AIP | The Journal of Chemical Physics

# Photolysis of Liquid Water at 1849 Å

Uriel Sokolov and Gabriel Stein

Citation: The Journal of Chemical Physics **44**, 3329 (1966); doi: 10.1063/1.1727233
View online: http://dx.doi.org/10.1063/1.1727233
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/44/9?ver=pdfcov
Published by the AIP Publishing

---

---

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 44, NUMBER 9 1 MAY 1966

# Photolysis of Liquid Water at 1849 Å

URIEL SOKOLOV AND GABRIEL STEIN*
*Department of Physical Chemistry, Hebrew University, Jerusalem, Israel*

(Received 9 December 1965)

The photolysis of pure water and of aqueous solutions of alcohols (methanol, ethanol, and isopropanol) at 1849 Å, when the light is absorbed by the water, proceeds according to

$$\begin{tikzcd} \mathrm{HOH}+h\nu \arrow[r, shift left] & (\mathrm{HOH})^* \arrow[l, shift left] \arrow[r] & (\mathrm{H}+\mathrm{OH}) \arrow[ll, bend left] \end{tikzcd}$$

$$(\mathrm{H}+\mathrm{OH})+\mathrm{RH}_2\rightarrow\mathrm{H}+\mathrm{H}_2\mathrm{O}+\cdot\mathrm{RH}.$$

The quantum yield for the formation of the geminate pair (H+OH) is $\phi=0.45$ at room temperature. Scavengers compete with the recombination of the geminate pair according to diffusive inhomogeneous kinetics. A value of $3.9\times10^{-6}$ sec$^{½}$ is obtained for the Noyes parameter $a$, in agreement with theory. The results exclude direct interaction between scavenger and excited water molecules and also exclude molecular processes in the formation of $H_2$. Solvated-electron formation has a quantum yield of $\leqslant 0.045$. Isotope experiments support the conclusions.

In the reaction with the alcohols, that of the OH radicals determines the competition with secondary geminate recombination. From the results a value of $k(\mathrm{dim})/k(\mathrm{dis})=6.6$ is obtained for the ratio of dimerization to disproportionation of $CH_2OH$ radicals.

THE photolysis of aqueous solutions above and below 2000 Å, where light is absorbed by the solutes, has been the subject of numerous investigations; the photolysis of liquid water itself, below 2000 Å, of very few. More data are available on the photolysis of water vapor where there is general agreement that the primary act following absorption in the first absorption band is

$$H_2O\xrightarrow{h\nu}H+OH, \tag{1}$$

with both radicals formed in their ground state.[1–3] As to the photolysis in the second absorption band there is evidence[4] that about 25% of the primary act is

$$H_2O\xrightarrow{h\nu}H_2+O. \tag{2}$$

Fricke and Hart[5] were the first to study the photolysis of liquid water in a work on the photochemistry and radiation chemistry of aqueous solution of methanol. They observed that in both cases the yield was independent of the radiation intensity. In this early work excited water molecules were assumed the active intermediates in both photo- and radiolysis. Weeks and Matheson[6] briefly mention that dilute aqueous solutions of formic acid behave similarly when irradiated by far-uv or x rays. They interpret the mechanism involving radical intermediates.

The only detailed investigation of the photolysis of liquid water (to exclude flash photolysis) is that of Barrett and Baxendale[7] who irradiated aqueous solutions of methanol and ethylacetate at 1849 Å. They explain their results according to the primary act (1) as do later workers on the flash photolysis of aqueous solutions.[8–10] The kinetics of the photochemical process was not studied. Other possible primary acts were not excluded.

We reinvestigated the photolysis of liquid water to study the kinetics of the radicals and to explore the possibilities of (a) molecular mechanism, (b) reaction of excited water molecules with the scavengers, and (c) the formation of electrons from the excited water molecule.

The complete purification of water is notoriously difficult, therefore most of the work was in the presence of radical scavengers. However, some experiments on the photolysis of highly pure water are described and correlated with those in the presence of scavengers.

## EXPERIMENTAL

### Materials

Pure water was prepared as follows: triple-distilled water was irradiated with x rays followed by irradiation with a low-pressure mercury lamp through a 0.1*M*

---

* Present address: Chemistry Department, Boston University, Boston, Mass.

[1] A. Y. M. Ung and R. A. Back, Can. J. Chem. **42**, 753 (1964); D. H. Volman, Advan. Photochem. **1**, 43 (1963).

[2] E. P. Del Greco and F. Kaufman, Discussions Faraday Soc. **33**, 128 (1962).

[3] L. F. Phillips and H. I. Schiff, J. Chem. Phys. **37**, 1233 (1962).

[4] J. R. McNesby, I. Tanaka, and H. Okabe, J. Chem. Phys. **36**, 605 (1962).

[5] H. Fricke and E. J. Hart, J. Chem. Phys. **4**, 418 (1936).

[6] J. L. Weeks and M. S. Matheson (unpublished) cited by M. S. Matheson, Proc. U.N. Intern. Conf. Peaceful Uses At. Energy 2nd Geneva, 1958 **29**, 385 (1958).

[7] J. Barrett and J. H. Baxendale, Trans. Faraday Soc. **56**, 37 (1960).

[8] J. H. Baxendale and A. L. Mansell, Nature **190**, 622 (1961).

[9] J. H. Baxendale, Radiation Res. **17**, 312 (1962).

[10] J. K. Thomas and E. J. Hart, J. Phys. Chem. **68**, 2414 (1964).

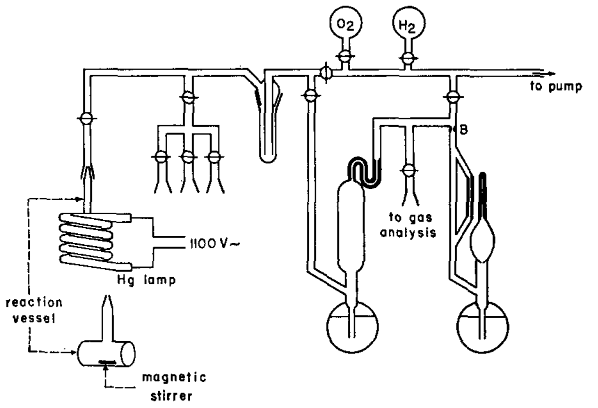

FIG. 1. The vacuum system and irradiation arrangements with spiral lamp.

