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# CAGE EFFECTS AND SCAVENGING MECHANISMS IN THE PHOTOCHEMISTRY OF THE IODIDE ION IN AQUEOUS SOLUTIONS

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Scavenging mechanisms in the photochemistry of the iodide ion were investigated. The nature of the scavenged species is discussed. An iodine atom-electron pair is formed from the primary excited state.  $H^+$  ions promote specifically the formation of H atoms from these electrons.  $H^+$  ion and aliphatic alcohols were employed as scavengers for the H atoms. At high scavenger concentration a limiting quantum yield of  $0.290 \pm 0.005$  was observed at  $25^\circ$  and  $2537 \text{ \AA}$ , independent of the nature of the scavenger. Application of specific scavengers made discrimination possible between H atoms and their precursors formed from the dissociation of the excited state of the ion. The dependence of the quantum yield on the scavenger concentration was found to be in agreement with general scavenging equations.

## Introduction

In previous work<sup>1</sup> the photochemistry of evacuated aqueous KI solutions was investigated. The pH dependence of the initial quantum yield, which was found to be independent of  $I^-$  concentration and light intensity, could be interpreted adequately by a diffusion controlled scavenging mechanism.<sup>2</sup> The introduction of H atoms into the bulk was found to be facilitated by  $H^+$  ions, acting as an efficient scavenger. However, we were unable to establish with certainty the nature of the species scavenged by the  $H^+$  ion. It was postulated that in the photochemical cage together with an iodine atom either an electron or an H atom is formed, and undergoes a random diffusion process. It may then be captured by the I atom, leading to a secondary recombination, scavenged by  $H^+$  ion, or diffuse into the bulk.

The purpose of the present work is the investigation of the nature of the fragments formed from the excited state of the ion. We attempt to discriminate between H atoms and their precursors by using specific scavengers. Further theoretical and experimental investigation of diffusion controlled scavenging mechanisms is presented.

## Theoretical

**Diffusion-Controlled Scavenging.**—Radicals produced in pairs in the liquid phase by a thermal, radiation-chemical, or photochemical process may undergo primary recombination which is kinetically equivalent to thermal deactivation of the excited state. Radicals escaping primary recombination may undergo secondary diffusive recombination with their original partners or diffuse into the bulk.

Various semiquantitative treatments were presented for the effects of an efficient scavenger on secondary recombination.<sup>2-9</sup> The experimental results of our work will be treated by applying the general approach of Noyes.<sup>2,3</sup>

The total reaction probability of the two original partners is given by

$$\beta' = \int_0^\infty h(t) dt \quad (1)$$

In the presence of a scavenger capable of reacting with one of the radicals the probability of this radical being scavenged, instead of it recombining with another radical in a secondary geminate recombination, is

$$\int_0^\infty (1 - e^{-k_s[S]t})h(t) dt \quad (2)$$

where  $[S]$  is the scavenger concentration and  $k_s$  is the long time rate constant for the scavenging reaction. The dependence of the reactivity on the "age" of the radicals produced<sup>2,10</sup> was not considered in the present treatment.

The residual yield  $\gamma_r$  is defined as the quantum yield in the presence of the scavenger at concentration which is sufficient to prevent radical recombination in the bulk, but is too low to compete with secondary recombination. We denote by  $\Gamma$  the cross-section for radical production, *i.e.*, the quantum yield of radical pairs escaping primary recombination. Thus we set

$$\gamma_r = \Gamma (1 - \beta') \quad (3)$$

$$\beta' = 1 - \frac{\gamma_r}{\Gamma} \quad (3a)$$

The total quantum yield for radical scavenging obtained in the presence of a scavenger S at a concentration at which it prevents radical recombination in the bulk and competes with secondary recombination will be denoted by  $\gamma$ , and given by

$$\gamma = \gamma_r + \Gamma \int_0^\infty h(t)(1 - e^{-k_s[S]t}) dt \quad (4)$$

In Noyes' early treatment<sup>2</sup>  $h(t)$  was introduced in the form

$$h(t) = 0 \quad 0 < t < 4a^2/\beta'^2 \quad (5)$$

$$h(t) = at^{-3/2} \quad t > \frac{4a^2}{\beta'^2}$$

(10) R. M. Noyes, *J. Phys. Chem.*, **65**, 763 (1961).

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

(2) R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955).

(3) R. M. Noyes, *ibid.*, **78**, 5486 (1956).

(4) A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).

(5) J. C. Roy, R. R. Williams, and W. H. Hamill, *J. Am. Chem. Soc.*, **76**, 3274 (1954).

(6) R. A. Wijsman, *Bull. Math. Biophys.*, **14**, 121 (1952).

(7) L. Monchick, *J. Chem. Phys.*, **24**, 381 (1956).

(8) H. A. Schwarz, *J. Am. Chem. Soc.*, **77**, 4960 (1955).

(9) H. Fricke, *Ann. N. Y. Acad. Sci.*, **59**, 567 (1955).

Substitution of (5) in (4) leads to Noyes' formula<sup>2</sup>

$$\gamma = \gamma_r + 2a\Gamma\sqrt{\pi k_s[S]} - \frac{\Gamma 4a^2 k_s[S]}{\beta'} + \dots \quad (6)$$

for low [S] values

$$\gamma = \gamma_r + \alpha\Gamma\sqrt{[S]} \quad (6a)$$

where

$$\alpha = 2a\sqrt{\pi k_s}$$

This equation yields the theoretical basis for the linear dependence of the quantum yield on the square root of the scavenger concentration at low [S], and it was previously applied by us.<sup>1</sup> However, at high scavenger concentrations deviations from linearity in the plot  $\gamma$  vs. [S] appear.

