is endothermic to the extent of 0.6 e.v., and so could only occur before electrons have slowed down to thermal energies. From early experiments in the gas phase, the probability of electron capture in this reaction reaches a maximum at 0.5 e.v.[17] but more recent work indicates that the probability is at a maximum at a slightly higher value.[18] The recent data are more extensive, and in better agreement with the thermochemistry of the system. To calculate the yield for electron capture we may accept provisionally the figure of 5×10^{-4} for the maximum probability of capture at a collision.[17] For simplicity of calculation we can further assume that the capture probability is 3×10^{-4} in the range 1.5–0.5 e.v., and zero outside this range. Now if we assume with Magee[19] that an electron loses about 2% of its energy per collision (the exact value depends on the medium, but no value is available for cyclohexane), then the electron collides about fifty times in slowing down from 1.5 to 0.5 e.v. For the highest hydrogen chloride concentration employed in our experiments, about 1%, the number of collisions with HCl would be 0.5. Hence the probability of a given electron being captured by hydrogen chloride is at most 1.5×10^{-4}. Assuming a yield of $G = 3$ for the production of electrons, the yield for electron capture by HCl is $G < 4.5 \times 10^{-4}$, which is negligible. The principal uncertainties in this calculation are the assumption of the values of 3×10^{-4} for the capture probability and of 2% for the percentage energy loss per collision, but these values between them would have to be low by at least a factor of 10^{-3} to affect the argument, and this seems unlikely. The argument so far applies to the gas phase. In the liquid phase it is possible that electron capture by "solvated" hydrogen chloride might be associated with the formation of molecular hydrogen in the reaction

$$e + C_6H_{12}\cdot HCl \longrightarrow C_6H_{11} + H_2 + Cl^-$$

but this reaction is endothermic to the extent of 0.1 e.v., and the above argument still applies. The conclusion that hydrogen chloride does not capture electrons in the present system is reinforced by our results with ultraviolet light of a wave length which could not produce ionization. The effects obtained are very similar to those with γ-rays, showing that the γ-ray result should be explicable without postulating electron capture.

In view of the above process of elimination we are inclined to conclude that the radiolysis products must arise in some way from the reactions of excited molecules. Unfortunately no reactions seem to have been reported in the literature which could provide a precedent for the present case. The simplest reaction scheme would be

$$C_6H_{12} \longrightarrow C_6H_{12}^*$$

$$C_6H_{12}^* + HCl \longrightarrow C_6H_{11}Cl + H_2$$

$$C_6H_{12}^* \xrightarrow{HCl} C_6H_8 + 2H_2$$

but this is highly speculative and further work is required. It may well be that similar reactions of excited molecules are occurring in other systems, for example those studied by Williams and Hamill, but that knowledge of their existence has so far been obscured by other possibilities.

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[17] N. E. Bradbury, *J. Chem. Phys.*, **2**, 827 (1934); H. S. W. Massey, "Negative Ions," 2nd edition, Cambridge, 1950, p. 76.

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[19] J. L. Magee, *Ann. Rev. Nuclear Sci.*, **3**, 171 (1953).

THE MECHANISM OF OXIDATION BY HYDROGEN ATOMS IN AQUEOUS SOLUTION. I. MASS TRANSFER AND VELOCITY CONSTANTS

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The conditions of the oxidation of various scavengers in aqueous solution by atomic hydrogen introduced from the gas phase were investigated experimentally and theoretically. Approximate equations are derived for the kinetics in the case of purely diffusion controlled mass transfer of H atoms and for the case of forced convection. First-order reaction with the scavenger in competition with second-order recombination, as well as consecutive scavenging mechanisms are considered. The results are compared with the treatment based on homogeneous kinetics.

In the investigation[1] of the reactions of H atoms with various scavengers atomic hydrogen was produced in the gas phase and introduced into the aqueous solution containing the scavenger. In this heterogeneous system we assumed, in view of the vigorous bubbling and stirring occurring under our experimental conditions, that homogeneous kinetics will provide a good approximation to the actual situation. In the present paper this assumption is examined and the conditions under which our work is carried out is investigated both experimentally and theoretically.

