The decomposition of chloroacetic acid in aqueous solutions by atomic hydrogen. I. Comparison with radiation chemical data

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THE DECOMPOSITION OF CHLOROACETIC ACID IN AQUEOUS SOLUTIONS BY ATOMIC HYDROGEN. I. COMPARISON WITH RADIATION CHEMICAL DATA

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The decomposition of aqueous solutions of chloroacetic acid in acid and neutral solutions by H atoms was investigated. The rate constants for hydrogen and chloride abstraction from the chloroacetic acid and from the chloroacetic anion by H atoms were derived. It was found that H atoms as such react with chloroacetic acid mainly by hydrogen abstraction. The comparison of these results with radiation chemical data yields evidence for the nature of the reducing radicals produced in the radiolysis of water. The acid form of these reducing radicals involves the H atom as such.

Introduction

Recent experimental studies indicate that the reducing radicals formed in the radiolysis of water can exist in two forms, exhibiting widely different reactivity with specific scavengers, e.g., H_2O_2,[1,2] N_2O,[3] organic alcohols, and ketones[4] and chloroacetic acid.[5,6] It was shown[2] that the form of H atom equivalent produced by irradiation of neutral aqueous solutions differs from the species produced by the oxidation of H_2 by OH radicals, and from those produced by radiolysis of acid aqueous solutions.[1,7] The possible pairs of the reducing species considered were e_{aq} and H, or alternately H atom and H_2^+ ion. Radiation chemical data do not make it possible so far to discriminate unambiguously between these possibilities.[1,2,6]

Comparative studies of the reactivity of H atoms generated as such and introduced into the solution[8] and of the reducing species produced in the radiolysis of water may yield information concerning the nature of the reducing radicals produced in irradiated solutions under various experimental conditions. Recent studies[8f] of the decomposition of aqueous solutions of H_2O_2 by H atoms showed that the acid form of the reducing radical involves a hydrogen atom as such. In order to provide further evidence for the nature of these species, the decomposition of aqueous solutions of chloroacetic acid by atomic hydrogen was investigated. Radiation-chemical studies of this system were recently carried out.[5,6] In the present work the radiation chemical data are compared with experimental results for the decomposition of acid and neutral chloroacetic solutions by atomic hydrogen.

Experimental

Production of H-Atoms.—Atomic hydrogen was generated by a method previously described,[8] by an electrodeless discharge in H_2 gas at 30 mm. pressure. The pumping velocity was 150 l. min.$^{-1}$. Atomic hydrogen was passed

for 15 min. through 25 cc. of the evacuated solution kept at 4°.

Determination of dose of H atoms was carried out by reduction of 10^{-3} M ferricyanide solution.[8c] During the runs the dose rate of H atoms was checked. The mean dose in this series of experiments was 1×10^{-6} mole l.$^{-1}$ sec.$^{-1}$ (2.5×10^{-8} mole sec.$^{-1}$). After using the ferricyanide dosimeter, it was found necessary to pass atomic hydrogen through pure water in order to obtain reproducible results.

Analysis.—Chloride was determined by a turbidometric method. The reagent solution consisted of $0.01N$ $AgNO_3$ in $2 N$ HNO_3. Equal volumes of the reagent solution with the analyzed solution were mixed at room temperature, 25°. The turbidity was measured at 400 mμ with a Beckman DU spectrophotometer. The optical density increases with time, reaching a maximum value after 20–30 min. depending on Cl^- and chloroacetic acid concentration. The maximum reading was taken. The measured optical density is linear with Cl^- concentration up to o.d. 0.8, for a 1-cm. light path.

The method is adequate for microdetermination of inorganic chloride in the concentration region 5×10^{-5}–10^{-3} M. The results were found to depend on chloroacetic concentration higher than 0.5 M, and were duly corrected. The accuracy of the method is $\pm 3\%$. At chloroacetic acid concentrations above 3 M, the chloride production during the analysis was very fast and no experiments were carried out in this region.