NaCl filter to decompose the $H_2O_2$ formed. The alcohols used were of Analar grade.

### Analysis

The gas evolved was analyzed by a method based on the selective absorption on silica gel at liquid-air temperature.[11] $H_2O_2$ was determined spectrophotometrically,[12] formaldehyde by chromotropic acid,[13] and ethylene glycol by periodic acid.[14]

### Actinometry

The light intensity was determined[15] through the measurement of the hydrogen evolved from de-aerated 5*M* aqueous ethanol. The value for the quantum yield given by Farkas and Hirshberg[15] is erroneous, since they neglected absorption by the pure water. In the present work, a corrected[16] value of $\phi=0.63$ was used. From the present work an identical value may be derived, supporting this recent suggestion.[16]

### Irradiation Arrangements

The light sources were low-pressure mercury lamps actuated by 1100 Vac. The work at the highest light intensities was done with a 5-turn spiral lamp with an inner diameter of 7 cm manufactured by Thermal Syndicate Ltd., as were all reaction vessels and other lamps. The reaction vessel was a cylinder made of high-transmittance silica, 4.5-cm diameter and 5-cm length, positioned in the center of the lamp (Fig. 1). Attempts to produce different light intensities by changing the current through the lamp did not yield reproducible results, therefore the experiments with different light intensities were carried out using a different lamp and changing the distance between the lamp and the reaction vessel (Fig. 2). A flat spiral lamp (2.5-cm diam) was positioned on an optical bench. The reaction vessel, a cylinder with a diameter of 2 cm and 10-cm length connected to a sapphire window through a sapphire–Pyrex graded seal, was mounted on the slides. Its distance from the lamp could thus be changed reproducibly. The advantage of a sapphire window is its high transmittance of the 1849-Å wavelength relative to silica.

Using the full light of the lamps, the light intensity in the cylindrical spiral lamp was $4.6\times10^{-8}$ einstein $sec^{-1}$ absorbed in the vessel which contained 50 ml of solution, while with the flat spiral lamp it was varied from $25.2\times10^{-10}$ einstein $sec^{-1}$ to $2.22\times10^{-10}$ einstein $sec^{-1}$ absorbed in the vessel which contained 35 ml of solution.

The low-pressure mercury lamps emit 90% of the uv light at 2537 Å, and about 10% at 1849 Å. To ascertain whether the 2537-Å line influences the results, we repeated some experiments with monochromatic light of 1849 Å, filtering out the 2537-Å line with the help of an LiF disk irradiated with $\gamma$ rays.[17] This absorbs all of the 2537 Å and transmits about 50% at 1849 Å.

### Procedure

The solutions were degassed by short openings to the vacuum line through a liquid-air-cooled trap. The gases produced were collected for analysis by a Töpler pump into a McLeod gauge equipped with a silica-gel cold finger. In the experiments with $N_2O$ (which was purified by bulb-to-bulb distillation) the gas was equilibrated with the solution for 5 h. After the irradiation, the gas evolved was trapped in a liquid-air cold trap. Then the trap was warmed to room temperature, the water vapor trapped by cooling with $CO_2$/acetone mixture, and only then the $N_2O$ was retrapped by replacing the $CO_2$/acetone trap by a liquid-air trap. The reason for this somewhat complicated procedure is

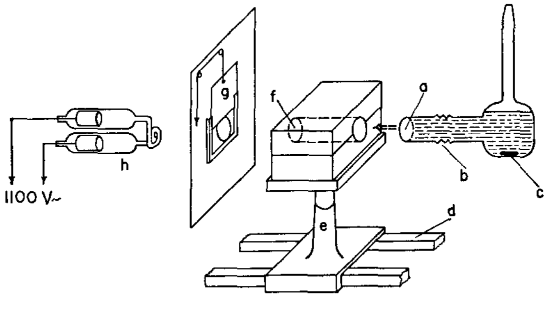

FIG. 2. Irradiation arrangement with variable light intensity.

---

[11] U. Sokolov and G. Stein, Anal. Chem. **36**, 1882 (1964).

[12] C. J. Hochanadel, J. Phys. Chem. **56**, 587 (1952).

[13] C. E. Bricker and H. R. Johnson, Ind. Eng. Chem. (Anal. Ed.) **17**, 400 (1945).

[14] E. Adams and J. H. Baxendale, J. Am. Chem. Soc. **80**, 4215 (1954).

[15] L. Farkas and Y. Hirshberg, J. Am. Chem. Soc. **59**, 2450 (1937).

[16] J. Hagege and C. Vermeil, J. Chim. Phys. **62**, 403 (1965); A. Bernas, M. Bodard, and D. Sagghattchian, *ibid.*, p. 1418.

[17] R. Kato, S. Nakushima, K. Nakamura, and Y. Uchida, J. Phys. Soc. Japan **15**, 2111 (1960).

that[18] when a mixture of nitrogen and water vapor is quickly cooled to liquid-air temperature some of the nitrogen is trapped with the ice.

## RESULTS

### Photochemistry in the Presence of Aliphatic Alcohols

Alcohols, $RH_2$, react with OH radicals according to

$$RH_2+OH \rightarrow RH+H_2O \quad (3)$$

and with H atoms according to

$$RH_2+H \rightarrow RH+H_2, \quad (4)$$

thus yielding molecular hydrogen. The radicals RH may then dimerize or disproportionate.

