The rate constants ratios k_2/k_1 and k_2'/k_1' indicate that H atoms as such react with chloroacetic acid mainly by hydrogen abstraction. These results should be compared with recent radiation chemical studies of this system.[5,6] Radiation chemical investigations of aqueous chloroacetic acid solutions were interpreted by Hayon and Weiss[5] by assuming that transient negative ions formed as primary products in the radiolysis of water react with monochloroacetic acid with the formation of chloride ion. These species are the precursors of H atoms which react by dehydrogenation. The quantitative study of this system by Hayon and Allen[6] indicates that the reducing radical formed from the radiolysis of water yields Cl^- ion. H^+ and chloroacetic acid compete for this radical. The product of the reaction with H^+ ion is another radical which reacts with the acid to form either Cl^- or H_2. These studies cannot determine unambiguously the nature of the two reducing radicals.[6]

The experimental results obtained in the present work in the acid region indicate no pH dependence of the chloride yield in the pH region 0.4–2. This result rules out the formation of H_2^+ under our experimental conditions, and the participation of this radical in dehydrogenation reactions. The concentration dependence of $R(Cl^-)$ at pH 1.9 and 3.3 (Table I) cannot be adequately interpreted in terms of H atoms reacting at pH > 3 and of H_2^+ reacting at pH < 2. It thus appears that the H_2^+ molecule ion is of no kinetic importance in this system. This conclusion is consistent with the low rate of formation of this species in acid solution.[8b] The rate constants ratio $k_2/k_1 = 0.5$ obtained in our experiments using H atoms as such is in good agreement with the rate constants ratio 0.55 derived by Hayon and Allen[6] for the reactivity of the acid form of H atoms (denoted as H′ by Allen)[1,2] in irradiated solutions of chloroacetic acid. This agreement indicates that the acid form of the reducing radical formed in the radiolysis of water involves an H atom as such.

Our experimental results obtained in the neutral pH region indicate that about 90% of the H atoms scavenged by chloroacetic acid lead to dehydrogenation. On the other hand, radiation chemical studies[6] indicate that at pH 5.5 the chloride yield is $G(Cl^-) = 2.8$ at 0.01 M chloroacetic acid.[6] This value is near to the standard yield of the reducing radicals in neutral solutions, obtained from the hydrogen–oxygen[14] and ethanol–oxygen[15] systems. Thus the reducing radical formed as the *main* product by radiolysis in the neutral pH region exhibits reactivity different from the H atoms. This H atom precursor is presumably the solvated electron e_{aq}. The reaction mechanism in irradiated aqueous solutions of chloroacetic acid involves the reactions

$$e_{aq} + CH_2ClCOOH \longrightarrow Cl^- + CH_2COOH \quad (6)$$

$$e_{aq} + CH_2ClCOO^- \longrightarrow Cl^- + CH_2COO^- \quad (6')$$

$$e_{aq} + H^+ \longrightarrow H \quad (7)$$

and H atoms reacting by reactions 1 and 2.

These conclusions are consistent with the results of a previous work[8f] where the reactivity of H atoms in H_2O_2 solutions was compared with the reactivity of the reducing species formed from the radiolysis of water.[1,2] The results of the present and the previous study[8f] of the reactivity of H atoms in aqueous solutions make possible an unambiguous identification of the acid form of the reducing radical produced in the radiolysis of water. These conclusions are consistent with recent tentative identifications of the pair of the reducing radicals.[4,5] The primary reducing species e_{aq} has a sufficiently long lifetime to react with active scavengers. The conversion of e_{aq} to H atoms proceeds by reaction 7 rather than by reaction with a water molecule.

NOTE ADDED IN PROOF.—Recently, kinetic salt effects were utilized (G. Czapski and H. A. Schwarz, *J. Phys. Chem.*, 66, 471 (1962)) as an evidence that the reducing radical produced in the radiolysis of neutral aqueous solutions may be identified as the solvated electron. This conclusion is in complete agreement with the results of the present work.

