quad (7)$$

$$(I + H)_{II} \longrightarrow I + H \qquad \gamma_r^{II} \quad (8)$$

When the pH is decreased below 3 the radical pair $(I + H)_{II}$ is formed, in the solvent cage. In the absence of an efficient scavenger for H atoms they will undergo a secondary recombination lowering γ below the limiting value Γ. It is assumed (and will be further discussed) that N_2O is a poor scavenger for H atoms. An increase of $\gamma(I_2)$ is observed at pH < 2 as the H^+ concentration increases, reaching a value sufficient for efficient scavenging of H atoms by H^+ ions.[1] These results can be quantitatively accounted for by considering a general model for parallel scavenging.

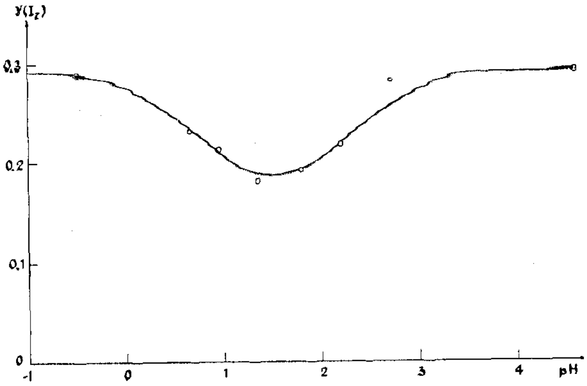

Fig. 3.—The pH dependence of $\gamma(I_2)$ in the presence of $1.6 \times 10^{-2}\ M$ N_2O: open circles, experimental data; solid curve, calculated from eq. 12.

Parallel Scavenging Model.—We consider a system where $i = 1 \ldots n$ efficient scavengers react with a radical undergoing secondary recombination. The parallel scavenging reactions are pseudo first order with rate constants $k_{S_i}[S_i]$. Applying the general considerations presented in previous work[1] the quantum yield for the depletion of the scavenger S_1 will be given by

$$-\frac{1}{J}\frac{d[S_i]}{dt} = \frac{k_{S_i}[S_i]}{\sum\limits_{i = 1 \ldots m} k_{S_i}[S_i]}\Gamma(1 - \beta' e^{-(2a/\beta')\sqrt{\pi \sum_{i=1 \ldots m} k_{Si}[Si]})} \quad (9)$$

Parallel Scavenging by N_2O and H^+.—The pH dependence of the quantum yield of iodine production at relatively high N_2O concentration was investigated. For $C_{N_2O} > 3 \times 10^{-3}$ mole l.$^{-1}$ the results in neutral solution indicate that $\sqrt{[N_2O]} >> \beta'/2a\sqrt{\pi k_{N_2O + e}}$; thus the exponential term in eq. 9 can be neglected.

The total quantum yield is thus presented in the form

$$\gamma(I_2) = \gamma_r^{I} + (\Gamma - \gamma_r^{I})\,\delta + (\Gamma - \gamma_r^{I})(1 - \delta)(1 - \beta_{II}'\, e^{-(2a_{II}/\beta_{II}')\sqrt{\pi k_{H + H^+}[H^+]}} \quad (10)$$

where

$$\delta = \frac{k_{(N_2O + e)}[N_2O]}{k_{(N_2O + e)}[N_2O] + k_{(H^+ + e)}[H^+]}$$

In deriving this equation it is assumed that cage I yields a constant residual yield γ_r^{I} which is totally scavenged in the bulk contributing to the I_2 yield. The rest of the electrons in cage I are subjected to parallel scavenging by H^+ and N_2O. The fraction δ scavenged by N_2O fully contributes to the total yield while $1 - \delta$ is the relative efficiency for H atom production in cage II. Assuming that all the electrons are scavenged from cage I, the cross-section for the formation of cage II is $(\Gamma - \gamma_r^{I})(1 - \delta)$. H atoms are then scavenged according to the ordinary eq. 4. Equation 10 can be transformed into the form

$$\gamma = \Gamma - (\Gamma - \gamma_r{}^I)(1 - \delta)\beta_{II}{}' e^{-(2a_{II}/\beta_{II}{}')\sqrt{\pi k_{H+H^+}[H^+]}} \quad (11)$$

Inserting the numerical data previously obtained[1]

$$\beta_{II}{}' = 1;\ \frac{2a_{II}}{\beta_{II}{}'}\sqrt{\pi k_s} = 2.6\ \text{mole}^{-1/2}\ \text{l.}^{1/2};$$

$$\Gamma = 0.29_3;\ \gamma_r{}^I = 0.08$$

we obtain

$$\gamma = 0.29_3 - \frac{0.21e^{-2.6[H^+]}}{1 + \dfrac{k_{(N_2O+e)}[N_2O]}{k_{(H^+ + e)}[H^+]}} \quad (12)$$

In Fig. 3 the experimental results are compared with the theoretical curve based on eq. 12. Fair agreement was obtained setting the rate constants ratio $k_{H^+ + e}/k_{N_2O + e} = 1\text{–}5$. The best agreement was obtained setting this rate constants ratio to 2, used in Fig. 3. These results are consistent with the comparison of the results for electrons scavenged by H^+ and by N_2O presented in Table II.