### Experiments in the Presence of Methanol

The quantum yield for the formation of hydrogen was measured as a function of dose and light intensity in the concentration range of $10^{-6}$ to $10^{-1}M$. The dependence on $p$H is discussed separately. The oxidation products were determined for three different concentrations of the methanol: $10^{-4}$, $10^{-3}$, and $10^{-2}M$.

The dependence of the quantum yield of hydrogen—the only gas produced—on the dose is given in Fig. 3. The yield decreases with increasing dose. Calculation showed that if the only reason for the decrease with the dose were the decrease in alcohol concentration, the effect should have been much greater. We conclude that the oxidation products are also efficient scavengers for H atoms. Comparison of the appropriate rate constants supports this conclusion. The results of the analysis of the products at three different concentrations of methanol are shown in Table I. The results are in good agreement with previous work[7] and give a reasonable material balance. As can be seen at the higher concentration of the alcohol the percentage of the formaldehyde is somewhat higher. The reason for this is probably that at this concentration there is some little direct light absorption by the alcohol, and it is known[15] that photolysis of methanol in aqueous solutions produces formaldehyde.

TABLE I. Analysis of irradiated methanol solutions.

| Methanol concentration ($M$) | $H_2$ ($\mu$M) | $H_2CO$ ($\mu$M) | $(H_2COH)_2$ ($\mu$M) |
|---|---|---|---|
| $10^{-2}$ | 3.82 | 0.65 | 3.10 |
| $10^{-3}$ | 4.21 | 0.51 | 3.60 |
| $10^{-4}$ | 3.22 | 0.42 | 2.60 |

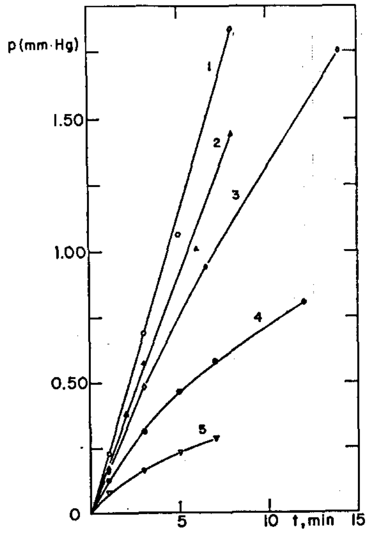

FIG. 3. Dependence of hydrogen yield on dose in methanol solutions. (1) $5M$ (actinometer), (2) $10^{-1}M$, (3) $10^{-2}M$, (4) $10^{-3}M$, (5) $10^{-4}M$.

The results in Table I enable us to calculate the ratio of the rate constants of the dimerization and disproportionation of $CH_2OH$ radicals,

$$k(\text{dim})/k(\text{dis})=6.6.$$

$H_2O_2$ could not be detected. To check the possibility that $H_2O_2$ may be produced by a molecular process, but is then destroyed by the 2537-Å radiation, a solution of $10^{-3}M$ methanol and $10^{-5}M$ $H_2O_2$ was irradiated for 5 min with the full light of the lamp, after which no $H_2O_2$ could be detected. When similar methanol solutions are irradiated with ionizing radiations[19] $H_2O_2$ is formed but it is not attacked. We then repeated the experiments with an irradiated LiF filter[17] which transmits about half of the intensity of 1849 Å and filters out completely the 2537-Å line. No $H_2O_2$ was produced. However, $H_2O_2$ introduced initially could be partially recovered after 5-min irradiation. The conclusion is, therefore, that there is no molecular yield of $H_2O_2$. The reduction in hydrogen yield in these experiments was equal to the reduction in the light intensity of 1849 Å. Using unfiltered light, and increasing the light intensity by a factor of 200, the initial quantum yield of hydrogen remained the same. The initial quantum yields of hydrogen at the various methanol concentrations are summarized in Table II.

These results cannot be interpreted by homogeneous reaction kinetics, in which scavengers would react with the excited state of the water molecule or would react with radicals homogeneously distributed through the solution. They are shown to agree quantitatively with inhomogeneous scavenger kinetics, in which scavengers compete with the recombination of geminate radical pairs,[20] for example (H+OH) produced by dissociation of the excited water molecule.

Such inhomogeneous distribution of radicals, and thus inhomogeneous kinetics, was demonstrated, e.g., in the photolysis of aqueous solutions of iodide ions

---

[18] M. Ottolenghi, Ph.D. thesis, Jerusalem, 1963.

[19] G. Scholes (unpublished results).

[20] R. M. Noyes, Progr. Reaction Kinetics **1**, 131 (1961); J. Am. Chem. Soc. **80**, 4529 (1964).

TABLE II. Dependence of initial quantum yield of hydrogen on methanol concentration.

| Methanol ($M$) | $1\times10^{-6}$ | $5\times10^{-6}$ | $1\times10^{-5}$ | $5\times10^{-5}$ | $1\times10^{-4}$ | $5\times10^{-4}$ | $1\times10^{-3}$ | $5\times10^{-3}$ | $1\times10^{-2}$ | $1\times10^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $\phi$ H$_2$ | 0.11 | 0.13 | 0.14 | 0.19 | 0.25 | 0.30 | 0.37 | 0.47 | 0.49 | 0.54 |

where the pair $(\mathrm{I}+e_{aq}^{-})$[21,22] is formed. In our case, we consider the behavior of the pair of radicals (H+OH).

According to Noyes,[20] such kinetics are characterized by obeying the scavenging equation

$$\phi=\phi r+\Phi 2a(\pi k_S[\mathrm{S}])^{\frac{1}{2}},$$

where $\phi$ is the experimental quantum yield, $\Phi$ the limiting quantum yield, i.e., the quantum yield at high scavenger concentration when geminate recombination is totally suppressed, $k_S$ the rate constant for the scavenging, [S] the concentration of the scavenger, and $\phi r$ the residual yield at vanishing scavenger concentration given by $\phi r=\Phi(1-\beta')$. $a$ and $\beta'$ are parameters characterizing the photochemical properties of the geminate-pair formation.[20–22] This equation is valid only over a limited range of low concentrations. Jortner, Ottolenghi, and Stein[21] developed an extended equation valid for a wider range of concentrations,

$$\ln[1-(\phi/\Phi)]=\ln[1-(\phi r/\Phi)]-(2a/\beta')(\pi k_S[\mathrm{S}])^{\frac{1}{2}}.$$

Another characteristic of such kinetics is that the quantum yield of the scavenging reaction is independent of the light intensity.[21,22] Agreement with the scavenging equation, independence of the quantum yield of the light intensity, and, finally, direct chemical evidence are our criteria in concluding whether or not the photolysis of water at 1849 Å obeys inhomogeneous diffusion-controlled scavenger kinetics.