Mass transfer problems in heterogeneous systems are of great interest in several fields of chemical kinetics. They have been investigated[2–5] mainly

[1] (a) G. Czapski and G. Stein, *Nature*, **182**, 598 (1958); (b) G. Czapski and G. Stein, *J. Phys. Chem.*, **63**, 850 (1959); (c) G. Czapski, J. Jortner and G. Stein, *ibid.*, **63**, 1769 (1959); (d) G. Czapski and G. Stein, *ibid.*, **64**, 219 (1960).

[2] L. L. Bircumshaw and A. C. Riddeford, *Quart. Rev.*, **6**, 157 (1952).

[3] T. K. Sherwood, "Mass Transfer between Phases," Pennsylvania State University, 1959.

[4] P. V. Danckwerts, *Trans. Faraday Soc.*, **46**, 300 (1950).

to establish the rate of transfer of the reacting species under the effect of chemical reaction. Under our experimental conditions there is vigorous bubbling and stirring by the H_2 gas. We assume that under these conditions the actual rate of introduction of atomic H will be independent of changes in scavenger concentration. We also assume that scavenger concentration is constant and scavenger depletion does not occur during the reaction. Thus not the "film theory"[3] which predicts linear increase of the mass transfer coefficient with the scavenger concentration for pseudo first-order reactions, but an approach similar to that of the "penetration theory"[3] will be adopted.

In our case there is competition between the second-order recombination of H atoms and their first-order reaction with the dissolved scavenger. The application of non-homogeneous kinetics to this system will enable us to establish the reaction mechanisms and determine the rate constants in the extreme case of completely non-homogeneous conditions; compare these values with those obtained from treatment assuming homogeneous conditions and to estimate how far under our experimental conditions one or other of these extreme cases is approached.

Experimental

Under our conditions atomic hydrogen is produced by a high frequency discharge in pure H_2 gas at pressures of ~30 mm. and it reaches the reaction vessel, being pumped through it at a velocity of the order of 150 liter min.$^{-1}$. H atoms are by then present in high dilution in the H_2 gas. The bubbling introduces H atoms by repeated brief exposures of the surface elements of the liquid phase. The exposure period is of the order of 0.1 sec. Vigorous stirring occurs and mass transfer is by diffusion and forced convection. We assume accordingly continuous renewal of the phase boundary.

Efficiency of Forced Convection.—To investigate the efficiency of stirring by bubbling stroboscopic photography was used under usual conditions of operation. Photographs were obtained using a Dumont Oscillograph Record Camera Type 321-A at film travel velocities of 3600 and 10800 inches per minute. The light source used was Strobolux Type 618-A, the trigger circuit was Strobotac Type 631-B58, both instruments manufactured by General Radio Co. Flash duration was 5×10^{-6} sec. The time intervals used were $^1/_{60}$ and $^1/_{180}$ sec. From consecutive photographs obtained at known time intervals and from the known dimensions of the reaction vessel we estimate that the velocity of the liquid under stirring is of the order of 100 cm. sec.$^{-1}$.

Effect of Changing Bubbler Size.—The reduction of Ag^+ ions by H atoms is independent of Ag^+ concentration in the region above 0.05 M.[6] In this concentration region it was found that changing the bubbler diameter from 1 to 6 mm. had no effect on the reduction yield. There was no change in the reduction yield when the solution volume was changed by a factor of three. These observations indicate that the dose of H atoms is constant.

The effect of mass transport was investigated in the oxidation of 10^{-2} M Fe^{2+} solutions in 0.8 N H_2SO_4 by H atoms. In this region the oxidation yield is dependent on Fe^{2+} ion concentration. The inlet tube was exchanged for one ending above the surface of the solution. When the gas was passed above the quiescent solution about 20% of the oxidation yield under bubbling conditions was obtained. Next, arrangements were made for stirring with a magnetic stirrer. When the solution was vigorously stirred and the gas passed above it the yield was about 50% of that obtained under bubbling conditions. These results show the importance of mass transfer processes in these systems. However when the gas was bubbled through the solution, additional vigorous stirring with a magnetic stirrer had no effect on the yield. This indicates that the assumption of constant scavenger concentration is justified.