In the pH region where competition occurs between scavenging by H^+ and N_2O the quantum yield is expected to depend on N_2O concentration over the whole range employed by us, in contrast to the behavior at neutral pH where at high N_2O concentration the quantum yield is constant. The experimental results entirely confirm this prediction. In Table IV the dependence of $\gamma(I_2)$ on N_2O concentration at $pH < 3$ is presented.

Table IV

The Dependence of $\gamma(I_2)$ on N_2O Concentration at $pH < 3$

P_{N_2O}, mm.	$10^3C_{N_2O}$, mole l.$^{-1}$	$\gamma(I_2)$ expt.	pH	$\gamma(I_2)$ calcd. Eq. 13	$\gamma(I_2)$ calcd. Eq. 12
500	16	0,218	2.2	0.195	0.220
293	9.2	.164	2.2	.165	.184
155	4.9	.132	2.2	.133	.172
285	9.0	.105	1.8	.130	.140

The comparison of the experimental results with the prediction of eq. 12 setting $k_{H^+ + e}/k_{H_2O + e} = 2$ is reasonable. However the calculated values are somewhat too high. We attribute this discrepancy to the approximation involved in the derivation of the consecutive scavenging model.[1] Besides, the application of eq. 12 is based on the assumption that every H atom introduced into the bulk by scavenging by H^+ oxidizes another I^- ion. This may not be applicable for pH 2.2 and 1.8. Therefore we have estimated the dependence of $\gamma(I_2)$ on N_2O concentration by applying our previous experimental results for evacuated solutions.[1,5] The quantum yield was represented in the form

$$\gamma(I_2) = \delta\Gamma + (1 - \delta)s\Gamma \quad (13)$$

where s represents the ratio of the quantum yield at the given pH in evacuated solution to the cross-section Γ. Agreement was obtained by applying eq. 13 at relatively low N_2O concentration.

The decrease of the quantum yield and its dependence on N_2O concentration at $pH < 3$ indicates that H atoms produced at this pH do not act efficiently with N_2O. These results can be interpreted by assuming the conversion of electrons to H atoms. These results cannot be interpreted by the hypothesis of Dainton, *et al.*,[2,3] who assumed conversion of H atoms to H_2^+ molecule ion. If H_2^+ would have been formed in this pH region the quantum yield for I_2 production would remain unchanged, as this species efficiently oxidizes I^- ions.[10]

Discussion

Chemical Evidence for Solvated Electrons in Water.—The photochemical results presented in this work yield chemical evidence for the formation of H atom precursors in water differing in their reactivity from H atoms as such. Recent radiation chemical data point in the same direction.

The fate of electrons, formed in the primary ionization process in the radiolysis of aqueous solutions, has been discussed previously.[11–12] Experimental evidence has recently been accumulating indicating the existence of two different forms of H atoms in irradiated solutions exhibiting different reactivity with specific scavengers. Barr and Allen[13] have shown that H_2O_2 is efficiently decomposed by the reducing species produced by ionizing radiation in neutral solutions, while H_2O_2 is less reactive with the species formed by the reaction

$$H_2 + OH \longrightarrow H + H_2O \quad (14)$$

or by ionizing radiation in acid solution.[13] An investigation of the decomposition of H_2O_2 by atomic hydrogen generated in the gaseous phase[14] indicated the identity of H atoms as such with the "acid form" produced by ionizing radiation and with the species produced by the reaction of OH radical with molecular hydrogen. The results of Allan and Scholes[15] and those obtained by the use of H atoms[14] led to the conclusion that the "neutral form" produced by ionizing radiation is the solvated electron. The result of radiation chemical investigation of aqueous solutions of monochloroacetic acid[16] was similarly interpreted. The relative radiation stability of nitrous oxide in irradiated acid solution[2] was attributed to the acid form of H atoms, which was assumed to be H_2^+.[2] However this conclusion is not consistent with the relative slow rate of formation of H_2^+.[9] The results of Dainton and Peterson[2] can be interpreted[4] in terms of an efficient decomposition of N_2O by solvated electrons and its stability to decomposition by genuine H atoms.

Kinetic evidence in the gas phase indicates that the activation energy for the reaction

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[10] G. Czapski, J. Jortner, and G. Stein, *J. Phys. Chem.*, **64**, 1792 (1960).