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THE DECOMPOSITION OF CHLOROACETIC ACID IN AQUEOUS SOLUTIONS BY ATOMIC HYDROGEN. II. REACTION MECHANISM IN ALKALINE SOLUTIONS

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The reactivity of atomic hydrogen in alkaline solutions of chloroacetic acid was investigated. The pH and concentration dependence yield kinetic evidence for the formation of H_2O^- in alkaline solutions: $H + OH^- \rightarrow H_2O^-$ with $k_{H+OH^-} = 6 \times 10^5$ l. mole^{-1} sec.$^{-1}$. These results are correlated with radiation chemical data, and the nature of the H_2O^- radical is discussed.

Introduction

In the preceding work[1] it was shown that H atoms generated in an electrodeless discharge and the reducing radicals produced by radiolysis of aqueous solutions at neutral pH[2,3] differ in their reactivity with chloroacetic acid. Aqueous solutions of

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(2) E. Hayon and J. Weiss, *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva*, **29**, 80 (1958).

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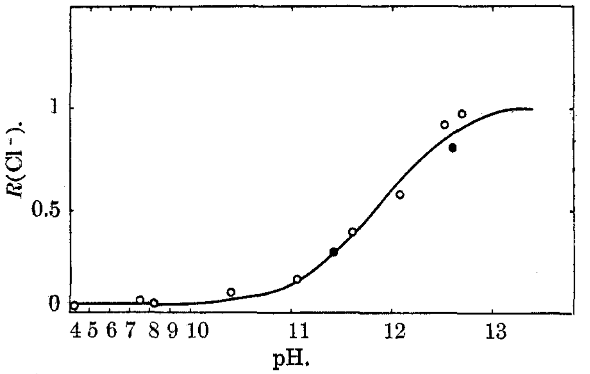

Fig. 1.—The pH dependence of $R(Cl^-)$: $[CH_2ClCOO^-] = 0.01\ M$; temperature 4°; dose rate of H atom 10^{-6} mole l.$^{-1}$ sec.$^{-1}$; volume of solution 25 cc.; duration of run 15 min.; open circles, pH adjusted with KOH; full circles, 0.25 M Na_2CO_3 added; curve calculated from eq. VI.

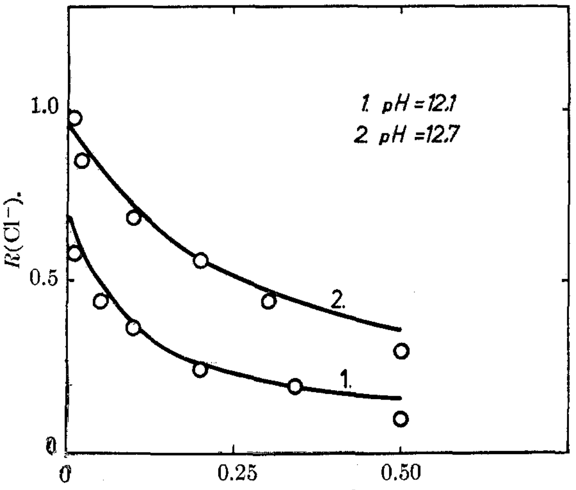

Fig. 2.—The concentration dependence of $R(Cl^-)$ at alkaline pH: experimental condition is stated in Fig. 1; curves calculated from eq. VI.

chloroacetic acid manifest different reactivity with the two forms of H atom equivalent[1-3] and are convenient for the study of H atoms in solutions. We have recently investigated the decomposition of chloroacetic acid in alkaline solutions. A preliminary report of this work was given.[4] In alkaline solutions an enhancement of chloride abstraction was observed. These results were interpreted in terms of a mechanism involving an interaction of the H atom and the OH^- ion. The species thus formed reacts with chloroacetic acid by chloride abstraction. In the present work, we present our detailed results of the reactivity of H atoms in alkaline solutions of chloroacetic acid.

Experimental

The experimental technique was the same as described in the previous work.[1] Freshly prepared solutions were always used. Solutions of chloroacetic acid in the pH region 8–13 were prepared by adjusting the pH with KOH while the solution was kept at 0°. The solutions were kept at this temperature before and after passing H atoms, which was carried out at about 4°. Blank experiments were run parallel with the analysis of irradiated solutions and corrections for hydrolysis were introduced. Chloroacetic acid solutions in the concentration region 0.01–0.05 M were found to be stable under these conditions, the amount of Cl^- did not exceed $2 \times 10^{-5}\ M$. In the concentration region 0.1–0.5 M the chloride content of the blank solutions did not exceed $2 \times 10^{-4}\ M$. Chloroacetic acid, KOH, $NaHCO_3$, Na_2CO_3, and formic acid used were of Analar grade. Water was triply distilled. Solutions were prepared in freshly boiled water. As only a negligible effect of added Na_2CO_3 on the experimental results was observed, no further precautions were necessary. pH measurements were carried out with a Metrohm pH meter equipped with an "alkaline" electrode.