Materials and Solution.—A.R. grade chloroacetic acid (Hopkin & Williams), sulfuric acid, and KOH were used. The pH usually was adjusted by H_2SO_4 and KOH. In some cases 10^{-3} M phosphate buffer was employed. Solutions were freshly prepared and kept in ice until used. The initial chloride concentration of solutions up to 0.5 M did not exceed 2.5×10^{-5} M chloride. Solutions in the concentration region 1–3 M did not contain more than $2 \times 10^{-4} M$ chloride.

Results

The decomposition of chloroacetic acid by atomic hydrogen was followed by measuring the formation of inorganic chloride. It was found convenient to define the *reaction yield R* for the product in terms of

$$R(Cl^-) = \frac{[Cl^-]V}{At} \qquad (I)$$

where A is the dose rate of H atoms expressed in mole sec.$^{-1}$, V the volume of the solution expressed in l., and t the duration of the run. The values of $R(Cl^-)$ were obtained as mean values of at least three runs, and were reproducible within $\pm 20\%$ or better.

Reaction Yields in Acid Solutions.—The experimental results for $R(Cl^-)$ obtained in acid solutions from pH 0.4 to pH 2 are presented in Table I. In acid solutions $R(Cl^-)$ is dependent on chloroacetic acid concentration leveling off at high concentration. The limiting value observed is

(1) A. O. Allen and H. Schwarz, *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva*, **29**, 30 (1958).

(2) N. F. Barr and A. O. Allen, *J. Phys. Chem.*, **63**, 928 (1959).

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

(4) J. T. Allan and G. Scholes, *ibid.*, **187**, 218 (1960).

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

(6) E. Hayon and A. O. Allen, *J. Phys. Chem.*, **65**, 2181 (1961).

(7) J. T. Sworski, *J. Am. Chem. Soc.*, **76**, 4687 (1954).

(8) (a) G. Czapski and G. Stein, *J. Phys. Chem.*, **63**, 850 (1959); (b) G. Czapski, J. Jortner, and G. Stein, *ibid.*, **63**, 1769 (1959); (c) G. Czapski and G. Stein, *ibid.*, **64**, 219 (1960); (d) G. Czapski, J. Jortner, and G. Stein, *ibid.*, **65**, 956 (1961); (e) **65**, 960 (1961); (f) **65**, 964 (1961).

$R^0(\text{Cl}^-) = 0.33$. At constant chloroacetic acid concentration, the chloride yield is independent of pH in the region 0.4–2.0.
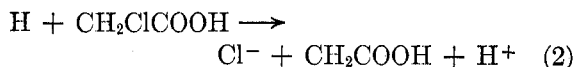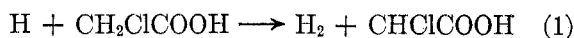
Reaction Mechanism in Acid Solutions.—The limiting chloride reaction yield reaches the value of 0.33 at high scavenger concentrations. Thus the experimental results are interpreted by assuming competition between two first-order scavenging reactions, which involve hydrogen and chloride abstraction from chloroacetic acid.

TABLE I

CHLORIDE YIELDS FROM AQUEOUS SOLUTIONS OF CHLORO-
ACETIC ACID AT 4°

Dose of H atoms/10^{-6} mole l.$^{-1}$ sec.$^{-1}$; duration of run 900 sec.

pH	[CH₂ClCOOH], mole l.$^{-1}$	$R(\text{Cl}^-)$
0.4	0.5	0.18
.4	.05	.032
.4	.005	.02
1.0	3.5	(.33)
1.0	3.3	(.33)
1.0	2.5	.33
1.0	1.0	.21
1.0	0.5	.15
1.0	.2	.08
1.0	.1	.07
1.0	.05	.02
1.2	.5	.18
1.9	3.5	(.28)
1.9	0.5	.16
1.9	.05	.02
3.3	.4	.07
3.3	.05	.06
4.2	.87	.08
4.2	.44	.07
4.2	.01	.03
4.4	.5	.08
4.4	.05	.07
7.4	.01	.04

$$\text{H} + \text{CH}_2\text{ClCOOH} \longrightarrow \text{H}_2 + \text{CHClCOOH} \quad (1)$$

$$\text{H} + \text{CH}_2\text{ClCOOH} \longrightarrow$$
$$\text{Cl}^- + \text{CH}_2\text{COOH} + \text{H}^+ \quad (2)$$