The results of Table II are plotted in Fig. 4 according to the Noyes equation. The plot is linear in the lower concentration range as required. For analysis in terms of the extended scavenging equation the value of $\Phi$ is required, taking into account the fact that as the concentration of the methanol increases, direct absorption of light will occur resulting in H$_2$ formation. The limiting quantum yield $\Phi$ from water was calculated from the equation $\phi\mathrm{H}_2=\phi_m\alpha+(1-\alpha)\Phi$, where $\alpha$ is the fraction of light absorbed by methanol molecules and $\phi_m$ the quantum yield of H$_2$ in this process.

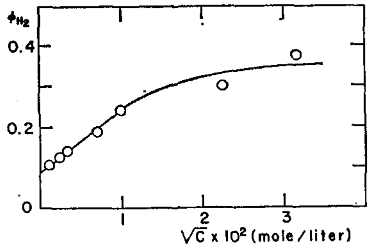

FIG. 4. Photolysis of methanol solutions, Noyes plot.

This is based on the assumption that $\phi_m$ is independent of the alcohol concentration, which is correct for the case of methanol. The use of $\Phi$ is justified since we applied the equation only in the range where the concentration of the alcohol is high enough to eliminate completely any geminate recombination. As can be seen in Fig. 5 the results indeed obey the extended scavenging equation over a wider range of concentrations.

The fact that the results obey the scavenging equations and that the quantum yield is independent of the light intensity prove that the initial geometrical distribution of the radicals in the solution is inhomogeneous, and we can describe the reaction scheme as follows[23–26]:

$$\mathrm{H_2O}\overset{h\nu}{\rightleftharpoons}(\mathrm{H_2O})^{*}\rightarrow(\mathrm{H}+\mathrm{OH}),\qquad\text{(a)}$$

$$(\mathrm{H}+\mathrm{OH})\rightarrow\mathrm{H_2O},\qquad\text{(b)}$$

$$(\mathrm{H}+\mathrm{OH})+\mathrm{CH_3OH}\rightarrow\mathrm{CH_2OH}+\mathrm{H_2O}+\mathrm{H},\qquad\text{(c)}$$

$$\mathrm{CH_3OH}+\mathrm{H}\rightarrow\mathrm{CH_2OH}+\mathrm{H_2},\qquad\text{(d)}$$

$$\mathrm{CH_3OH}+\mathrm{OH}\rightarrow\mathrm{CH_2OH}+\mathrm{H_2O},\qquad\text{(e)}$$

$$2\,\mathrm{CH_2OH}\rightarrow\mathrm{CH_2O}+\mathrm{CH_3OH},\qquad\text{(f)}$$
$$\phantom{2\,\mathrm{CH_2OH}}\rightarrow(\mathrm{CH_2OH})_2$$

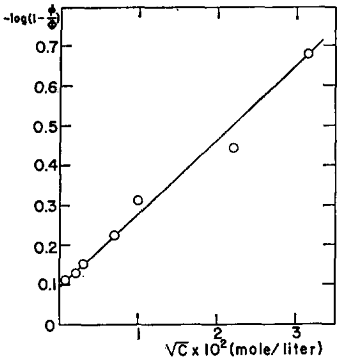

FIG. 5. Photolysis of methanol solutions, extended equation plot.

---

[21] J. Jortner, M. Ottolenghi, and G. Stein, J. Phys. Chem. **66,** 2029, 2037, 2042 (1962).

[22] G. Stein, Advan. Chem. **50,** 230 (1965); and (to be published).

[23] E. J. Hart, J. K. Thomas, and S. Gordon, Radiation Res. Suppl. **4,** 74 (1964).

[24] M. Anbar and D. Meierstein (unpublished results).

[25] J. H. Merz and W. A. Waters, J. Chem. Soc. Suppl. **1949,** S-15.

[26] C. Lifshitz and G. Stein, J. Chem. Soc. **1962,** 3706.

TABLE III. Dependence of initial quantum yield of hydrogen on ethanol concentration.

| Ethanol ($M$) | $1\times10^{-6}$ | $5\times10^{-6}$ | $1\times10^{-5}$ | $5\times10^{-5}$ | $1\times10^{-4}$ | $1\times10^{-3}$ |
|---|---|---|---|---|---|---|
| $\phi H_2$ | 0.10 | 0.11 | 0.13 | 0.19 | 0.24 | 0.37 |

The results for aqueous solutions of ethanol were similar to those in methanol solutions and are shown in Figs. 6 and 7. The quantum yield of hydrogen formation was independent of the light intensity over a tenfold change. The initial quantum yields for the hydrogen formation are summarized in Table III.

In the case of isopropanol solutions, results were again similar except at relatively high concentrations of the alcohol. Here the initial quantum yield for the formation of hydrogen did not continue to increase, but reaches a maximum then a minimum after which the yield increases rapidly at very high concentrations up to pure isopropanol (Fig. 8). The difference in behavior is probably due to a difference in the mechanism of the direct photolysis of the different alcohols in aqueous solution.

For comparison with the alcohol solutions we analyzed, in the terms of the scavenging equation, the results[7] of Barrett and Baxendale on the photolysis of dilute aqueous solutions of ethylacetate. The parameters calculated for all the scavengers are summarized in Table IV.