Results

Chloride Yields at Alkaline pH.—The decomposition of chloroacetic acid by atomic hydrogen was investigated over the pH region 8–13 varying the chloroacetic concentration in the region 2×10^{-3}–0.5 M. From the amount of chloride produced and the dose of H atoms, the reaction yields[1] $R(Cl^-)$ for Cl^- production were obtained. The experimental results are presented in Fig. 1 and 2. These results indicate that at constant chloroacetic acid concentration, the reaction yield for Cl^- production increases with increasing pH in the pH region above 11. In this region the reaction yield for Cl^- production decreases with increasing chloroacetic acid concentration at constant pH.

We attempted to ascertain that the increase of the chloride yield at pH > 11 is not due to the hydrolysis of the reaction products, which as indicated by previous results[1,3,4] are presumably chloro derivatives of carboxylic acids. A 0.01 M chloroacetic acid solution was decomposed by H atoms at pH 7 and the pH of the solution was then adjusted to 12.6 by addition of KOH. No increase of the Cl^- concentration was observed after 1 hr. This conclusion also is consistent with the observed concentration dependence at high pH. In the previous work[1] it was shown that in the neutral pH region the chloride yield is independent of chloroacetic acid concentration in the concentration region 0.05–0.5 M. Thus in this concentration region at neutral pH, the yield of the chlorodicarboxylic acids is constant. However, in the alkaline region the concentration dependence is entirely different. These considerations rule out the above mentioned trivial mechanism of chloride production in alkaline pH.

Effects of Some Added Solutes.—In order to establish the reaction mechanism, the effect of carbonate and bicarbonate ions on the chloride yields was investigated. Experiments were carried out in the presence of $NaHCO_3$ and Na_2CO_3 (Table I). No enhanced decomposition in the presence of carbonate and bicarbonate ions was observed. On the contrary, $R(Cl^-)$ in the presence of 0.25 M Na_2CO_3 at pH 12.6 is about 15% lower than obtained at this pH in its absence.

Recent radiation chemical studies[5] indicate that H atom precursors (*i.e.*, solvated electrons) react with the HCO_3^- ion with the formation of the CO_2^- ion. It may be argued that the CO_2^- radical ion is formed in alkaline solutions by decomposition of HCO_3^- or CO_3^{-2} ion by H atoms, and that this species reacts with chloroacetic acid with Cl^- formation. This argument is not consistent with the fact that $R(Cl^-)$ is not increased by added $NaHCO_3$ and Na_2CO_3. Besides, a decrease in the chloride yield was observed in the presence of

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formate ion (Table I). This result indicates that the formate ion, $HCOO^-$, competes with the decomposition of chloroacetic acid. As dehydrogenation of the $HCOO^-$ anion leads to the formation of CO_2^-, these results indicate that this radical ion probably does not react with chloroacetic acid.

TABLE I

EFFECTS OF ADDED SOLUTES ON Cl^- YIELD IN ALKALINE SOLUTIONS OF CHLOROACETIC ACID DECOMPOSED BY ATOMIC HYDROGEN AT 4°

Dose rate of H atoms 10^{-6} mole l.$^{-1}$ sec.$^{-1}$; volume of solution 25 cc.; duration of run 15 min.

pH	CH_2Cl-COOH, mole l.$^{-1}$	Added solutes	$R(Cl^-)$
7.5	0.010	10^{-3} *M* sodium phosphate 0.25 *M* formic acid	(0.01)
7.5	.010	10^{-3} *M* sodium phosphate	.04
8.15	.010	10^{-3} *M* sodium phosphate	.05
		0.25 *M* sodium bicarbonate	.05
8.10	.010	10^{-3} *M* sodium phosphate	
11.43	.010	0.25 *M* sodium carbonate	.30
11.4	.010	KOH	.30
12.66	.010	0.25 *M* sodium carbonate	.80
12.7	.010	KOH	.95