The present data were obtained at a relatively high dose rate of H atoms, thus second-order radical recombination reactions have to be included. The concentration dependence of $R(\text{Cl}^-)$ is attributed to the recombination reaction

$$2\text{H} \longrightarrow \text{H}_2 \quad (3)$$

Evaluation of the Experimental Results.—In a previous work[8d] approximate kinetic expressions were derived for the reactivity of H atoms introduced from the gaseous phase into the solution. By application of the diffusion model[8d] the sum of the reaction yields for H₂ and Cl⁻ production is

$$R(\text{Cl}^-) + R(\text{H}_2) = \frac{\Delta}{W} \quad (\text{II})$$

where Δ is obtained from the cubic equation

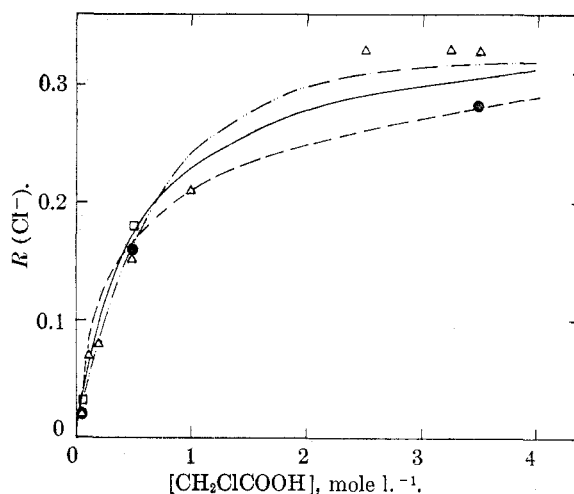$$2\Delta^3 + 3\Delta^2 + \Delta = W \quad (\text{III})$$

Fig. 1.—Chloride reaction yields in acid solutions: □, pH 0.4; △, pH 1; ●, pH 1.9. Calculated curves: — ·· —, homogeneous kinetics; ———, diffusion treatment; — — —, forced convection treatment.

The parameter W is expressed using the same notation as in previous work[8d]

$$W = \frac{k_3 A}{6\{(k_1 + k_2)[\text{CH}_2\text{ClCOOH}]\}^{1/2}D^{1/2}\varphi} \quad (\text{IV})$$

where A is the dose rate of H atoms, D their diffusion coefficient, and φ the mean surface area for mass transport.

The chloride yield can be expressed in terms of the limiting yield $R^0(\text{Cl}^-)$

$$R(\text{Cl}^-) = R^0(\text{Cl}^-)(\Delta/W) \quad (\text{V})$$

Setting the experimental value for the dose rate $A = 2.5 \times 10^{-8}$ mole sec.$^{-1}$ and using the constants[8d,8e] $D = 4 \times 10^{-5}$ cm.^{2}/sec. and $k_3 = 10^{13}$ mole^{-1} cm.^{3} sec.$^{-1}$, we obtain

$$W = \frac{6.6 \times 10^6}{\{(k_1 + k_2)\varphi^{2/3}\}^{1/2}[\text{CH}_2\text{ClCOOH}]^{1/2}} \quad (\text{VI})$$

Best agreement with experimental data was obtained setting $(k_1 + k_2)\varphi^{2/3} = 1.3 \times 10^5$ mole^{-1} l. sec.$^{-1}$ cm.$^{4/3}$ Analysis of the results according to the forced convection mechanism[8c] leads to

$$R(\text{Cl}^-) = R^0(\text{Cl}^-)\frac{(k_1 + k_2)\varphi\mu[\text{CH}_2\text{ClCOOH}]}{k_3 A} \times$$

$$\ln\left\{1 + \frac{k_3 A}{(k_1 + k_2)\varphi\mu[\text{CH}_2\text{ClCOOH}]}\right\} \quad (\text{VII})$$