We attempt to derive a scavenging equation adequate for the whole concentration region.  $h(t)$  is described by the continuous function<sup>3</sup>

$$h(t) = at^{-3/2} e^{-\pi a^2/\beta' t} \quad (7)$$

Substitution in eq. 4 leads to the result

$$\gamma = \Gamma \left( 1 - \int_0^\infty at^{-3/2} e^{-\pi a^2/\beta' t} e^{-k_s[S]t} dt \right) \quad (8)$$

The Laplace transform  $f(k_s[S])$  of  $h(t)$  is given by

$$f(k_s[S]) = \int_0^\infty e^{-k_s[S]t} h(t) dt = \beta' e^{-(2a/\beta')\sqrt{\pi k_s[S]}} \quad (9)$$

Thus the general expression for the quantum yield is obtained

$$\gamma = \Gamma(1 - \beta' e^{-(2a/\beta')\sqrt{\pi k_s[S]}}) \quad (10)$$

Application of eq. 3 leads to the result

$$\ln \left( 1 - \frac{\gamma}{\Gamma} \right) = \ln \left( 1 - \frac{\gamma_r}{\Gamma} \right) - \frac{2a}{\beta'} \sqrt{\pi k_s[S]} \quad (11)$$

For the limiting cases eq. 10 and 11 reduce to

$$\begin{aligned} S << \frac{\beta'^2}{4a^2\pi k_s}; \gamma &\longrightarrow \gamma_r \\ S &\longrightarrow \infty; \gamma &\longrightarrow \Gamma \end{aligned} \quad (12)$$

The general scavenging equation is reduced to Noyes' equation for relatively low scavenger concentration. When

$$\frac{2a}{\beta'} \sqrt{\pi k_s[S]} < 1 \quad (13)$$

the exponent in eq. 10 can be expanded leading to

$$\left( 1 - \frac{\gamma}{\Gamma} \right) = \beta' \left( 1 - \frac{2a}{\beta'} \sqrt{\pi k_s[S]} \right) \quad (14)$$

leading to eq. 6.

Thus the linear dependence of  $\gamma$  on  $\sqrt{[S]}$  will hold for  $S << \beta'^2/\alpha^2$ . For typical values of  $\alpha = 1 \text{ l.}^{1/2} \text{ mole}^{-1/2}$  obtained in this work Noyes' relation will hold within 5% or better up to scavenger concentrations of 0.1 M.

It is interesting to compare the results of Noyes' treatment with the equation of Roy, Hamill, and Williams<sup>5</sup> which is based on similar assumptions. Their equation can be written in the form

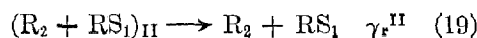
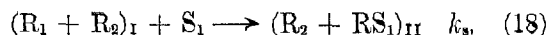
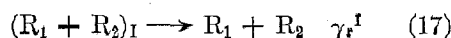
$$\ln \gamma = A + B \sqrt{[S]} \quad (15)$$

where  $A$  and  $B$  represent constants related to microscopic diffusion parameters. For low [S] values (15) is identical with (6) if

$$A = \ln \gamma_r; B = \frac{\alpha\Gamma}{\gamma_r} \quad (16)$$

All cage-scavenging models of this type lead to the conclusion that the quantum yield should be independent of light intensity.

The species formed in the scavenging process may be a reactive radical. In the presence of added scavengers consecutive scavenging may occur, in which a species formed by the interaction of one of the scavengers with a radical originally produced reacts with a second scavenger specifically. To treat this mechanism we consider the general reaction scheme



The radical pair  $R_1$  and  $R_2$  in cage I may undergo diffusion into the bulk with quantum yield  $\gamma_r^I$ , or the radical  $R_1$  may be scavenged by  $S_1$  leading to a new radical pair in cage II. The scavenging of the radical  $RS_1$  by  $S_2$  from cage II should be treated by application of the general eq. 10. Assuming that the scavenger concentrations  $[S_1]$  and  $[S_2]$  are sufficiently high to prevent any radical recombination in the bulk the general expression for the quantum yield for the products formation is given by

$$\gamma = \gamma_r^I + \Gamma_{II}(1 - \beta_{II}' e^{-(2a_{II}/\beta_{II}')\sqrt{\pi k_{s2}[S_2]}}) \quad (21)$$

where  $\Gamma_{II}$ , the cross-section for radical production, in cage II is related to  $\Gamma$  by

$$\Gamma_{II} = \Gamma(1 - \beta_I' e^{-(2a_I/\beta_I')\sqrt{\pi k_{s1}[S_1]}}) - \gamma_r^I$$

$\beta_I'$  and  $\beta_{II}'$  present the total reaction probabilities in cages I and II.  $\gamma_r^I$  is the residual yield from cage I presented by eq. 3. The residual yield from cage II is presented in an analogous way

$$\gamma_r^{II} = \Gamma_{II}(1 - \beta_{II}') \quad (22)$$

In this approximation  $\Gamma_{II}$  depends on  $[S_1]$ , reaching at high  $S_1$  concentration the limiting value  $(\Gamma - \gamma_r^I)$ . For sufficiently low  $S_2$  concentration and at constant  $[S_1]$  the extended form of Noyes' relation is obtained

$$\gamma = \gamma_r^I + \gamma_r^{II} + \Gamma_{II} 2a_{II} \sqrt{\pi k_{s2}[S_2]} \quad (23)$$

This result indicates that within the framework of the present approximation Noyes' relation holds

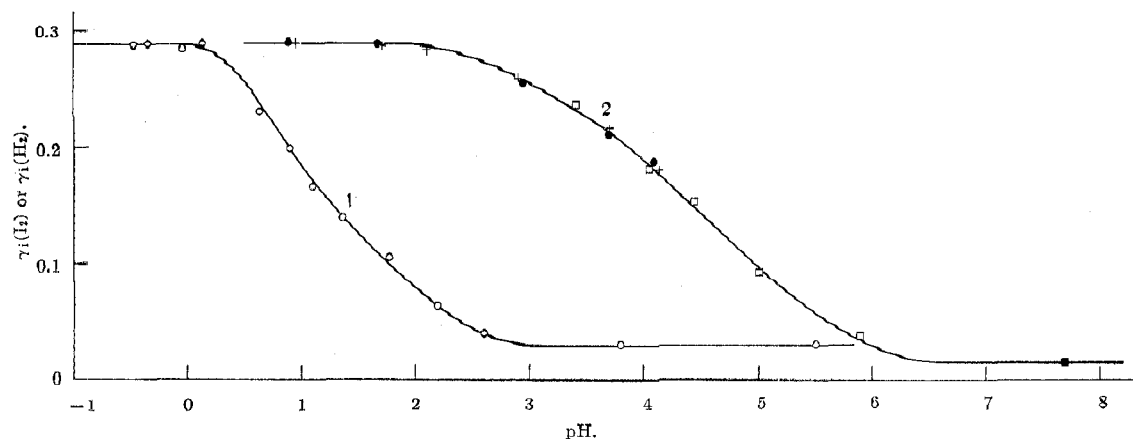


Fig. 1.—The pH dependence of initial quantum yields. (1) Iodine and hydrogen yields in evacuated solutions. The pH values below pH 0 represent  $-\log [H^+]$ . (2) Hydrogen yield in the presence of alcohols: ●, 1 *M* methanol,  $H_2SO_4$  solutions; +, 1 *M* isopropyl alc.,  $H_2SO_4$  solutions; □, 1 *M* isopropyl alc.,  $5 \times 10^{-3}$  *M* acetic acid-acetate buffer; ■, 1 *M* isopropyl alc.,  $5 \times 10^{-3}$  *M* sodium monophosphate buffer.

for both ordinary and consecutive scavenging mechanisms.