The fact that in all the systems studied, $\Phi$, the value of the limiting quantum yield approached at high scavenger concentration, is less than unity rules out the possibility of a direct reaction of the scavenger with the excited water molecule. The agreement with the scavenging equation, and the fact that the quantum yield is independent of the light intensity, prove that the radicals formed are not distributed homogeneously but are formed in pairs (direct chemical evidence for this fact is given later). Now, if this is true, then the kinetic parameters should be independent of the specific scavenger and this is indeed the case both for $\beta'$ and $\Phi$ (Table IV). The parameter $a$ is obtained in the form of $a(\pi k_s)^{\frac{1}{2}}$, containing the specific rate constant $k_s$. We note that there is a difference of about 30% in the values of $a(\pi k_s)^{\frac{1}{2}}$ derived from the Noyes equation and the extended scavenging equation, respectively. This difference is the same as in the case of the photolysis of iodide solution[21] and originates in the different mathematical approximations used to derive these equations. If $a$, as Noyes predicts, is independent of the scavenger, then the ratio of the parameters $a(\pi k_s)^{\frac{1}{2}}$ obtained with different scavengers should give the correct ratio of the rate constants.

The results in Table V show that the present results for $k_s$ agree fairly well with those derived from other systems, taking the value for methanol as the basis of comparison. Thus $a$ is independent of the scavenger, and is a specific parameter of the photochemical (H+OH) pair formation. We conclude that the rate-determining step is indeed the competition between geminate recombination and the scavenging of OH radicals. Finally $a$, which is independent of scavenger, has the value of $3.9\times10^{-6}$ sec$^{\frac{1}{2}}$, in agreement with the value predicted theoretically by Noyes.[20]

Until now experimental information on this parameter was not available. In the cases involving photochemical $e_{aq}^-$ formation, the value of $a$ is higher.[22]

## Irradiations of Ethanol Solutions in Heavy Water

Ethanol solutions in heavy water were irradiated and the isotopic composition of the gas produced was determined. Typical results are given in Table VI. In all these experiments, the fraction of light absorbed by the alcohol was negligible. The reactivity of the hydroxylic hydrogen in the abstraction reaction is small. It is seen that the formation of $D_2$ is very small. Thus there is no appreciable molecular yield, since if hydrogen would have been produced by a nonradical mechanism, $D_2$ should have been formed. The small amount of $D_2$ found is probably due to the attack on the OD group. If not, it gives an upper limit of 0.005 for the molecular yield.

That almost no $D_2$ is produced proves also that radicals are inhomogeneously distributed throughout the solution. Namely, if the distribution were homo-

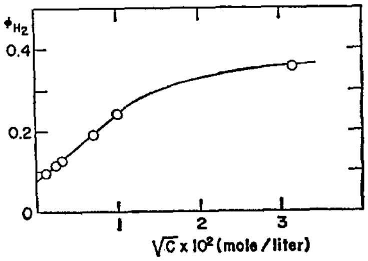

FIG. 6. Photolysis of ethanol solutions, Noyes plot.

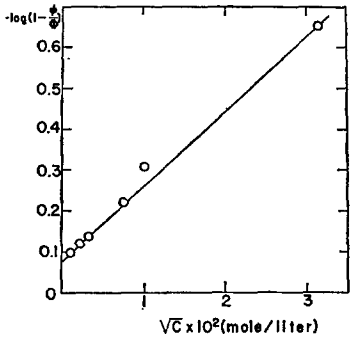

FIG. 7. Photolysis of ethanol solutions, extended equation plot.

TABLE IV. Parameters for the photochemical pair formation (H+OH).

| Scavenger | Noyes' equation $\Phi$ | $\phi r$ | $\beta'$ | $2a(\pi k_S)^{\frac{1}{2}}$ | Extended equation $\phi r$ | $\beta'$ | $2a(\pi k_S)^{\frac{1}{2}}$ |
|---|---|---|---|---|---|---|---|
| Methanol | 0.47 | 0.09 | 0.91 | 0.33 | 0.09 | 0.91 | 0.47 |
| Ethanol | ··· | 0.08 | 0.92 | 0.36 | 0.08 | 0.92 | 0.46 |
| Isopropanol | 0.44 | 0.08 | 0.92 | 0.31 | 0.09 | 0.92 | 0.39 |
| Ethylacetate | 0.45 | 0.06 | 0.94 | 0.10 | ··· | ··· | ··· |
| Mean value | 0.46 | 0.08 | 0.92 | | 0.09 | 0.92 | |

geneous, the following reactions would have taken place in the bulk:

$$D+OD \rightarrow D_2O, \qquad (A)$$

$$D+D \rightarrow D_2, \qquad (B)$$

$$OD+OD \rightarrow D_2O_2, \qquad (C)$$

$$RH_2+D \rightarrow RH+HD, \qquad (D)$$

$$RH_2+OD \rightarrow RH+HOD. \qquad (E)$$

The concentration of the alcohol in these experiments is below that required for total scavenging of the radicals. If homogeneous distribution prevailed, not only would $D_2$ be produced, but the ratio of $D_2/HD$ would have been dependent on the alcohol concentration because of the competition between Reactions (B) and (D). This is not the case; rather, the results indicate the prevalence of (A) as the chief radical-recombination process. This provides chemical evidence in favor of the inhomogeneous distribution. This argument is valid since $k_A \cong k_B \cong k_C$. If $k_A \gg k_B \cong k_C$, no $D_2$ could have been produced in any case.