where μ is the velocity of the liquid. Reasonable agreement was obtained setting $(k_1 + k_2)\varphi\mu = 2.5 \times 10^5$ l. mole^{-1} sec.$^{-1}$ cm.^{3} sec.$^{-1}$. Finally, the homogeneous kinetic treatment was employed

$$R(\text{Cl}^-) = R^0(\text{Cl}^-)\frac{V\tau[\text{CH}_2\text{ClCOOH}]^2}{A} \times$$

$$\left\{\left(1 + \frac{2A}{V\tau[\text{CH}_2\text{ClCOOH}]^2}\right)^{1/2} - 1\right\} \quad (\text{VIII})$$

where $\tau = (k_1 + k_2)^2/2k_3$ and V is the volume of the solution. The experimental results were fitted by setting $\tau = 10^{-6}$ l.$^{-1}$ mole sec.$^{-1}$. The comparison of the experimental results and calculated data is presented in Fig. 1.

Derivation of "Absolute Rate Constants."—In a previous analysis[8c] it was shown that the homogeneous kinetic treatment yields the lower limit for the rate constants. The scavenging rate constants were estimated from the result of the diffusion model. The effective surface area for introduction of H atoms was estimated as 10-20 cm.[2,8d,8e] Setting $\varphi^{2/3} = 10$ cm.$^{4/3}$ we obtain $k_1 + k_2 = 1.3 \times 10^4$ l. mole^{-1} sec.$^{-1}$. This estimation is based on the values of k_3[8,9] and of φ.

Alternatively, similar conclusions can be derived by comparing the present results with the kinetic data previously obtained[8e] under similar experimental conditions for the oxidation of Fe^{+2} ion by H atoms. We have calculated the ratio $k_1 + k_2/k_{H+Fe^{+2}}$ using the three kinetic models. The calculation of the rate constants ratio $k_1 + k_2/k_{H+Fe^{+2}}$ yielded 1.42×10^{-2} using homogeneous kinetics, 1.74×10^{-2} using the diffusion model, and 1.67×10^{-2} applying the forced convection model.

These rate constants ratios are independent of the value chosen for k_3. The rate constants ratio for H atom scavenging in these two different systems is not changed by the kinetic treatment employed. This conclusion yields further support to the validity of the kinetic data obtained[8] by using this experimental method. Using the rate constant $k_{H+Fe^{+2}} = 6.7 \times 10^5$ mole l.$^{-1}$ sec.$^{-1}$ obtained[10] from comparison of radiation chemical results with gaseous phase data,[10] we obtain $k_1 + k_2 = 10^4$ l. mole^{-1} sec.$^{-1}$. Thus the two independent methods lead to similar results.

In the present treatment only the recombination reaction 3 was considered. The recombination of H atoms with the radicals CH$_2$COOH and CHCl-COOH was not included. The nature of this approximation will be considered briefly. Assuming equal reaction rates of H atoms with these radicals and equal rates for the recombination of these radicals, the kinetic scheme should include the reactions

$$H + B \longrightarrow HB \qquad (4)$$

$$2B \longrightarrow B_2 \qquad (5)$$

where B represents both CHClCOOH and CH$_2$-COOH.

At relatively high chloroacetic acid concentrations, the steady state concentration of H atoms is determined by the first-order scavenging reactions 1 and 2, and thus the effect of reaction 4 is negligible. The greatest effect of the recombination reactions 4 and 5 is manifested in the low concentration region of the scavenger. It can be shown that the sum of the rate constants $k_1 + k_2$ may then be altered by a factor of 2 only. This will not affect the general conclusions of the present kinetic analysis.

The rate constants ratio k_2/k_1 was obtained from the limiting value $R^0(Cl^-) = 0.33$ at pH < 2. Thus we calculated

$$\frac{k_2}{k_1} = \frac{R^0(Cl^-)}{1 - R^0(Cl^-)} = 0.5 \pm 0.1$$

(9) H. L. Friedman and A. H. Zeltman, J. Chem. Phys., **28**, 878 (1959).

(10) P. Riesz and E. J. Hart, J. Phys. Chem., **63**, 859 (1959).