The Steady-state Treatment.—The mathematical treatment of the problem is based on the assumption that the concentration change at a certain point is due to transport processes and chemical reaction occurring simultaneously

$$\partial c/\partial t = (\partial c/\partial t)_{\text{transport}} + (\partial c/\partial t)_{\text{reaction}} \qquad (1)$$

We consider now the kinetic scheme

$$H + S \longrightarrow \text{products} \quad k_S \qquad (2.1)$$

$$2H \longrightarrow H_2 \quad k_r \qquad (2.2)$$

where k_S denotes the velocity constant of the reaction of H atoms with the scavenger, S, and k_r that of the recombination reaction. Thus

$$-(\partial[H]/\partial t)_{\text{reaction}} = k_S[S][H] + k_r[H]^2 \qquad (3)$$

the rate constants being in units of mole^{-1} cm.^{3}.

Throughout this treatment steady state is assumed. The justification of this assumption in some simple cases will be given. Setting

$$\partial[H]/\partial t = 0 \qquad (4)$$

we get

$$(\partial[H]/\partial t)_{\text{transport}} = k_S[S][H] + k_r[H]^2 \qquad (5)$$

The solution of equation 5 has to be subjected to the boundary conditions

$$X \longrightarrow \infty \ [H] = 0 \text{ and } d[H]/dX = 0 \qquad (6)$$

where X represents the distance from the boundary, and subject to the law of mass conservation

$$\int(\partial[H]/\partial t)_{\text{transport}}\, dV = A \qquad (7)$$

where V is the total volume of the system and A is the rate of introduction of atomic hydrogen expressed in moles sec.$^{-1}$ A one-dimensional model for transport processes will be employed. Thus we set

$$dV = \varphi\, dX \qquad (8)$$

where φ is the mean surface area for the mass transfer process.

The Diffusion Model.—First we shall assume that during the brief exposure of the surface mass transfer occurs by diffusion only

$$(\partial[H]/\partial t)_{\text{transport}} = D(\partial^2[H]/\partial X^2) \qquad (9)$$

where D is the diffusion coefficient of H atoms, for which we assume a value of 4×10^{-5} cm.^{2} sec.$^{-1}$. Two simple cases will be considered. For a first-order reaction, as in 2.1, from equations 5 and 9.

$$\partial^2[H]/\partial X^2 = \beta[H] \qquad (10)$$

where $\beta = k_S[S]/D$, leading to the solution

$$[H] = [H]_0 e^{-\beta^{1/2}X} \qquad (11)$$

where $[H]_0$ is the concentration of H atoms at the surface, $X = 0$, obtained by applying condition 7.

$$[H]_0 = A/\sqrt{k_S[S]D\phi} \qquad (12)$$

For a second-order reaction as in equation 2.2

$$\partial^2[H]/\partial X^2 = \alpha[H]^2 \qquad (13)$$

where $\alpha = k_r/D$. The solution is

$$[H] = 1/\{(1/[H]_0) + \sqrt{(\alpha/6)}\,X\}^2 \qquad (14)$$

where

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(5) A. Wheeler, *Advances in Catalysis*, **3**, 249 (1951).