Reaction Mechanism in Alkaline pH.—The increased chloride yields at alkaline pH are attributed to the interaction of H atom and OH^- ion with the formation of a species which will be denoted H_2O^-.

$$H + OH^- \longrightarrow H_2O \qquad (1)$$

This "alkaline" form of H atoms will react with chloroacetic acid anion by chloride formation:

$$H_2O^- + CH_2ClCOO^- \longrightarrow Cl^- + CH_2COO^- + H_2O \qquad (2)$$

Reaction 1 competes with the first-order scavenging reactions of H atoms by chloroacetic acid

$$CH_2ClCOO^- + H \longrightarrow H_2 + CHClCOO^- \qquad (3)$$

$$CH_2ClCOO^- + H \longrightarrow Cl^- + H^+ + CH_2COO^- \qquad (4)$$

At low chloroacetic acid and OH^- ion concentrations, H atom recombination should be considered

$$2H \longrightarrow H_2 \qquad (5)$$

This mechanism accounts properly for the pH and concentration dependence of $R(Cl^-)$.

Evaluation of Experimental Data.—The experimental results were treated by application of the diffusion model,[6] which is probably most adequate for semiquantitative evaluation of rate constants from such experiments. Neglecting the diffusion of the active intermediate H_2O^-,[6] the concentration of H atoms is given by the expression

$$D\frac{\partial^2[H]}{\partial X^2} = k_5[H]^2 + P[H] \qquad (I)$$

where

$$P = k_3\left\{\left(1+\frac{k_4}{k_3}\right)[CH_2ClCOO^-] + \frac{k_1}{k_3}[OH^-]\right\} \qquad (II)$$

In the present treatment the concentration of OH^- ion will be defined by $[OH^-] = 10^{-14+pH}$.

Following the notation used in previous work,[1,6] the total reaction yield for H_2 and Cl^- production is given by

$$R(Cl^-) + R(H_2) = \Delta/W \qquad (III)$$

where

$$2\Delta^3 + 3\Delta^2 + \Delta = W = \frac{k_5A}{6P^{3/2}D^{1/2}\varphi} \qquad (IV)$$

Setting the experimental value $A = 2.5 \times 10^{-8}$ mole sec.$^{-1}$, $D = 4 \times 10^{-5}$ cm.^{2} sec.$^{-1}$, and using the rate constants ratio[1] $k_4/k_3 = 0.09$ we get

$$W = \frac{6.6 \times 10^6}{\left\{1.09[CH_2ClCO_2^-] + \frac{k_1}{k_3}[OH^-]\right\}^{3/2}(k_3\varphi^{2/3})^{3/2}} \qquad (V)$$

The reaction yield for chloride production is given by

$$R(Cl^-) = \frac{0.09[CH_2ClCO_2^-] + \frac{k_1}{k_3}[OH^-]}{1.09[CH_2ClCO_2^-] + \frac{k_1}{k_3}[OH^-]}\,\frac{\Delta}{W} \qquad (VI)$$

An estimation of the rate constants ratio k_1/k_3 was carried out by using the experimental results at pH 12.7. At high OH^- concentration, H atom recombination can be neglected and then $\Delta/W = 1$. Applying this simplifying assumption, eq. VI can be written in the form

$$\frac{k_1}{k_3}[OH^-](1 - R(Cl^-)) = [CH_2ClCOO^-](1.09\,R(Cl^-) - 0.09) \qquad (VII)$$

A plot of the experimental results at pH 12.7 according to eq. VII (Fig. 3) yields a straight line with an intercept of zero, as required by eq. VI. From the slope we obtain $k_1/k_3 = 4.5 \pm 1$.

The pH dependence and the concentration dependence of $R(Cl^-)$ in alkaline solution could be adequately fitted by eq. VI setting $k_1/k_3 = 4.5$; $(k_3\varphi^{2/3})^{3/2} = 3 \times 10^9$ l.$^{3/2}$ mole$^{-3/2}$ sec.$^{-3/2}$ cm.^{2}. The value of $k_3 = 1.4 \times 10^5$ l. mole^{-1} sec.$^{-1}$ obtained by setting $\varphi^{2/3} = 10$ cm.$^{4/3}$ is consistent with the value estimated from the experimental results at neutral pH.[1]

Discussion

The comparison between the experimental results and the calculated data according to eq. VI is presented in Fig. 1 and 2. It thus appears that the experimental results are satisfactorily accounted for by the proposed mechanism involv-

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[6] G. Czapski, J. Jortner, and G. Stein, *J. Phys. Chem.*, **65**, 956 (1961).