The apparent separation factors $S'$ in the table are calculated from the expression $S' = (D/H)_l/(HD/H_2)_g$. They are not the true factors because of the different absorption coefficients of $D_2O$ and HDO at 1849 Å. (The concentration of $H_2O$ under these conditions is negligible.[27]) If there were no isotopic effect in the quantum yields and in the decomposition of HDO, the isotopic composition of the gas would be given by

$$HD/H_2 = (\alpha_{D_2O} + \tfrac{1}{2}\alpha_{HDO})/\tfrac{1}{2}\alpha_{HDO},$$

where $\alpha_{D_2O}$ is the fraction of light absorbed by $D_2O$, and $\alpha_{HDO}$ that absorbed by HDO. The true isotopic separation factors are therefore given by[28]

$$S'' = \frac{\{[(\alpha_{D_2O} + \tfrac{1}{2}\alpha_{HDO})/\tfrac{1}{2}\alpha_{HDO}](HD/H_2)_g\}}{S'},$$

where $S'$ are the values in the table.

The following factors are contributing to the isotopic separation factors: (a) The isotope effect in the decomposition of HDO into radicals. At this energy most probably H+OD are the main products. (b) The smaller initial separation of D+OD than that of H+OD. This difference is due to the higher bond energy of O–D than of OH resulting in less kinetic energy, ($h\nu -$bond energy). (c) The higher diffusion coefficient of H relative to D. As a result, D is less likely to escape geminate to recombination.

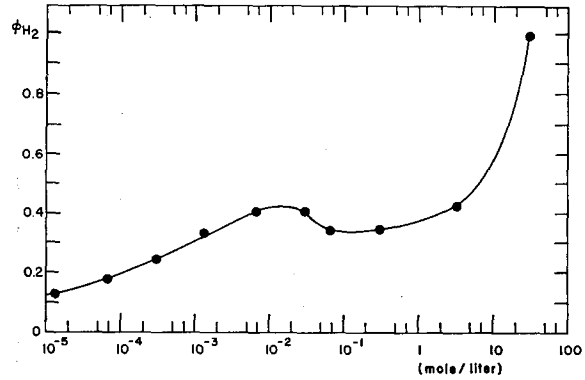

FIG. 8. Photolysis of isopropanol solutions. Dependence of initial $H_2$ yield on concentration.

## Are Solvated Electrons Formed in the Photochemical Reaction?

The formation of solvated electrons was proved lately in the case of solution of anions.[21,29] The electrons were identified kinetically by the use of scavengers and by their absorption spectrum. Matheson[30] deduces from the fact that the quantum yield for the formation of hydrogen is roughly the same in the photolysis of aqueous methanol solution and in the case of the pho-

TABLE V. Rate constants of OH radicals with scavengers, calculated relative to methanol.

| Scavenger | $k_S$ (mole$^{-1}\cdot$sec$^{-1}$) | Ref. | Values calculated from present work |
|---|---|---|---|
| Methanol | $1.8\times10^9$ | 23 | $1.8\times10^9$ |
| Ethanol | $3.0\times10^9$ | 24[a] | $1.9\times10^9$ |
| Isopropanol | $9.0\times10^8$ | 23 | $1.5\times10^9$ |
| Ethylacetate | $3.5\times10^8$ | 25[a] | $1.6\times10^8$ |

[a] Values obtained at acid *p*H.

---

[27] C. Urey, J. Chem. Soc. **1947**, 562.

[28] H. Basseches, Ph.D. thesis, Ohio State University, 1951.

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

[30] M. S. Matheson, Radiation Res. Suppl. **4**, 12 (1964).

TABLE VI. Photolysis of $CH_3CH_2OH$ in $D_2O$.[a]

| Ethanol ($M$) | Time of irrad. (min) | %D in solution | % Composition of gas | | | Separation factors | |
|---|---|---|---|---|---|---|---|
| | | | $H_2$ | HD | $D_2$ | $S'$ | $S''$ |
| $0.8\times10^{-3}$ | 30 | 92 | 41.5 | 57.5 | 2 | 12 | 6.3 |
| $1.6\times10^{-3}$ | 30 | 98 | 21.5 | 77.5 | 1 | 14 | 4.4 |

[a] High-intensity spiral lamp used.

tolysis of formic acid solution that the main reducing species in the photolysis of water are hydrogen atoms. Actually, the difference in the quantum yields is about 25% thus setting an upper limit of 25% for the formation of electrons. But owing to uncertainty in the actinometry, these figures are not reliable enough for a firm conclusion to be reached.

In their study of the flash photolysis of aqueous solutions, Matheson, Mulac, and Rabani,[29] deduce that electrons are produced from water since they observed a weak absorption band of $e_{aq}^-$ which disappeared when $O_2$, an electron scavenger, was added. However, they irradiated $0.2M$ methanol solutions and not pure water. At this concentration, the methanol absorbs about half of the incident light below 2000 Å. The ionization potential of methanol is lower than that of water,[31] so that there is no certainty to assume that the electrons originate from water. Thomas and Hart,[10] comparing the flash photolysis and pulse radiolysis of pure water and aqueous solutions of methanol and formic acid, deduced that electrons, if formed at all, are not more than 10% of the reducing species. In view of the uncertainty, we decided to study the possibility that electrons are produced from excited water molecules at 1849 Å. We used $N_2O$ as the efficient electron scavenger with[32] $k_{N_2O+e}=5\times10^9$ yielding molecular nitrogen which is conveniently determined.

The reaction of $N_2O$ with atomic hydrogen also produces $N_2$ but it is slow,[33] $k_{N_2O+H}=1.2\times10^4$. Nevertheless, it is necessary to work in the presence of an efficient scavenger for atomic hydrogen. We choose isopropanol since we already know the yields for the formation of $H_2$ by atomic hydrogen from its solutions. Of the three alcohols it is the fastest,[34] with $k=5\times10^7$, to react with H atoms.

The photolysis of $N_2O$ in the gas phase produces $N_2$. To check whether the photolysis of $N_2O$ in solution also produces $N_2$, we irradiated a solution of $N_2O$ in which about half of the incident light is absorbed by the $N_2O$. Considerable amounts of $N_2$ were evolved. Therefore, only $N_2O$ concentrations less than $1.5\times10^{-4}M$ may be used so that $N_2O$ does not absorb directly. On the other hand, we cannot use lower concentrations than $1\times10^{-4}M$ since water itself would compete for the electrons.