(6) G. Czapski and G. Stein, to be published.

$$[\mathrm{H}]_0 = (1/\varphi^{2/3})(3A^2/2k_rD)^{1/3} \qquad (15)$$

We attempt now to consider the general case where competition between second-order recombination and first-order scavenging reaction occurs. We obtain the equation

$$\partial^2[\mathrm{H}]/\partial X^2 = \alpha[\mathrm{H}]^2 + \beta[\mathrm{H}] \qquad (16)$$

the proper solution of which is

$$[\mathrm{H}] = (6\beta/\alpha)\{(ae^{-\sqrt{\beta}X})/(1 - ae^{-\sqrt{\beta}X})^2\} \qquad (17)$$

where

$$a = \left\{\left(\frac{2}{3}\,\alpha[\mathrm{H}]_0 + \beta\right)^{1/2} - \beta^{1/2}\right\} \Big/ \left\{\left(\frac{2}{3}\,\alpha[\mathrm{H}]_0 + \beta\right)^{1/2} + \beta^{1/2}\right\} \qquad (18)$$

$[\mathrm{H}]_0$ is again determined by applying equation 7 in the form

$$A = \int(k_r[\mathrm{H}]^2 + k_S[\mathrm{S}][\mathrm{H}])\,\mathrm{d}V \qquad (19)$$

Applying the expressions

$$\int[\mathrm{H}]\,\mathrm{d}X = (6\beta^{1/2}/\alpha)\,\{a/(1 - a)\} \qquad (20)$$
$$\int[\mathrm{H}]^2\,\mathrm{d}X = (6\beta^{3/2}/\alpha^2)(3a^2 - a^3)/(1 - a)^3$$

equation 19 is now obtained in the form

$$2\Delta^3 + 3\Delta^2 + \Delta = W \qquad (21)$$

where

$$\Delta = a/(1 - a) \qquad (22)$$

$$W = (k_rA)/\{6(k_S[\mathrm{S}])^{3/2}D^{1/2}\varphi\} \qquad (23)$$

The yield, Y, of the scavenging reaction 2.1 will be given by

$$Y = k_S[\mathrm{S}]\int[\mathrm{H}]\,\mathrm{d}V \qquad (24)$$

Thus we obtain

$$Y = A\Delta/W \qquad (25)$$

Y is expressed in units of mole sec.$^{-1}$.

In practice equation 21 was solved numerically for values of W from 100 to 0.001. The best value of $k_S\varphi^{2/3}$ was obtained by trial and error. Using selected values of $k_S\phi^{2/3}$, W was calculated from eq. 23 and then Δ was obtained. Hence Y was calculated from eq. 25. This procedure was repeated until best agreement with experiment was obtained.

It is of interest to test the limiting values of the solutions of eq. 21.

For high concentrations of S, $W \rightarrow 0$ and thus $\Delta \rightarrow 0$. Therefore $\Delta >> \Delta^2$, Δ^3 and thus $\Delta = W$ and $Y = A$. For very low concentrations of S, $W \rightarrow \infty$ and thus $\Delta = (^1/_2 W)^{1/3}$. We then obtain

$$Y_{([\mathrm{S}]\rightarrow 0)} = k_S[\mathrm{S}]\phi^{2/3}(18DA/k_r^2)^{1/3} \qquad (26)$$

This result can be readily obtained from equations 14 and 24.

Time Dependent Solution.—In order to test the adequacy of the steady-state treatment the time dependent solution was considered, for the first-order reaction. Equation 27

$$\partial[\mathrm{H}]/\partial t = D\partial^2[\mathrm{H}]/\partial X^2 - k_S[\mathrm{S}][\mathrm{H}] \qquad (27)$$

can be solved using Danckwerts' treatment[4] or the Laplace transform method.[7] Equation 27 is solved under the initial conditions of $[\mathrm{H}] = 0$ for $t = 0$, and $[\mathrm{H}] = [\mathrm{H}]_0$ for $t > 0$ at $X = 0$. The solution is obtained in the form

$$[\mathrm{H}] = ([\mathrm{H}]_0/2)\,[\exp(-X\sqrt{k_S(\mathrm{S})/D})\,\mathrm{erfc}\,\{(X/2\sqrt{Dt}) - (k_S[\mathrm{S}]t)\} + \exp(X\sqrt{k_S(\mathrm{S})/D})\,\mathrm{erfc}\,\{(X/2\sqrt{Dt}) + (k_S[\mathrm{S}]t)\}] \qquad (28)$$