The most serious approximation involved in the present treatment is the assumption that  $\gamma_r^I$  is a constant independent of  $S_1$  concentration. The simple treatment of scavenging from a photochemical cage by  $S_1$  does not discriminate between radicals scavenged in the bulk and in the solvent cage. However when consecutive scavenging is considered the spatial distribution of the radicals formed by interaction with the scavenger  $S_1$  should be taken into account. At extremely high  $S_1$  concentration the cross-section for the formation of cage II may reach the limiting value  $\Gamma$  and then the simple scavenging eq. 10 will be applicable and the residual yield will be due to diffusion from cage II. Because of this difficulty it is not easy to determine quantitatively the source of the residual yield, which may be due to diffusion from both cages I and II. We have used the two limiting approximations (a),  $\gamma_r^I$  is constant independent of  $S_1$  so that  $\Gamma_{II} = \Gamma - \gamma_r^I$ ; (b),  $\gamma_r^I = 0$  so that  $\Gamma_{II} = \Gamma$ . It was found that the parameter  $2a_{II}\sqrt{\pi k}$  is not very susceptible to the approximation involved.

### Experimental

Photochemical experiments were carried out at 2537 Å., using a low pressure mercury lamp. The experimental technique was substantially that previously used.<sup>1</sup> Experiments were carried out at 25°.

**Materials and Solution.**—Solutions at high acid concentrations were prepared by evacuation of freshly prepared neutral KI solutions and the acid solutions in two different vessels and mixing in the vacuum system. The initial  $I_2$  concentration did not exceed  $2 \times 10^{-7}$  *M*. The pH below 4.5 was adjusted by  $H_2SO_4$ . In the pH region 3.4–5.9,  $5 \times 10^{-3}$  *M* acetic acid-sodium acetate buffer was employed while at pH 7–8,  $5 \times 10^{-3}$   $KH_2PO_4$ - $Na_2HPO_4$  buffer was used. At certain pH values the acetate and the sulfate systems were used in alternate experiments and identical results obtained. Thus acetate has no specific influence on the results. All chemicals used were of Analar grade. The water used was triply distilled from alkaline potassium permanganate and phosphoric acid.  $D_2O$  was prepared by distillation from alkaline permanganate followed by distillation from potassium hydrosulfate (to remove traces of permanganate), and two final distillations.

**Analysis.**—The analytical procedures for the determination of hydrogen and iodine were described previously.<sup>1</sup> Formaldehyde was identified and determined in irradiated

aqueous methanol solutions by chromotropic acid.<sup>11</sup> The deuterium content of the gas evolved from methanol- $D_2O$  solutions was determined by mass-spectrographic analysis.

### Results and Discussion

**The pH Dependence of  $\gamma_i$  in Evacuated Solutions.**—In ref. 1 the pH dependence of the initial quantum yields,  $\gamma_i$ , in evacuated solutions was investigated in the pH region 0.6–7. In the present work the  $H^+$  concentration region was extended and experiments were carried out up to 4 *N*  $H_2SO_4$ . Figure 1 curve 1 represents the dependence of  $\gamma_i$  on  $[H^+]$  over the whole region in the absence of any other scavenger. The hydrogen yields observed were equal to the  $I_2$  yields. At high acid concentration the quantum yield reaches an upper limiting yield  $\gamma_{i\text{lim}} = 0.290 \pm 0.005$  at 25°. Such behavior is theoretically predicted for efficient scavenging competing with secondary recombination. At relatively low pH the analysis of the bulk reactions in this system indicates<sup>1</sup> that every H atom introduced into the bulk oxidizes another  $I^-$  ion. Thus the limiting value obtained for the quantum yield of  $I_2$  and  $H_2$  production in this system leads to the value  $\Gamma = 0.29$  for the cross-section for photodissociation.

**The pH Dependence of  $\gamma_i$  in the Presence of Aliphatic Alcohols.**—The photochemistry of the iodide ion in aqueous solutions in the presence of isopropyl alcohol and methanol was investigated. These aliphatic alcohols were chosen, as recent radiation chemical investigations indicate that they act as specific scavengers for hydrogen atoms.<sup>12</sup> The initial quantum yields for  $H_2$  evolution from these solutions were found to depend on pH and alcohol concentration (Fig. 1, 2, 3). Figure 1 curve 2 represents the pH dependence of the initial quantum yields for  $H_2$  evolution investigated over a wide pH region in the presence of aliphatic alcohols. These results were obtained at high alcohol concentration where the quantum yield is independent of this scavenger concentration. Identical results were obtained in 1 *M* methanol and 1 *M* isopropyl

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

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

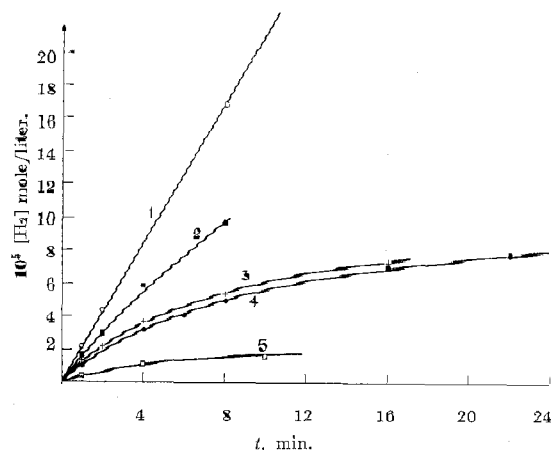


Fig. 2.—Hydrogen yields in isopropyl alc. solutions: (1) 1.01 *M* isopropyl alc., pH 1.72; (2)  $2.1 \times 10^{-3}$  *M* isopropyl alc., pH 2.92; (3)  $1.01 \times 10^{-3}$  *M* isopropyl alc., pH 1.72; (4)  $1.45 \times 10^{-3}$  *M* isopropyl alc., pH 2.92; (5)  $1.4 \times 10^{-4}$  *M* isopropyl alc., pH 2.92.