Decomposition by H Atoms at Neutral pH.—Low chloride yields were obtained at the neutral pH region 3-8. The experimental results are presented in Table I. The analytical accuracy is somewhat less satisfactory in this region, and only semi-quantitative conclusions can be derived. $R(Cl^-)$ was found to be independent of pH over this whole region. The reaction yield was found to be independent of chloroacetate concentration in the region 0.05-1 M. The limiting yield in this region was found to be $R^0(Cl^-) = 0.08 \pm 0.02$.

As the dissociation constant of monochloroacetic acid is $pK = 2.8$, the change of the reactivity when passing from acid to neutral solutions is attributed to the change of the reacting species from the undissociated acid CH$_2$ClCOOH to the anion CH$_2$-ClCOO$^-$. The reaction mechanism in the neutral pH region is presented in the form

$$CH_2ClCOO^- + H \longrightarrow H_2 + CHClCOO^- \qquad (1')$$

$$CH_2ClCOO^- + H \longrightarrow$$
$$Cl^- + CH_2COO^- + H^+ \qquad (2')$$
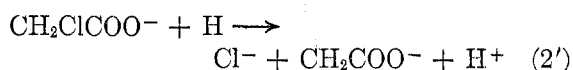
Application of eq. XI and the experimental value of $R^0(Cl^-)$ leads to $k_2'/k_1' = 0.09$.

The levelling-off of $R(Cl^-)$ at lower concentrations at the neutral pH region than in the acid region indicates that the sum of the scavenging rate constants $k_1' + k_2'$ is higher for the anion than the corresponding sum for the acid. Using the approximate value $R(Cl^-)/R^0(Cl^-) = 0.5$ at 0.02 M, then by application of the diffusion model we estimate $(k_1' + k_2')\varphi^{2/3} = 1.5 \times 10^6$ l. mole^{-1} sec.$^{-1}$ cm.$^{4/3}$; hence $k_1' + k_2' = 1.5 \times 10^5$ l. mole^{-1} sec.$^{-1}$.

Discussion

The rate constants for the decomposition of chloroacetic acid by atomic hydrogen are presented in Table II.

These results indicate the enhanced reactivity of the anion compared to the acid in the dehydrogenation and chloride abstraction reaction by H atoms. Recent data indicate that the relative efficiency of the dehydrogenation of the anion compared with the acid may be general for the case of aliphatic acids. The most extreme case is that of formic acid where $k_{H+HCOO^-}/k_{H+HCOOH} > 100$.[11] The increased reactivity of the formic acid anion compared with the conjugated acid was demonstrated in some other radical reactions.[12,13]

TABLE II

RATE CONSTANTS FOR SCAVENGING OF H ATOMS BY CHLOROACETIC ACID

Reacting species	k_1, l. mole^{-1} sec.$^{-1}$	k_2, l. mole^{-1} sec.$^{-1}$
CH$_2$ClCOOH	9×10^3	4×10^3
CH$_2$ClCOO$^-$	1.3×10^5	1.3×10^4

In the case of the reactivity of acetic acid with H atoms it was found that $k_{H+CH_3COO^-}/k_{H+CH_3COOH} = 3$.[13] Until recently, the different reactivity of H atoms with acids and their conjugated anions was not taken into account in radiation chemical studies of such systems.

(11) J. Rabani, ibid., **66**, 361 (1962).
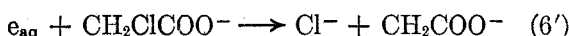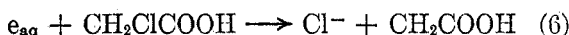
(12) E. J. Hart, J. Am. Chem. Soc., **83**, 567 (1961).

(13) J. Rabani and G. Stein, to be published.

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.

(14) C. J. Hochanadel, *J. Phys. Chem.*, **56**, 587 (1952).

(15) G. G. Jayson, G. Scholes, and J. Weiss, *J. Chem. Soc.*, 1358 (1957).

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

(1) J. Jortner and J. Rabani, *J. Phys. Chem.*, **66**, 2078 (1962).

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

(3) E. Hayon and A. O. Allen, *J. Phys. Chem.*, **65**, 2181 (1961).