The total amount of H atoms absorbed per unit time is given by

$$\int D\,\mathrm{grad}\,[\mathrm{H}]\,\mathrm{d}\varphi = ([\mathrm{H}]_0/\sqrt{k_S[\mathrm{S}]D})\,\{(\mathrm{erf}\,\sqrt{k_S[\mathrm{S}]t}) + \exp(-k_S[\mathrm{S}]t)/\sqrt{\pi k_S[\mathrm{S}]t}\} \qquad (29)$$

For a sufficiently high value of t, when erf $\sqrt{k_S[\mathrm{S}]t} \cong 1$, expressions 28 and 29 reduce to equations 11 and 12 obtained under steady-state approximation. The required condition is that

$$t \sim (k_S[\mathrm{S}])^{-1} \qquad (30)$$

Under our experimental conditions k_S is of the order of 10^5 liter mole^{-1} sec.$^{-1}$, $[\mathrm{S}] \sim 10^{-3}$ to 1 M, so that the steady-state approximation appears to be reasonable. It is interesting to point out that the condition of 30 is almost identical with the condition for the application of steady-state treatment in homogeneous kinetics, which we considered previously.[1c] However this solution yields only the lower limit for the time required for the establishment of steady-state conditions.

Forced Convection Model.—In the preceding treatment we restricted the role of stirring to ensure quasi homogeneous scavenger concentration and assumed that scavenger depletion can be neglected. We shall now consider the effect of stirring on the mass transfer process. The quantitative treatment for forced convection will be based on the well known general equation

$$(\partial[\mathrm{H}]/\partial t)_{\mathrm{transfer}} = D\,\mathrm{div}\,\mathrm{grad}\,[\mathrm{H}] - \mathcal{V}\,\mathrm{grad}\,[\mathrm{H}] \qquad (31)$$

where $\mathcal{V}$ is the velocity vector of the liquid with component u parallel to the x axis. For the one-dimensional case under steady-state conditions

$$D(\partial^2[\mathrm{H}]/\partial X^2) - u(\partial[\mathrm{H}]/\partial X) - k_S[\mathrm{S}][\mathrm{H}] - k_r[\mathrm{H}]^2 = 0 \qquad (32)$$

In the case when recombination may be neglected eq. 32 reduces to

$$\partial^2[\mathrm{H}]/\partial X^2 - \gamma(\partial[\mathrm{H}]/\partial X) - \beta[\mathrm{H}] = 0 \qquad (33)$$

where $\gamma = u/D$. The solution is

$$[\mathrm{H}] = (A\eta/k_S[\mathrm{S}]\varphi)e^{-\eta X} \qquad (34)$$

where

$$\eta = -u/2D + \{(u^2/4D^2) + (k_S[\mathrm{S}]/D)\}^{1/2} \qquad (35)$$

It will be seen that transport by diffusion can be neglected compared with transport by convection, when

$$u^2/4D^2 \gg k_S[\mathrm{S}]/D \qquad (36)$$

or alternatively when

$$u \gg 2\sqrt{k_S[\mathrm{S}]D} \qquad (36)$$

Using the numerical values of $k_S[\mathrm{S}] = 10^4$ sec.$^{-1}$ and $D = 4 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ it is found that when $u >> 1.2$ cm. sec.$^{-1}$ mass transport by convection only has to be considered. For these relatively high u values eq. 34 is reduced to the form

$$[\mathrm{H}] = (A/u\varphi)e^{-k_S[\mathrm{S}]X/u} \qquad (34')$$

We shall now consider the general case when diffusion can be neglected in comparison by convection. Equation 32 will be given in the form

$$\partial[\mathrm{H}]/\partial X + \omega[\mathrm{H}] + \epsilon[\mathrm{H}]^2 = 0 \qquad (37)$$

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(7) J. Crank, "The Mathematics of Diffusion," Oxford Univ. Press, 1956, p. 18ff.

where $\omega = k_S[S]/u$ and $\epsilon = k_r/u$. The solution is

$$[H] = \omega b e^{-\omega X}/(1 - b\epsilon e^{-\omega X}) \qquad (38)$$

where $b = [H]_0/(\omega + \epsilon[H]_0)$. Application of condition 7 gives

$$b = Au/(k_S[S]\varphi u + k_r A) \qquad (39)$$

and by using eq. 24 the yield is given by

$$Y = (k_S[S]\varphi u/k_r) \ln \{1 + (Ak_r/k_S[S]\varphi u)\} \qquad (40)$$

Experimental results can be fitted to equation 40 by choosing the best value for the parameter $(k_S\varphi u)$.