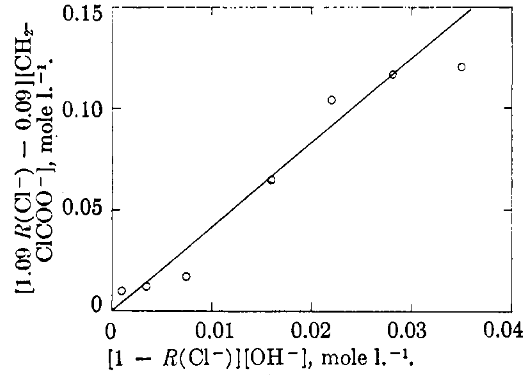

Fig. 3.—Graphical determination of the rate constants ratio k_1/k_3 according to eq. VII.

ing H_2O^- formation. The rate constant for the formation of this species is 6×10^5 l. mole^{-1} sec.$^{-1}$.

These results yield kinetic evidence for the interaction of H atom with OH^- ion in alkaline solutions. The nature of the species thus formed, which we denote H_2O^-, should be briefly considered. The product of the reaction with chloroacetic acid of the species produced under our experimental conditions is identical with that of the reducing species produced by the radiolysis of neutral aqueous solutions.[1-3] The latter species is identified as the solvated electron. The problem of electron binding in water[7-9] and in non-aqueous solutions[10,11] was treated by the application of a continuous dielectric model for the system.

The most plausible picture is an electron bound by the polarization of the dielectric medium. The electron solvated according to this model is delocalized and its charge distribution is distributed over few solvent molecules. This picture was applied for electrons produced in irradiated neutral solutions.[7-9] On the other hand, the species H_2O^- where the unpaired electron is localized on a single water molecule (presumably in a $3s\sigma$ orbital) is not stable in the gaseous phase. Experimental[12] and theoretical[13] evidence indicates that a single water molecule in the gaseous phase does not exhibit a positive electron affinity. However, in a polar medium the species H_2O^- may be stabilized by solvation. It is not clear at present whether the species produced by reaction 1 does lead to electron delocalization. We can only conclude at present that the similar reactivity of the alkaline form of H atoms produced under our experimental conditions, and of H atom precursors in radiation chemistry, may indicate their identity.

In the concentration region of chloroacetic acid below 10^{-2} M at constant high pH, a decrease of the chloride yield was observed. At pH 12.1 at 0.01 M CH_2ClOO^-, we get $R(Cl^-) = 0.58$, decreasing to $R(Cl^-) = 0.47$ at 0.005 M CH_2ClCOO^-. At pH 12.7, $R(Cl^-)$ decreased from 0.98 at 0.01 M CH_2ClCOO^- to $R(Cl^-) = 0.66$ at 0.002 M CH_2ClCOO^-. The decrease is outside of the experimental uncertainty and should be considered as significant. The reaction scheme proposed above postulates that the species H_2O^- once produced reacts with the acid with Cl^- production. However, when the chloroacetic acid concentration is reduced, alternative mechanisms for the disappearance of H_2O^- have to be considered.

The decomposition reactions of H_2O^- without chloride production may proceed by the recombination reactions $2H_2O^- \rightarrow H_2 + 2OH^-$ and $H + H_2O^- \rightarrow H_2 + OH^-$, which were not considered in the kinetic scheme. Besides, at low scavenger concentrations, the reaction products may compete for the H_2O^- without chloride production.

The present results yield the first evidence for the enhanced reactivity of H atoms in alkaline solution. Reaction 1 was previously postulated in radiation chemical studies.[2,14] However, these experimental results can be accounted for adequately by the formation of e_{aq} (or H_2O^-) as a *primary* product in irradiated solutions.

In a previous work from this Laboratory[15] no enhanced decomposition of H_2O_2 at pH 13 relative to pH 7 was observed. However, the dissociation constant of H_2O_2 is $pK = 11.8$ at 20°.[16,17] Thus under these experimental conditions the decomposition of the HO_2^- ion was investigated. Therefore the interpretation of those experimental results would require the consideration of two possible superimposed pH effects.

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