[11] (a) A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953); (b) G. Stein, *Discussions Faraday Soc.*, **12**, 243 (1952).

[12] R. L. Platzman and H. Frohlich, *Phys. Rev.*, **92**, 1152 (1953).

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[16] E. Hayon and J. Weiss, *Proc. Int. Conf. Peaceful Uses At. Energy*, **29**, 80 (1958).

$$N_2O + H \longrightarrow N_2 + OH \qquad (15)$$

is 16.6 kcal. mole^{-1},[17] in agreement with an approximate previous estimation.[18] As the frequency factor for this reaction is 4×10^{11} l. mole^{-1} sec.$^{-1}$ [17] this reaction proceeds slowly in the gas phase at room temperature. The analysis[4] of some kinetic data[2] for the reactivity of H atoms in acid solution containing N_2O indicates that reaction 15 in aqueous solution is a relatively slow process, in agreement with the gas phase experiments. Two studies of negative ion formation in N_2O were published recently. The results of electron impact experiments[19] indicate that O^- ions are produced in N_2O with an onset at zero electron energy. The results of a mass spectrometric investigation[20] confirm these conclusions. These results indicate that in the gaseous phase the reaction

$$N_2O + e \longrightarrow N_2 + O^- \qquad (16)$$

proceeds efficiently. In the liquid phase the O^- ion will be stabilized by solvation. This independent evidence yields further support to our conclusions regarding N_2O as specific scavenger for electrons in aqueous solutions. The rate constants ratio $k_{H^+ + e}/k_{N_2O + e} = 2\text{–}5$ obtained from our photochemical experiments appears to be consistent with the radiation chemical results of Dainton and Peterson.[2]

In the present photochemical investigation we tried to select various specific scavengers for the discrimination between H atoms as such and their precursors. H^+ ion was found to act as an efficient scavenger for H atom precursors, *i.e.*, solvated electrons. The reaction

$$H^+_{aq} + e_{aq} \longrightarrow H \qquad (17)$$

appears to be efficient, in agreement with recent radiation chemical data.[15,16,21] This may proceed by direct electron capture by the hydroxonium ion, or by a general acid-catalyzed mechanism

$$H_3O^+ + H_2O + e_{aq} \longrightarrow H_2O + H_2O + H \qquad (17')$$

The increase of the quantum yield in the presence of the monophosphate ion at pH 5.9[1] may indicate the operation of such a mechanism. However at present this suggestion should be considered as tentative.

The nature of the solvated electrons formed in the photochemical system should be briefly considered. The most probable model involves an electron bound in the polarization field of the dielectric medium.[22-24] The time required for the solvation process of the electron is of the order of the relaxation time of the solvent molecules. A similar model is applicable for the thermalized electrons produced by ionizing radiation in water.[11b,24] The lifetime of this species is long enough in aqueous solutions to make its detection possible by reaction with specific active scavengers.

Mechanism of Primary Radical Formation.—The photochemical results presented in this work can be unambiguously interpreted by assuming the operation of a cage mechanism, and the decrease of the quantum yield with decreasing scavenger concentration should be assigned to secondary recombinations. The independence of the quantum yield on light intensity definitely rules out any bulk recombination mechanism. In our previous work[5] we have pointed out that the alternative mechanism involving the interaction of H^+ ion with the excited state followed by electron scavenging with direct formation of H atoms is not favored by the experimental data. At high scavenger concentration a limiting quantum yield of 0.290 ± 0.005 at 25° is obtained independent of the nature of the scavenger.

The absolute value of this limiting quantum yield probably is accurate within 10%, as it was determined by chemical actinometry using independently uranyl and ferrous oxalate actinometers. This result indicates that under our experimental conditions the limiting quantum yield of radicals which can be scavenged at 25° is about 33%. Thus the cross-section for primary radical formation is smaller than unity. This result rules out the direct interaction of the scavenger with the spectroscopic excited state of the ion, indicating that the fragments which can be scavenged are formed by a secondary process.

The photochemical results can be correlated with the spectroscopic data for this system. Recent experimental and theoretical investigations[25-27] indicate that the excited state can adequately be described by a spherical symmetrical excited orbital involving a considerable charge expansion. The role of the hydration configuration in formation of this excited state has been repeatedly stressed.[25,27] The upper limit for the lifetime of the first spectroscopic excited state is the relaxation time of the solvent molecules. During the relaxation process the electron is detached from the excited state of the absorption center resulting in the formation of two distinct species: an I atom and a solvated electron.

The detachment of the electron competes with deactivation of the excited state, which probably proceeds by a radiationless transition to the ground state. The cross-section for radical formation should be dependent on temperature and on the solvent. Our results on these problems will be published separately.