Comparison with Homogeneous Kinetics.—The results of the present treatment based on heterogeneous kinetics will now be compared with the homogeneous kinetic treatment. The steady-state treatment of the competitive reactions of equations 2.1 and 2.2 based on homogeneous kinetics leads to

$$Y = \tau[S]^2V\{\sqrt{1 + (2A/\tau[S]^2 V)} - 1\} \qquad (41)$$

where $t = k_S{}^2/2k_r$. In the scavenger concentration region where [S] is sufficiently low and the steady state concentration of the H atoms is determined by the recombination reaction, the homogeneous kinetic treatment leads to the result

$$Y_{([S]\rightarrow 0)} = k_S[S](AV/k_r)^{1/2} \qquad (42)$$

The most reliable values for the scavenging rate constant were obtained from experiments at low scavenger concentrations. We shall therefore compare the values of apparent rate constant obtained for the homogeneous treatment according to equation 42, with the value obtained in the case of purely diffusion controlled kinetics, for which at low scavenger concentrations equation 26 holds. We obtain for the ratio of the apparent rate constants obtained from homogeneous and diffusion controlled treatments

$$\frac{k_S{}^{\text{diff}}}{k_S{}^{\text{homo}}} = \frac{(k_rA)^{1/6}\ V^{1/2}}{18^{1/3}\ D^{1/3}\ \varphi^{3/3}} \cong \frac{500}{\varphi^{2/3}} \qquad (43)$$

where the numerical value is obtained by setting $A = 5 \times 10^{-8}$ mole sec.$^{-1}$ and $V = 25$ cm.^{3}. The effective area φ can only be approximately estimated under our conditions of bubbling; it is of the order of 10 cm.^{2}. Thus we conclude that were the situation such, that forced convection is completely absent and mass transfer is by diffusion only, the rate constant evaluated from homogeneous kinetics would be an underestimate by some two orders of magnitude.

We shall now compare with this most extreme case our actual experimental conditions where forced convection occurs. It was shown that when the linear velocity of stirring, u, exceeds 1.2 cm. sec.$^{-1}$, transport by convection outweighs transport by diffusion. Under these conditions at low scavenger concentrations we obtain for the yield

$$Y_{([S]\rightarrow 0)} = \frac{k_S{}^{\text{f.c.}}[S]\varphi u}{k_r} \ln \frac{Ak_r}{k_S{}^{\text{f.c.}}[S]\varphi u} \qquad (44)$$

and for the ratio of the apparent rate constants obtained from homogeneous and forced convection treatments

$$\frac{k_S{}^{\text{f.c.}}}{k_S{}^{\text{homo}}} = \frac{(AV/k_r)^{1/2}}{(\varphi u/k_r)(\ln Ak_r - \ln B)} \cong \frac{400}{\varphi u} \qquad (45)$$

where $B = k_S{}^{\text{f.c.}}[S]\varphi u$. As $[S]\rightarrow 0$, $-\ln B$ may be neglected compared with $\ln AK_r'$ and introducing then the numerical values the final result shown is obtained. We see that as expected the existence of forced convection expressed through the introduction of the stirring velocity, brings the constant obtained by the homogeneous treatment nearer to the true value. The treatment is necessarily very approximate, but it does show, that as the value of $\varphi u \rightarrow 100$ cm.^{3}sec.$^{-1}$, the experimental constants obtained under our conditions of forced convection will approach within an order of magnitude those obtained assuming homogeneous kinetics.