We conducted two series of experiments at $pH=7$ and one at $pH=2$. The procedure was as described above. The $p$H was adjusted by $HClO_4$ which, at the concentrations used, does not absorb light directly. The results are shown in Table VII. In addition to $H_2$, $N_2$ was also produced. We investigated the possibility that its origin might be in an attack of the alcohol radical on $N_2O$ in solution. An aqueous solution of $N_2O$ was irradiated with x rays and the $G_{N_2}$ determined, then the experiment repeated in the presence of the alcohol. The same value for $G_{N_2}$ resulted in both. We conclude therefore that the alcohol radicals do not attack $N_2O$.

The mean total yield ($N_2+H_2$) in the first two series, at neutral $p$H, is the same as the hydrogen yield in the absence of $N_2O$. In the third series, at $pH=2$, the total yield is higher, and is also about the same as in the absence of $N_2O$ at the same $p$H. However, taking into account the length of these experiments and the small amounts of gas involved, the experimental error might be significant. Particularly, a small leakage of air may occur into the apparatus during the long duration of the experiment. Therefore, the agreement found is perhaps to some extent fortuitous. Nevertheless, the fact that $N_2$ is produced and that its yield is significantly reduced in the presence of $H^+$ indicates that electrons *are* formed from the excited water molecule.

TABLE VII. Nitrogen formation from solutions containing $N_2O$ and isopropanol $1.3\times10^{-3}M$.[a]

| Expt No. | $N_2O$ pressure (mm) | $[N_2O]$ $M\times10^4$ | Irrad. (min) | $\%N_2$ in gas | $p$H |
|---|---|---|---|---|---|
| 1 | 3.3 | 1.04 | 6 | 7.1 | 7 |
| 2 | 3.3 | 1.04 | 12 | 6.5 | 7 |
| 3 | 3.3 | 1.04 | 18 | 7.7 | 7 |
| 4 | 4.0 | 1.26 | 6 | 15.4 | 7 |
| 5 | 4.0 | 1.26 | 12 | 13.7 | 7 |
| 6 | 4.0 | 1.26 | 18 | 12.1 | 7 |
| 7 | 3.7 | 1.17 | 6 | <4 | 2 |
| 8 | 3.7 | 1.17 | 12 | <4 | 2 |
| 9 | 3.7 | 1.17 | 18 | <4 | 2 |

[a] Low-intensity lamp.

---

[31] K. Watanabe, J. Chem. Phys. **26**, 542 (1952).

[32] M. C. Sauer, S. Arai, and L. Dorfman, J. Chem. Phys. **42**, 708 (1965).

[33] J. P. Keene, Discussions Faraday Soc. **36**, 304 (1963).

[34] J. L. Weeks, G.M.A.C. Meaburn, and S. Gordon, Radiation Res. **19**, 559 (1963).

TABLE VIII. Dependence of $\phi H_2$ on $p$H in solutions of methanol.

| $p$H | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|
| With $1\times10^{-2}M$ methanol | 0.49 | .049 | 0.49 | 0.49 | 0.49 |
| With $1\times10^{-4}M$ methanol | 0.33 | 0.37 | 0.30 | 0.27 | 0.24 |

Their yield is not more than 10% of the yield of the reducing species.

### Dependence of the Hydrogen Yield on *p*H

The change in the quantum yield for the formation of hydrogen when the $p$H was varied between 3–7, was measured for solutions of methanol, ethanol, and isopropanol at two concentrations: at $10^{-2}M$ (at which there is total scavenging of the radicals) and at $10^{-4}M$ (at which scavenging still competes with geminate recombination). The outcome is the same for both the alcohols. At the higher concentration, there is no dependence on $p$H, while at the lower, the yield is inversely proportional to the $p$H. The effect is more pronounced in the case of isopropanol. The results for the methanol solutions are shown in Table VIII. This behavior may be due to electrons formed from excited water molecules. In this case, the reason for the increase in the $H_2$ yield with decreasing the $p$H is that $e_{aq}^-$ is converted by hydrogen ion to H atom which reacts with the alcohol forming $H_2$. This is plausible since alcohol is a bad electron scavenger; consequently at alcohol concentrations below that sufficient for total scavenging, the alcohol would scavenge H atoms and not electrons. At high enough concentrations, the alcohol may possibly scavenge both H atoms and electrons. However, this implies that $k_{RH_2+e}$ should be of the order of $10^6$ liter mole$^{-1}\cdot$sec$^{-1}$ in order that water should not compete. All that is presently known is that this is an upper value.[32]

An alternative explanation is that $k_{RH_2+H}$ slightly depends on the $p$H. At the lower concentration, where the alcohol still has to compete with geminate recombination, this dependence is significant, while at the higher concentration where the alcohol is present in an excess over that required for total scavenging, this dependence is insignificant. These experiments lead to the same conclusion as before that electrons are probably formed with a yield not exceeding 10% of the total yield of the reducing species. Thus, experimental evidence indicates that probably electrons are formed from the excited water molecule. The ionization potential of water is 12.6 eV, and the quantum energy at 1849 Å is 6.8 eV. Evidently, a direct photoionization process is energetically impossible, and some exoergic step is essential to cover this difference (5.8 eV). The hydration energy of $e_{aq}^-$ alone is insufficient. Complete hydration cannot account for this since it is much too slow a process ($>10^{-11}$ sec) to compete with the vibrational decomposition of the excited molecule in $10^{-13}$ sec. However, the process

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$$

is an ion–molecule reaction which may be very fast ($10^{-14}$ sec) and is by 7.8 eV exoergic, thus covering the energy gap between the ionization potential and the quantum energy. It should be emphasized that the reaction product is the complex $H_3O^+$ and not the hydrate which is formed after the slower process of complete hydration. The process suggested is

$$H_2O + h\nu \rightarrow (H_2O)^{\ddagger} \xrightarrow{+H_2O} (OH + H_3O^+) + e_{aq}^-.$$

### Photolysis of Highly Purified Water

To check our conclusions, some experiments were carried out in the absence of any added scavenger in highly purified water.