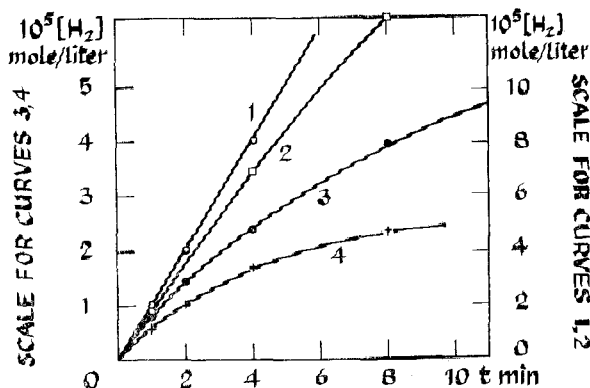


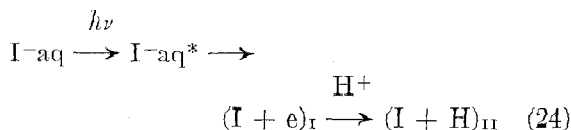
Fig. 3.—Hydrogen yields in methanol solutions: (1) 1 *M* methanol, pH 2.92; (2) 0.22 *M* methanol, pH 2.92; (3) 0.022 *M* methanol, pH 2.92; (4) 0.01 *M* methanol, pH 2.92.

alcohol solutions. Experiments carried out in  $\text{H}_2\text{SO}_4$  solutions and in the presence of  $5 \times 10^{-3}$  *M* acetate buffer did not reveal any specific anion effect on the mechanism of  $\text{H}_2$  evolution in the presence of alcohols.

The pH dependence of the initial  $\text{H}_2$  yields in this system indicates that these aliphatic alcohols may act as efficient scavengers only at relatively low pH. At pH < 2 the yield is independent of  $\text{H}^+$  ion concentration, and total scavenging occurs yielding the limiting value  $0.29 \pm 0.01$  which is identical with the yield in evacuated solutions at high acid concentration.

The pH dependence of  $\gamma(\text{H}_2)$  in the presence of an efficient scavenger for H atoms cannot be reconciled with any mechanism involving a direct H atom formation from the excited state of the ion.<sup>13,14</sup> These experimental results can be explained only if we assume the presence of two forms of "H atoms" formed in the photochemical system.<sup>1</sup> The acid form present at pH < 2 efficiently dehydrogenates the aliphatic alcohols while the other form does not, and reacts with the iodine atom leading mainly to a back reaction in the solvent

cage. Thus with decreasing pH the nature of the species available to the aliphatic alcohol is changed. These conclusions are consistent with the scheme for consecutive scavenging.<sup>1</sup>



where ( ) represents the solvent cage where particles may undergo secondary recombination.

In this scheme it is assumed that the atomic hydrogen precursor formed by the dissociation of the excited state of  $\text{I}^-$  is an electron, which does not lead to dehydrogenation of the aliphatic alcohol. This electron can undergo a secondary recombination process with the iodine atoms in the solvent cage I, or be scavenged by a  $\text{H}^+$  ion yielding a hydrogen atom, resulting in the formation of cage II. It will be shown later that the quantum yield for the processes in which H atoms as such are scavenged is also independent of light intensity. This shows that cage type recombination exists between I and H too and that the distribution of H atoms is not homogeneous. The pH dependent yield at high alcohol concentration represents the efficiency of electron scavenging by  $\text{H}^+$  from cage I. This pH dependence of  $\gamma_1$  (curve 2, Fig. 1) was analyzed according to the general scavenging mechanism. The experimental results were found to be in agreement with eq. 11. These results presented in Fig. 4 yield a support for the scavenging mechanism. From Fig. 4 we obtain for the scavenging reaction of electrons by  $\text{H}^+$  ions

$$\frac{2a}{\beta'} \sqrt{\pi k_{\text{H}^+ + \text{e}}} = 85 \text{ mole}^{-1/2} \text{ l.}^{1/2}, \beta' = 0.725 \text{ and}$$

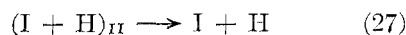
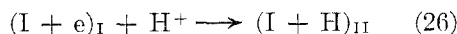
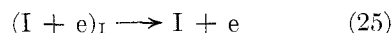
$$\text{hence } \gamma_1 = 0.08 \pm 0.005 \text{ and}$$

$$2a \sqrt{\pi k_{\text{H}^+ + \text{e}}} = 62 \text{ mole}^{-1/2} \text{ l.}^{1/2}$$

Application of the square root plot according to eq. 6 leads to a lower value of  $2a \sqrt{\pi k_{\text{H}^+ + \text{e}}} = 30 \pm 10 \text{ mole}^{-1/2} \text{ l.}^{1/2}$ . The difference obtained between these two treatments will be discussed.

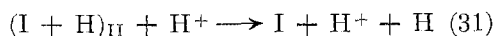
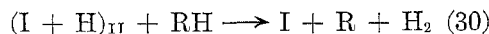
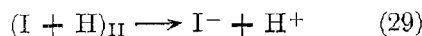
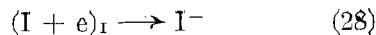
**Dependence of  $\gamma_1$  on Alcohol Concentration.**—Hydrogen atoms formed in cage II can be scavenged by any efficient scavenger for H atoms. To get a further insight into this reaction mechanism the dependence of the quantum yield,  $\gamma_1(\text{H}_2)$ , on the concentration of methanol and isopropyl alcohol was investigated. These results are presented in Fig. 5.

The dependence of the quantum yield on methanol concentration at constant pH indicates that down to 0.2 *M* methanol the quantum yield is independent of the scavenger concentrations. At lower concentrations the quantum yield decreases, indicating the effect of secondary recombination. The general mechanism for this system is in the form



(13) T. Rigg and J. Weiss, *J. Chem. Soc.*, 4148 (1952).

(14) J. Franck and F. Haber, *Sitzber. preuss. Akad. Wiss. Physik. Math. Klasse*, 250 (1931).



reactions 28 and 29 represent secondary recombinations in the solvent cage. The residual yield is due to reactions 25 and 27. The scavenging reaction 30 leads to the formation of  $H_2$ . These results will be treated by application of a general equation for consecutive diffusion controlled scavenging.