Consecutive Scavenging Mechanism.—We shall now examine the question whether the assumption of homogeneous kinetics in a case where diffusion and/or forced convection occur may lead to the derivation of reaction mechanisms which correspond to the true state of affairs.

We shall consider that the reactions of H atoms with scavengers may proceed by a composite mechanism involving the formation of a reactive intermediate. The general kinetic scheme can be represented as

$$H + S_1 \underset{k_{-S_1}}{\overset{k_{S_1}}{\rightleftarrows}} HS_1 \qquad (44)$$

$$HS_1 + S_2 \xrightarrow{k_{S_2}} \text{products}$$

$$2H \xrightarrow{k_r} H_2$$

Considering mass transfer by diffusion only we obtain

$$D(\partial^2[H]/\partial X^2) = k_{S_1}[S_1][H] + k_r[H]^2 - k_{-S_1}[HS_1] \qquad (45)$$

$$D'(\partial^2[HS_1]/\partial X^2) = -k_{S_1}[S_1][H] + k_{-S_1}[HS_1] + k_{S_2}[S_2][HS_1]$$

where D and D' are the diffusion coefficients of H atoms and of the HS_1 intermediate complex. Assuming no depletion of the scavengers S_1 and S_2 the yield will be

$$Y = k_{S_2}[S_2]\int[HS_1]dV \qquad (46)$$

The system of diffusion equations 45 was solved under the following simplifying assumptions: as $D>D'$ and $[H]>[HS_1]$, the diffusion of the active intermediate HS_1 was neglected and its concentration was expressed by ordinary steady-state expression. A similar approach was employed by Semenov[8] for some gas phase reactions. We obtain

$$[HS_1] = (k_{S_1}[S_1][H])/(k_{-S_1} + k_{S_2}[S_2]) \qquad (47)$$

The two diffusion equations are then replaced by the single one

$$\partial^2[H]/\partial X^2 = \alpha[H]^2 + \beta_1[H] \qquad (48)$$

$$\beta_1 = k_{S_1}[S_1]/(D\{(k_{-S_1}/k_{S_2}) + [S_2]\}) \qquad (49)$$

The expression obtained is identical with eq. 16. Solving according to condition 24 leads to

$$Y = A\Delta_1/W_1 \qquad (50)$$

$$W_1 = k_rA/6D^{1/2}k_{S_1}{}^{3/2}[S_1]^{3/2}\,e_{S_2}{}^{3/2} \qquad (51)(a)$$

$$e_{S_2} = [S_2]/\{(k_{-S_1}/k_{S_2}) + [S_2]\} \qquad (b)$$

Δ_1 is obtained from

$$2\Delta_1{}^3 + 3\Delta_1{}^2 + \Delta_1 = W_1 \qquad (52)$$

Considering now the case of forced convection

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(8) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Princeton Univ. Press, 1959.

when diffusion can be neglected, the corresponding equations are

$$-\partial[\mathrm{H}]/\partial X = k_{\mathrm{S}_1}[\mathrm{S}_1][\mathrm{H}] + k_r[\mathrm{H}]^2 - k_{-\mathrm{S}_1}[\mathrm{HS}_1]$$

$$-\partial[\mathrm{HS}_1]/\partial X = -k_{\mathrm{S}_1}[\mathrm{H}][\mathrm{S}_1] + k_{-\mathrm{S}_1}[\mathrm{HS}_1] + k_{\mathrm{S}_2}[\mathrm{S}_2][\mathrm{HS}_1] \quad (53)$$

and by applying equation 47 the yield is

$$Y = \{(k_{\mathrm{S}_1}\varphi[\mathrm{S}_1]e_{\mathrm{S}_2})/k_r\} \ln\{1 + (k_rA/k_{\mathrm{S}_1}\varphi[\mathrm{S}_1]e_{\mathrm{S}_2})\} \quad (54)$$

In the case of homogeneous kinetics the reaction scheme of consecutive scavenging leads to the expression

$$Y = (\tau_1 e_{\mathrm{S}_2}{}^2[\mathrm{S}_1]^2/V)(\{1 + (2AV/\tau_1 e_{\mathrm{S}_2}{}^2[\mathrm{S}_1]^2)\}^{1/2} - 1) \quad (55)$$

where $\tau_1 = k_{\mathrm{S}_1}{}^2/2k_r$.