Water that was purified as described above was irradiated at 1849 Å with the spiral lamp at the highest light intensity. The quantum yield of the formation of hydrogen, the only gas produced, decreased with the dose, probably because of the decrease in the amount of impurities. After some 16 h of continued irradiation, the results became reproducible. When this stage was reached the sample was irradiated for short periods of 1–10 min. The gas produced was pumped off after each irradiation and its pressure determined. The mean quantum yield in each separate irradiation was found to be inversely dependent on the time of the irradiation, probably due to the back reaction

$$H_2 + OH \rightarrow H_2O + H.$$

The initial quantum yield of hydrogen was found by extrapolating the mean value in each separate interval to zero time (Fig. 9). The value of 0.02 was obtained. The amount of $H_2O_2$ was always considerably less than required by material balance. However, we believe that the value of 0.02 is not meaningless, since it is exactly four times smaller than the value of the residual yield $\phi r$, in the presence of alcohols. This ratio is what one

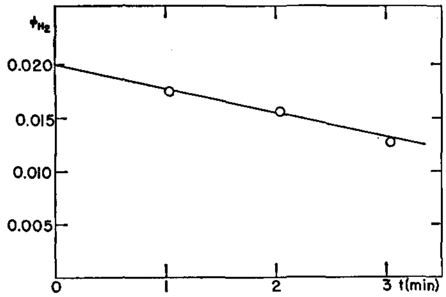

FIG. 9. Extrapolation of hydrogen yield to zero time in pure water.

might expect since in the presence of alcohols every H atom in the bulk leads to one molecule of $H_2$ according to $RH_2+H\rightarrow RH+H_2$, while in the case of pure water, the bulk reactions are

$$H+OH\rightarrow H_2O, \quad (I)$$

$$H+H\rightarrow H_2, \quad (II)$$

$$OH+OH\rightarrow H_2O_2, \quad (III)$$

and since the probability of Reaction (I) is twice that of (II) or (III), every four H atoms would lead to one molecule of $H_2$.

The correlation of the results is consistent with the primary act, $H_2O\rightarrow H+OH$, and is an additional evidence against the possibility of a molecular yield of $H_2$. Further support is the fact that the quantum yield was found to be independent of the light intensity. To confirm that there is no molecular yield of hydrogen, we repeated the irradiation in the presence of $5\times10^{-6}M$ $O_2$. No hydrogen was produced. This rules out the possibility that hydrogen is formed by any other mechanism but the recombination of H atoms. This excludes reactions of excited water molecules with each other or with unexcited water molecules, leading to $H_2$ formation and also the reaction $H_2O\rightarrow H_2+O(^3P)$.

## ACKNOWLEDGMENT

This research has been sponsored by the USAF School of Aerospace Medicine under Contract AF 61 (052)-655 through the European Office of Aerospace Research (OAR) U. S. Air Force.

---

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 44, NUMBER 9 1 MAY 1966

# Solvent Stark Effect and Spectral Shifts*

MARIO E. BAUR AND MALCOLM NICOL

*Department of Chemistry,† University of California, Los Angeles, California*

(Received 8 November 1965)

A theory is developed for the solvent shift in the electronic absorption spectrum of a nonpolar solute in a polar solvent. The shift is regarded as composed of two components, one of which arises from the same mechanism as the London forces and is taken successfully into account by the McRae theory. The second component, the solvent Stark effect, is treated in detail here by considering polarization fluctuations in a dipolar medium surrounding a cavity. A simple result for the contribution of this component in terms of the macroscopic dielectric properties of the solution is given. The model predicts in particular that the Stark contribution to the solvent shift becomes linear in the solution dielectric constant for large values of the latter. The theoretical expression obtained here is compared with the experimental data of Weigang and Wild for the $^1L_a$ transition of naphthacene, and a satisfactory fit is obtained.

## I. INTRODUCTION

IT is known that the electronic spectrum of a molecule immersed in a solvent medium in general suffers a shift in energy relative to the spectrum of the isolated molecule. This effect has been the subject of intensive investigation.[1–8] One would like ideally to construct a complete theory in which relations between solvent shifts and intermolecular forces are used in conjunction with knowledge of the effect of these forces on molecular distribution functions to relate all equilibrium properties of the solvent–solute system to the shift data; however, such a complete theory is scarcely practicable in view of the current primitive state of the theory of dense fluids. Work on this problem, therefore, has been directed towards establishing less general, systematic parametrizations of spectral solvent shifts in terms of macroscopic properties of the solvent (refractive index, dielectric constant). Such a parametrization assumes that the molecular interactions responsible for spectral solvent shifts can be expressed to a good approximation in terms of the quantities governing the interaction of isolated molecules with an external field, e.g., molecular polarizabilities and dipole moments. If this is the case, the problem is reduced to relating the macroscopic properties of the system to these individual molecular

---

* Supported by the National Institutes of Health Grant No. GM-11125-02 and the U.S. Atomic Energy Commission Contract AT (11-1)34, Project 88.

† Contribution No. 1881.

[1] Y. Ooshika, J. Phys. Soc. Japan **9**, 594 (1954).

[2] E. G. McRae, J. Phys. Chem. **61**, 562 (1957).

[3] N. Mataga, Y. Kaifu, and M. Koizumi, Bull. Chem. Soc. Japan **29**, 465 (1956).

[4] E. Lippert, Z. Naturforsch. **10a**, 541 (1955).

[5] H. C. Longuet-Higgins and J. A. Pople, J. Chem. Phys. **27**, 192 (1957).

[6] O. E. Weigang, J. Chem. Phys. **33**, 892 (1960).

[7] O. E. Weigang and D. D. Wild, J. Chem. Phys. **37**, 1180 (1962).

[8] O. E. Weigang, J. Chem. Phys. **41**, 1435 (1964).