**Scavenging of H Atoms by Methanol and Isopropyl Alcohol.**—The dependence of the quantum yield on methanol concentration is interpreted in terms of H atoms scavenging from cage II. In Fig. 6 the experimental results are plotted according to the scavenging equations. From the extended Noyes relation (23) we obtained  $\gamma_r^I + \gamma_r^{II} = 0.08 \pm 0.005$  and  $\Gamma_{II} 2a_{II} \sqrt{\pi k_{CH_3OH+H}} = 0.45 \text{ mole}^{-1/2} \text{ l}^{1/2}$ . At pH 2.9 the yield is 0.260 and by setting  $\gamma_r^I = 0.08$  obtained from Fig. 4 we get  $\Gamma_{II} = 0.26 - 0.08 = 0.18$ . Hence we obtain  $2a_{II} \times \sqrt{\pi k_{CH_3OH+H}} = 2.5 \text{ mole}^{-1/2} \text{ l}^{1/2}$ .

The general consecutive scavenging equation (21) was applied in the form

$$\ln \left( 1 - \frac{\gamma - \gamma_r^I}{\Gamma_{II}} \right) = \ln \beta_{II}' - \frac{2a_{II} \sqrt{\pi k_{CH_3OH+H}} [CH_3OH]}{\beta_{II}'} \quad (34)$$

with  $\gamma_r^I = 0.08$  and  $\Gamma_{II} = 0.18$ . This treatment leads to  $\beta_{II}' = 1$  and  $2a_{II} \sqrt{\pi k_{H+CH_3OH}} = 3.8 \text{ mole}^{-1/2} \text{ l}^{1/2}$ . A similar treatment for the scavenging of H atoms by isopropyl alcohol leads to  $\beta_{II}' = 1$ ;  $2a_{II} \sqrt{\pi k_{CH_3CHOHCH_3+H}} = 20 \text{ mole}^{-1/2} \text{ l}^{1/2}$ . The result  $\beta_{II}' = 1$  indicates that the scavenging of the electron by  $H^+$  to give an H atom has not significantly changed the probability of recombination in cage II. However this result does not mean that the residual yield from cage II is zero, since we have set  $\Gamma_{II} = \Gamma - \gamma_r^I$  in the present approximation.

**Consecutive Scavenging by  $H^+$  Ions.**— $H^+$  ions act in this system as scavengers in two consecutive steps. In the first step hydrogen atoms are formed in cage II through electron capture by  $H^+$  ions (eq. 17). The effect observed in the pH region 2.5–6 in the presence of organic scavengers is due to this (curve 2, Fig. 1). A pH dependence in evacuated solutions in the absence of organic scavengers (curve 1, Fig. 1) is observed in the pH region below pH 2.5. This pH dependence is interpreted in terms of H atom scavenging by hydroxonium ions,<sup>1</sup> given schematically by eq. 31. The scavenging of H atoms by  $H^+$  ions takes place in the pH region where complete scavenging of cage I has occurred already.

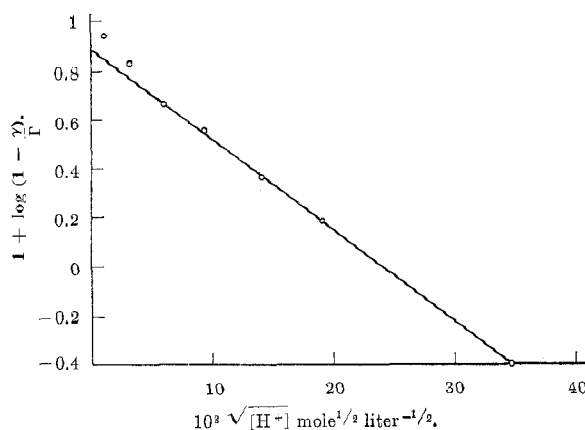


Fig. 4.—The dependence of  $\gamma(H_2)$  on  $\sqrt{[H^+]}$  according to eq. 11.

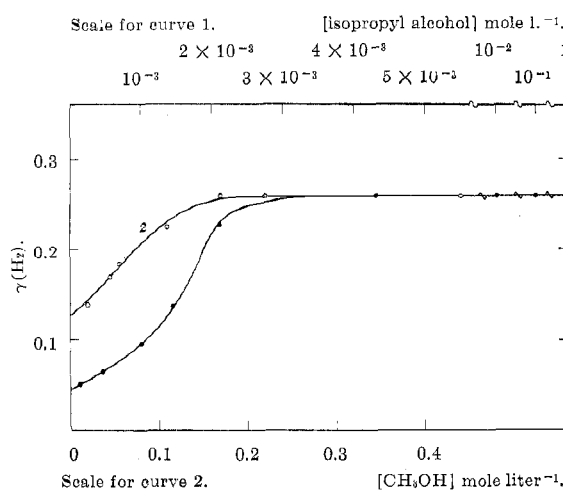


Fig. 5.—Dependence of  $\gamma(H_2)$  on alcohol concentration: (1) ●, isopropyl alc. solutions; (2) ○, methanol solutions.

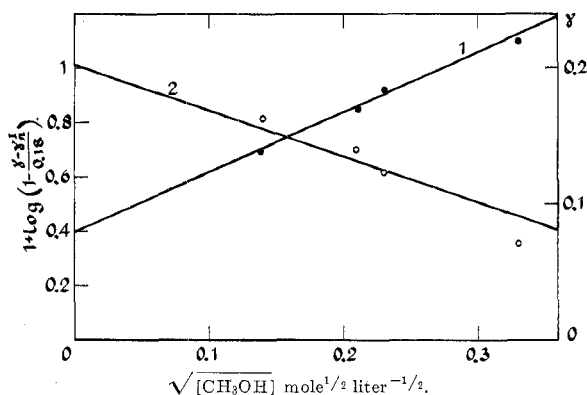


Fig. 6.—Scavenging equations for H atoms. Scavenging by methanol: (1) extended Noyes' eq. 23; (2) eq. 21.

It was shown<sup>1</sup> that the experimental results can be represented adequately by the Noyes relation. The parameters previously obtained<sup>1</sup> have to be interpreted in terms of eq. 23, setting  $\Gamma_{II} = \Gamma - \gamma_r^I = 0.21$ . Similar results have been obtained by application of the Roy-Hamill-Williams equation (Fig. 7). At high  $H^+$  concentration (pH < 0.7) deviation from Noyes' relation was observed<sup>1</sup> which is due to the inadequacy of eq. 23 at high scavenger concentration. The experimental results over the whole  $H^+$  concentration region were adequately

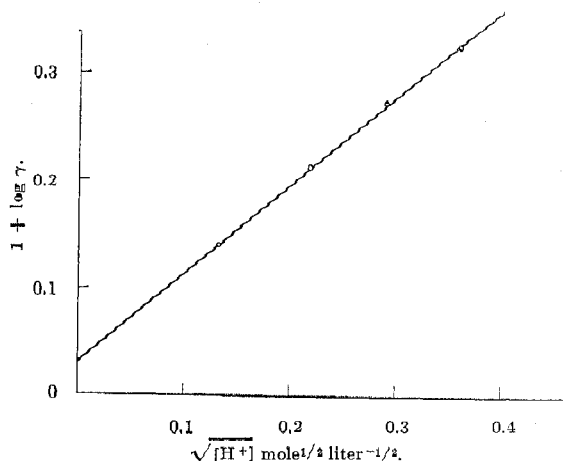


Fig. 7.—Roy-Hamill-Williams plot for scavenging of H atoms by  $H^+$  ions.