Some general conclusions may now be derived regarding these results for homogeneous and heterogeneous kinetics. For high S_2 concentrations $e_{\mathrm{S}_2} \rightarrow 1$ and the equations reduce to those obtained for the case of a single scavenger. Therefore the rate-determining step in this case involves the formation of the HS_1 intermediate complex. At lower S_2 concentrations e_{S_2} is less than unity and for $S_2 << k_{-\mathrm{S}_1}/k_{\mathrm{S}_2}$ the kinetic equations become equivalent to those obtained for the triple collision mechanism

$$\mathrm{H} + \mathrm{S}_1 + \mathrm{S}_2 \longrightarrow \text{products} \quad (56)$$

It is found then that in this approximation both heterogeneous and homogeneous treatments lead to the result that the yield is dependent on the concentration function $e_{\mathrm{S}_2}[\mathrm{S}_1]$ alone, when the consecutive scavenging mechanism is the actually operating one.

Conclusions

The impetus for the present investigation was given by one of the referees of the original draft of what forms now Part II of the present work. He requested detailed examination of those assumptions which were made in that and previous papers based on estimation of the experimental conditions, without a quantitative basis.

As the result of the present work we conclude regarding the absolute value of the rate constants, that under our conditions of vigorous stirring and bubbling the constants derived under the assumption of homogeneous kinetics are probably lower by not more than one order of magnitude than the true ones. As we cannot determine either u or φ accurately, no closer estimate is possible of the degree of agreement. However comparison of the values thus obtained by us with values derived from other experimental investigations support this conclusion. This point will be discussed in the following papers. Similarly, reaction mechanisms derived under these conditions under the assumption that homogeneous kinetics may be applied are the mechanisms arrived at also when heterogeneous kinetics are assumed.

In view of these conclusions homogeneous kinetics will be employed in some future papers, with due reference to the considerations now obtained.

THE MECHANISM OF OXIDATION BY HYDROGEN ATOMS IN AQUEOUS SOLUTION. PART II. REACTION MECHANISMS WITH DIFFERENT SCAVENGERS

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The mechanism of oxidation by hydrogen atoms of various acceptors is discussed. It is shown that two alternative pathways exist for the oxidation of ions dissolved in water. One involves the relatively slow reaction of H atoms with H^+_{aq} to form $H_2{}^+_{aq}$, which oxidizes acceptors, *e.g.*, I^-_{aq}. Alternatively other acceptors, *e.g.*, metal cations may directly form intermediate complexes with H, with faster rate constants. The intermediate hydride complex may react with H^+_{aq}, yielding molecular hydrogen. When this faster, hydride complex, pathway is available, the slower $H_2{}^+$ mechanism may not be of kinetic importance. The experimental results for the oxidation of Fe^{2+} ions by H atoms can be adequately explained by this mechanism. The results of radiation chemical and photochemical experiments are discussed.

Investigations of the radiation chemistry[1,2] of aqueous solutions of ferrous ions led to the assumption that H atoms may act as oxidizing agents in acid solutions. Evidence from the photochemistry of ferrous[3,4] and of iodide[5,6] ions was adduced to support this view. Recently using hydrogen atoms generated externally and introduced as such into the aqueous solutions it was shown that hydrogen atoms are indeed capable of oxidizing ferrous to ferric ions[7-9] and iodide to iodine.[10] The reaction was shown to be pH dependent.[9,10] However the actual mechanism was not finally established. Namely it was proposed[1,2] that the oxidation involves the formation of $H_2{}^+_{aq}$ ion according to

$$\mathrm{H} + \mathrm{H}^+_{aq} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{H}_2{}^+_{aq} \quad (1)$$

which acts as the actual oxidizing species

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