The electron thus formed by the dissociation of the excited state can be scavenged by specific scavengers, *e.g.*, H^+, N_2O, and O_2. This mechanism yields the major contribution to radical production. The present picture indicates that the major pathway of H atom production in this photochemical system does *not* involve a dissociative electron capture by a water molecule but electron capture by H^+. The scavenging

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experiments definitely rule out the mechanism of Franck and Haber[28] for this system.

The results with N_2O prove also that the role of the positive H^+ ion is not unique and that another, neutral electron scavenger can lead to a similar process.

The present picture involves a thermal electron detachment process from the excited state of the solvated negative ion, leading to the formation of a solvated electron in the aqueous solution. The formation of a thermalized electron is plausible in the case of an excited iodide ion, where the electron in the expanded orbital is acted upon only by the polarization field of the medium.

Franck and Scheibe[29] in their original work postulated a photodetachment process as the primary light absorbtion act of negative ions in solution. Our results show that this occurs only as the result of a secondary thermal process.

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THE EFFECT OF OXYGEN ON THE PHOTOCHEMISTRY OF THE IODIDE ION IN AQUEOUS SOLUTIONS

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The effect of O_2 on the photochemistry of aqueous iodide solutions was investigated. O_2 was found to act as a scavenger for both electrons and H atoms. The reaction mechanisms are discussed and kinetic data for the reaction of O_2 with electrons and H atoms are derived. The photochemical results are compared with data from radiation chemistry.

Introduction

Radiation chemical investigations[1] indicate that oxygen dissolved in aqueous solutions acts as an efficient scavenger for both solvated electrons and for H atoms.[1]

Following the preceding work,[2] the effect of O_2 on the photochemistry of the iodide ion was investigated. The investigation of the oxygen effect on this system is of importance for a further insight into the specific scavenging mechanisms of H atoms and their precursors.

Experimental

The experimental technique was similar to that previously employed.[2] Evacuated neutral potassium iodide solutions were equilibrated with air or oxygen for 2–3 hr. The pH was adjusted by acid added just before irradiation, which was carried out as fast as possible to avoid thermal oxidation. The kinetics of the post-irradiation effect in aerated solution were measured by the determination of the time dependence of the I_2 concentration in the reaction vessel after stopping the irradiation. The thermal oxidation was followed by a similar technique.

Results

Some experimental difficulties were encountered in the experimental investigation of this system at low pH. The effect of the thermal oxidation of I^- at pH < 2.5 is appreciable. Short irradiation times (15 sec.) were used, and corrections for thermal oxidation were introduced. The derivation of the experimental results for the initial quantum yields was further complicated by the observation of a post-irradiation effect in aerated solutions. It was assumed that this effect is due to the production of H_2O_2 in irradiated solutions. To confirm this hypothesis a kinetic study of this process was carried out. We measured the dependence of the I_2 concentration (determined as the optical density D_τ) on the time τ after stopping the irradiation. First-order kinetic curves were obtained by plotting ln $(D_\infty - D_\tau)$ as a function of τ (Fig. 1). The experimental values of D_τ were corrected for thermal oxidation. From the first-order rate constants k the second-order rate constants $k/[I^-]$ were obtained, in agreement with the result for thermal oxidation of I^- by H_2O_2.[3] These results indicate that H_2O_2 is produced in the photochemical system.

Table I

Post-Irradiation Effect in Irradiated KI Solutions

$[I^-] = 0.15\ M$, $J = 15 \times 10^{-7}$ einstein sec.$^{-1}$ l.$^{-1}$

pH	k, min.$^{-1}$	$k/[I^-]$, l. mole^{-1} min.$^{-1}$	D_0	D_∞
1.29	0.048	0.75	0.265 ± 0.02	0.48 ± 0.03
0.83	0.22	3.37	0.26 ± 0.02	0.50 ± 0.03

As the thermal oxidation of I^- by H_2O_2 during the short irradiation period is negligible, the initial $[I_2]_0$ concentration corrected for the post-irradiation effect was obtained from extrapolation of log $(D_\infty - D_\tau)$ to $\tau = 0$. We find (Table I) $2D_0 = D_\infty$, *i.e.*, $2[I_2]_0 = [I_2]_\infty$. Thus the quantum yield for H_2O_2 production is equal to that of I_2 during irradiation. The quantum yield at low pH could be evaluated by measuring $\gamma(I_2) + \gamma(H_2O_2)$. This was done by determination of I_2 yield after the completion of the post-irradiation effect about 60 min. after stopping the irradiation.

Dependence of γ on pH and O_2 Concentration—In Fig. 2 and 3 we represent the dependence of the initial quantum yield for I_2 production on pH and O_2 concentration. These quantum yields were corrected for thermal oxidation and do not include contribution of the oxidation by H_2O_2. γ_i at

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