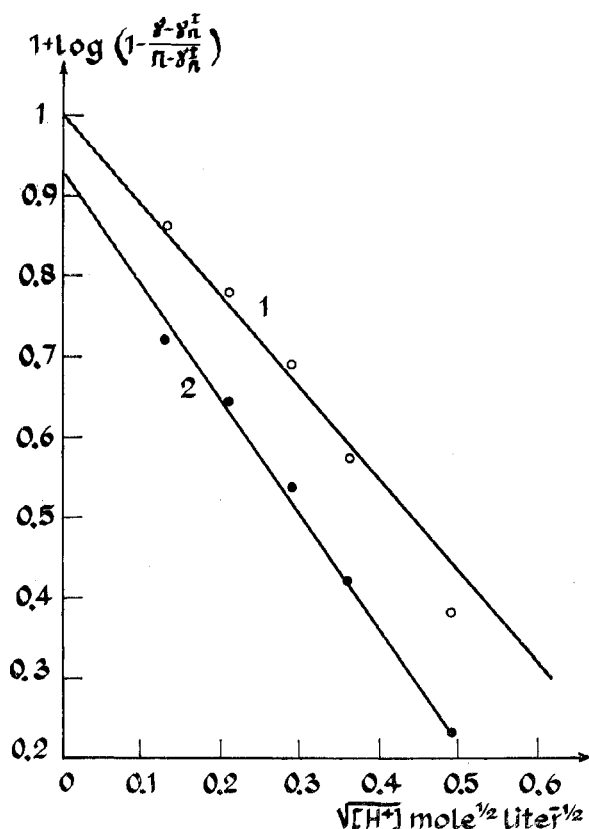


Fig. 8.—General equation for consecutive scavenging by  $H^+$  ions (eq. 35): (1)  $\gamma_r I = 0.08$ ; (2)  $\gamma_r I = 0$ .

represented by the consecutive scavenging equation

$$\ln \left( 1 - \frac{\gamma - \gamma_r I}{\Gamma - \gamma_r I} \right) = \ln \beta_{II}' - \frac{2a_{II}}{\beta_{II}'} \sqrt{\pi k_{H+H^+} [H^+]} \quad (35)$$

Two limiting approximations were applied for the treatment of eq. 35. (a) It was assumed that the residual yield  $\gamma_r I$  is given by its maximum value of 0.08. This treatment is analogous to that in the presence of alcohols. (b) As the experiments considered were carried out in the low pH region where,

as indicated by Fig. 3,  $H^+$  completely scavenges cage I we set  $\gamma_r I = 0$ . This is equivalent to the assumption that the cross-section for cage II is  $\Gamma$ , and eq. 35 is reduced to eq. 11.

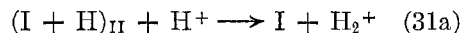
The results obtained from these treatments (Fig. 8) are presented in Table I. The two limiting approximations of eq. 35 yield identical scavenging constants. However these results do not make possible the identification of the source of the residual yield.

TABLE I  
SCAVENGING DATA FOR THE REACTION  $H + H^+$

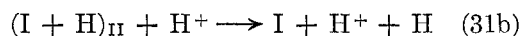
Eq.	$2a\sqrt{\pi k_{H+H^+}}$ , mole <sup>-1/2</sup> l. <sup>1/2</sup>	$\gamma_r I + \gamma_r II$	$\beta_{II}'$
23	1.57	$0.092 \pm 0.003$	
15	1.2	$0.100 \pm 0.01$	
35	2.6		1
11	2.55		0.8

The inspection of the results obtained for H atom scavenging by  $H^+$  and methanol indicates that the rate constants  $k_{H+H^+}$  and  $k_{H+MeOH}$  are comparable. Application of the "absolute" rate constant<sup>15</sup>  $k_{H+MeOH} = 10^5$  l. mole<sup>-1</sup> sec.<sup>-1</sup> obtained from radiation chemical study at low pH leads to the estimation  $k_{H+H^+} = 5 \times 10^4$  l. mole<sup>-1</sup> sec.<sup>-1</sup>, lower than our previous tentative estimation.<sup>1</sup>

The scavenging reaction 31 may proceed by the formation of  $H_2^+$



or alternatively by a charge transfer from H to  $H^+$ <sup>1</sup>



leading to the separation of H and I which is kinetically equivalent to scavenging.

In a previous work<sup>1</sup> we attempted to discard the mechanism involving  $H_2^+$  formation as it was previously shown that this reaction is a relatively slow process.<sup>16</sup> The kinetic treatment presented in that work<sup>16a</sup> involves a homogeneous kinetic treatment<sup>16b</sup> that leads to a lower limit for the rate constant,<sup>16b,c</sup> which may be underestimated by one order of magnitude. Thus the reaction mechanism 31a cannot be definitely excluded.<sup>17</sup>

**Scavenging Mechanism by the Aliphatic Alcohols.**—Hydrogen atoms will react with aliphatic alcohols by hydrogen atom abstraction. The scavenging mechanisms by the two alcohols will be presented in the form



(15) J. Rabani, *J. Phys. Chem.*, **66**, 361 (1962).

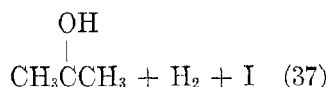
(16) (a) G. Czapski, J. Jortner, and G. Stein, *ibid.*, **63**, 1769 (1959); (b) **65**, 956 (1961); (c) **65**, 960 (1961).

(17) The charge transfer mechanism (31b) requires that in acid solutions, deuterium atoms should exchange with water at a rate which is at least as high as  $k_{H+H^+}$  observed in this work. The available experimental data show that this exchange reaction is slow. (T. W. Davis, S. Gordon, and E. J. Hart, *J. Am. Chem. Soc.*, **80**, 4487 (1958); H. L. Friedman and A. H. Zeltman, *J. Chem. Phys.*, **28**, 878 (1958); K. C. Kurien and M. Burton, Summary of Proceedings of the Fourth Informal Conference on the Radiation Chemistry of Water, University of Notre Dame, Indiana, 1961.) The lack of exchange in the case of  $H_2^+$  may be resolved, *e.g.*, by assuming that in the species usually referred to as the solvated hydrogen molecule ion the protons are not equivalent.

TABLE II

INITIAL QUANTUM YIELDS IN EVACUATED KI SOLUTIONS IN THE PRESENCE OF ALCOHOLS.  $[I^-] = 0.15 M$ 

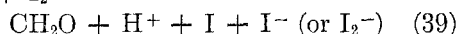
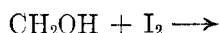
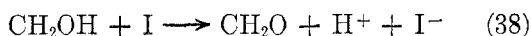
System	Concn., mole l. <sup>-1</sup>	pH	$\gamma(I_2)$	$\gamma(H_2)$	$\gamma(CH_2O)$
Isopropyl alc.	1	2.05	$10^{-3}$	$0.28 \pm 0.01$	
Isopropyl alc.	1	3.40	$10^{-3}$	$.24 \pm .01$	
Isopropyl alc.	$4.3 \times 10^{-3}$	2.92	$6 \times 10^{-3}$	$.26 \pm .01$	
Methanol	$2.2 \times 10^{-1}$	2.92	$10^{-3}$	$.26 \pm .01$	$0.27 \pm 0.02$



Very low  $I_2$  yields are obtained in the presence of alcohols. These results are summarized in Table II.

The low  $\gamma$  values for  $I_2$  production are due to back reactions.

In methanol solution the radical  $CH_2OH$  formed acts as a reducing agent in the reactions leading to the formation of formaldehyde.



The presence of formaldehyde in irradiated methanol solution was confirmed by analysis with chromotropic acid. The quantum yield of  $CH_2O$  in this system yields

$$\gamma(H_2) = \gamma(I_2) + \gamma(CH_2O)$$

The experimental results lead to a reasonable material balance.

**The Effect of Monophosphate Ion in the Presence of Alcohols.**—An interesting influence of the  $H_2PO_4^-$  ion on the reaction mechanism was observed in neutral solutions. At pH 6.25 we find  $\gamma(H_2) = 0.05$  in 1 *M* isopropyl alcohol solution in the presence of  $5 \times 10^{-3}$  *M*  $KH_2PO_4$ . This value is higher than  $\gamma(H_2) = 0.033$  obtained at this pH in the absence of the monophosphate ion. In the same system at pH 5.92 in the presence of 1 *M*  $KH_2PO_4$  we obtain  $\gamma(H_2) = 0.23$  compared with  $\gamma(H_2) = 0.040$  in the absence of monophosphate. These preliminary results indicate a specific effect of the monophosphate ion on the mechanism of the conversion of electrons of H atoms.

**The Nature of the Residual Yield in the Presence of Alcohols.**—The quantum yield  $\gamma(H_2)$  obtained in 1 *M* alcohol solutions at pH > 6 is much lower than the value 0.08 expected for the residual yield from the semiquantitative treatment of the scavenging mechanism. These results indicate that the species diffusing into the bulk are not efficiently scavenged by alcohols. Thus we conclude that the residual yield in the neutral pH region consists mainly of electrons diffusing into the bulk. The conversion of a small fraction of these electrons to H atoms, scavenged by the alcohols, may occur through the bulk reaction 32 or, alternatively, may involve a dissociative electron capture by  $H_2O^{18}$  leading to

H and  $OH^-_{aq}$ . The experimental data available in this pH region are not accurate enough to make a discrimination between these two processes possible. However, the small value of  $\gamma(H_2)$  in this region indicates that these reactions are not efficient. In alkaline solutions at pH 14 the quantum yield in the presence of 1 *M* methanol or isopropyl alcohol was found to be less than 0.005. Similar results on the effect of alkali on the residual yield were obtained by Norrish and Edgecombe.<sup>19</sup>

**Photochemistry of  $I^-$  in the Presence of Methanol in  $D_2O$ .**—The decrease of  $\gamma(H_2)$  with decreasing methanol concentration at constant pH is attributed to secondary recombination of I and H atoms. A further support to the assumption that this decrease is not due to bulk recombination reactions was obtained from experiments in  $D_2O$ . The isotopic composition of the gas produced by irradiation of  $I^-$  in 98%  $D_2O$  in the presence of  $CH_3OD$  is presented in Table III.

TABLE III

PHOTOCHEMISTRY OF 0.15 *M* KI IN 98%  $D_2O$  IN THE PRESENCE OF  $CH_3OD$ .  $H_2SO_4 = 1.4 \times 10^{-3}$  *N*

$CH_3OD$ , <i>M</i>	$\gamma$ in $D_2O$	$\gamma$ in $H_2O$	HD, %	$H_2$ , %	$D_2$ , %	(H/D) <sub>g</sub>
0.22	0.33	0.260	89.8	9.6	0.6	1.22
0.055	0.22	0.185	91.7	7.3	1	1.10

These results indicate that the quantum yields for gas evolution in  $D_2O$  are higher than in  $H_2O$ . The results for ordinary water are presented for comparison in the third column of Table III. These conclusions were confirmed by a detailed investigation of the photochemistry of  $I^-$  in  $D_2O$ .<sup>20</sup> In  $D_2O$  a similar dependence of  $\gamma$  on methanol concentration as in  $H_2O$  was observed. The main gaseous product is HD in agreement with the proposed scavenging mechanism by methanol. These results provide a further support for the cage effect in this system, ruling out the possibility that the decrease of  $\gamma$  is due to bulk recombination reactions. The minor content of  $D_2$  rules out any appreciable contribution of D atom recombination in the bulk. The increased H content in the gaseous phase compared to the hydrogen content of the solution is due to the photochemical isotope effect.<sup>21,22</sup> The results presented in Table III yield an isotope separation factor  $S = (D/H)_l \times (H/D)_g$  of the order of 5 in qualitative agreement with previous results.

**The Applicability of the Scavenging Equations.**—The experimental results of the present work can

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

(20) J. Jortner, M. Ottolenghi, and G. Stein, to be published.

(21) A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **34**, 1120 (1938).

(22) J. Jortner and G. Stein, *J. Appl. Radiation and Isotopes*, **7**, 193 (1960).

(18) D. M. Lea, "Action of Radiation on Living Cells," Cambridge University Press, 1947.



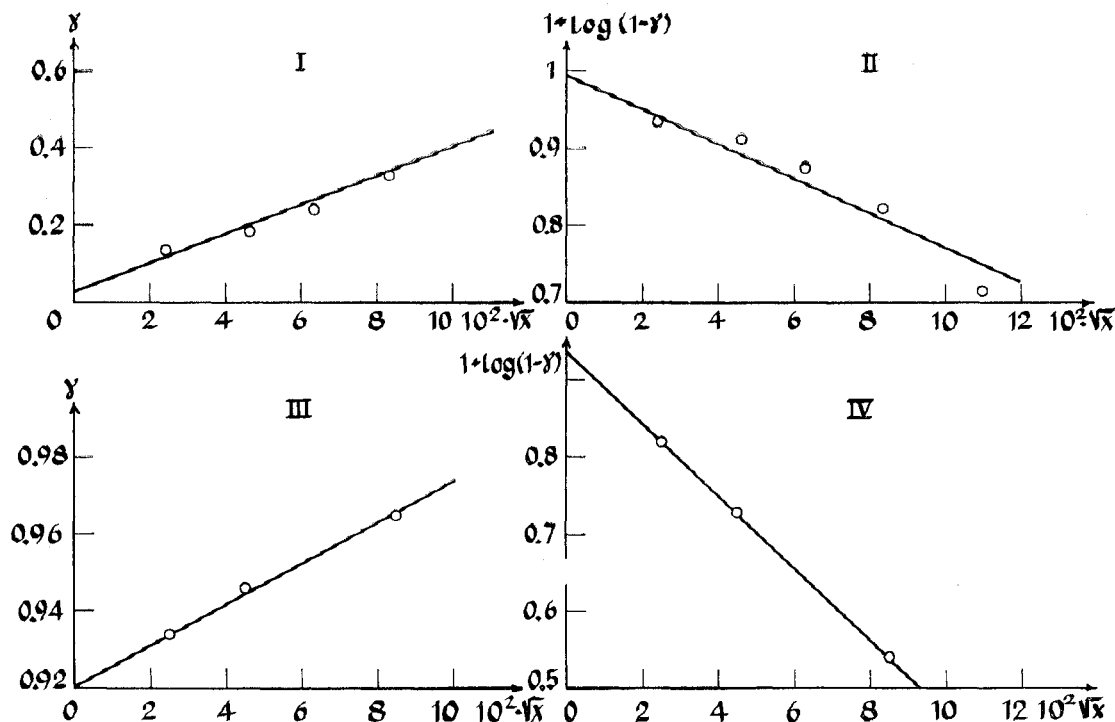


Fig. 9.—General analysis of some thermal and photochemical scavenging reactions: I, II, photolysis of azo-bis-isobutyronitrile<sup>25</sup>; I, eq. 6; II, eq. 11; III, IV, thermal decomposition of acetyl peroxide<sup>23</sup>; III, eq. 6; IV, eq. 11.

be interpreted in terms of scavenging mechanisms of two distinct species: the H atom precursors, (which presumably are electrons) and the genuine H atom. The treatment of the scavenging reaction by application of eq. 6 and 11 leads to somewhat differing results. The application of the Noyes relation (6) leads to results for the parameter  $2a\sqrt{\pi k}$  which are 30–50% lower than the results obtained from the more general eq. 11. In order to investigate this point further, the available literature,<sup>23–27</sup> which can be interpreted in terms of radical scavenging competing with secondary recombination of a radical pair, was treated by application of eq. 6 and 11. These results include the photolysis of azo-bis-isobutyronitrile<sup>25</sup> and the thermal decomposition of acetyl peroxide.<sup>23b</sup> The experimental results for the photodissociation of the trihalide ions<sup>23a</sup> were not applied as the value of  $\Gamma$  is not available. These experimental results are reproduced in Fig. 9 and in Table IV.

The scavenging parameters obtained for these two systems show the same trend as indicated by our results. We attribute the discrepancy between the results of eq. 6 and 11 to the approximations involved in our treatment. It was assumed that the reactivity of the radicals with the scavenger is independent of the time since its formation. However the rate constant  $^0k$  applicable

TABLE IV  
APPLICATION OF EQUATIONS 11 AND 6 TO  
DIFFUSION-CONTROLLED SCAVENGING PROCESSES

System	Scavenger	$\Gamma$	$\beta'$	$\gamma_r$	$2a\sqrt{\pi k}$ , mole <sup>1/2</sup> l <sup>-1/2</sup> , Eq. 6	Eq. 11
Photolysis of Azo-bis-isobutyronitrile in benzene soln. (ref. 25)	I <sub>2</sub>	1	~1	0.03	1.2	1.8
Thermal decomposition of acetyl peroxide in toluene soln. (ref. 23b)	I <sub>2</sub>	1	0.08	0.015	0.17	0.29

to the initial reactivity and the long-time rate constant  $k$  are related by<sup>2,10</sup>

$$k = ^0k(1 - \beta') \quad (40)$$

For the scavenging mechanism in the case of the iodide system we find  $\beta' = 0.7$ . Thus the scavenging rate constant decreases by a factor of 3 until its final long-time value is reached. The Noyes relations 6 and 23 are applicable for low scavenger concentration in the region where the long-time rate constant can be applied. On the other hand the slope of the curve obtained by application of eq. 11 is mainly determined by experimental results at high scavenger concentrations. This procedure leads to higher values of the scavenging rate constant. As this complication was not taken into account in the present work the treatment should be regarded as semiquantitative and the scavenging parameters as approximate.

The treatment presented in this work did not take into account ionic effects on reaction rates between the scavengers and the species scavenged. As this latter may be the negatively charged electron, the distribution of ionic scavengers and the presence of added ions may be of some influence.

**Acknowledgment.**—This work was sponsored by the Israel Atomic Energy Commission.

(23) (a) J. C. Roy, W. H. Hamill, and R. R. Williams, *J. Am. Chem. Soc.*, **77**, 2953 (1955); (b) *J. Phys. Chem.*, **60**, 823 (1956).

(24) D. L. Banbury, R. R. Williams, and W. H. Hamill, *J. Am. Chem. Soc.*, **78**, 6228 (1956).

(25) J. C. Roy, J. R. Nash, R. R. Williams, and W. H. Hamill, *ibid.*, **78**, 519 (1956).

(26) J. R. Nash, R. R. Williams, and W. H. Hamill, *ibid.*, **82**, 5974 (1960).

(27) H. A. Gillis, R. R. Williams, and W. H. Hamill, *ibid.*, **83**, 17 (1961).