

With these assumptions, the results in Table I indicate that di- and tribromoethanes are more often formed with  $^{82}\text{Br}$  than with  $^{80\text{m}}\text{Br}$  and suggest that hydrogen atom substitution proceeds more readily through a mechanism involving Auger electron emission. Conversely the scission of carbon-carbon bonds, and the substitution of bromine atoms in heavily scavenged systems, may be caused predominantly by atoms having recoil energy.

Besides the compounds listed, and carbon tetrabromide and tetrabromoethane,<sup>13</sup> small yields of compounds containing more than two carbon atoms have been found in this system. Since such products may be important in determining reaction mechanisms, a fuller discussion is withheld until complete analyses can be reported.

(13) W. E. Harris, *Can. J. Chem.*, **39**, 121 (1961).

NUCLEAR PHYSICS LABORATORY  
OXFORD, ENGLAND

T. E. GILROY  
GEORGE MILLER  
P. F. D. SHAW

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### Kinetic Evidence for $\text{H}_3\text{O}$ as the Precursor of Molecular Hydrogen in the Radiolysis of Water<sup>1</sup>

Sir:

$G_{\text{H}_2\text{O}_2}$ <sup>2a</sup> and  $G_{\text{H}_2}$ <sup>2b</sup> for the decomposition of water by  $^{60}\text{Co}$   $\gamma$ -radiation and  $G_{\text{H}_2}$ <sup>3</sup> for the decomposition of water by fission recoils are markedly dependent on solute concentration. This is attributed to reaction of solute with free-radical precursors, e.g., reaction with OH radicals before they combine to form  $\text{H}_2\text{O}_2$ .<sup>2a</sup> Attempts to derive the observed dependence from the "diffusion-kinetic" model have resulted<sup>4</sup> in a quantitative inconsistency. We have found that the precursor of molecular  $\text{H}_2$  disappears by a first-order process. Therefore, homogeneous kinetics can be substituted for diffusion kinetics to express the dependence of  $G_{\text{H}_2}$  on solute concentration.

Evidence to support this suggestion resulted from further examination of the striking effect<sup>5</sup> of  $\text{NO}_3^-$  on  $\text{Ce}^{4+}$  reduction in sulfuric acid solutions.  $\text{Tl}^+$  increases  $G(\text{Ce}^{3+})$  from  $2G_{\text{H}_2\text{O}_2} + G_{\text{H}} - G_{\text{OH}}$  to  $2G_{\text{H}_2\text{O}_2} + G_{\text{H}} + G_{\text{OH}}$ .  $\text{NO}_3^-$  at concentrations greater than 0.01  $M$  markedly enhances  $G(\text{Ce}^{3+})$  both in the presence and in the absence of  $\text{Tl}^+$ , the effect being equal in both cases. The  $\text{NO}_3^-$  effect is not pH dependent; no significant difference was observed between 0.08 and 0.8  $N$  sulfuric acid. The enhancement,<sup>6</sup>  $\Delta G(\text{Ce}^{3+})$ , for  $\text{NO}_3^-$  concentrations from 0.1 to 5.0  $M$  is quantitatively expressed by eq. I.

$$1/\Delta G(\text{Ce}^{3+}) = 0.185 + 0.0804/[\text{NO}_3^-] \quad (\text{I})$$

(1) This research was sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

(2) (a) T. J. Sworski, *J. Am. Chem. Soc.*, **76**, 4687 (1954); *Radiation Res.*, **2**, 227 (1955); (b) J. A. Ghormley and C. J. Hochanadel, *ibid.*, **2**, 227 (1955).

(3) J. W. Boyle, W. F. Kiefer, C. J. Hochanadel, T. J. Sworski, and J. A. Ghormley, *Proc. Intern. Conf. Peaceful Uses At. Energy*, **7**, 576 (1957).

(4) A. Kupperman in "The Chemical and Biological Action of Radiations," Vol. 5, M. Haissinsky, Ed., Academic Press, New York, N. Y., 1961, Chapter III.

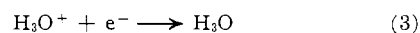
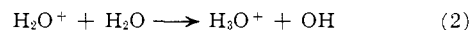
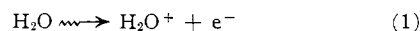
(5) T. J. Sworski, *J. Am. Chem. Soc.*, **77**, 4689 (1955).

(6) H. A. Mahlman, *J. Phys. Chem.*, **64**, 1598 (1960).

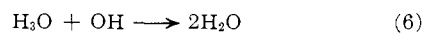
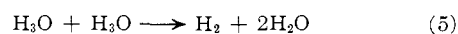
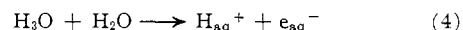
The  $\text{NO}_3^-$  effect is attributed to a decrease in  $G_{\text{H}_2}$  with a concomitant increase in  $G_{\text{H}_2\text{O}_2}$ . Quantitatively, these results are consistent with the assumption that an intermediate in the spur disappears by a first-order process in competition with reaction with  $\text{NO}_3^-$ . This is a pseudo-unimolecular process since the  $\text{NO}_3^-$  effect is temperature independent and not proportional<sup>7</sup> to  $T/\eta$ .

Plausible arguments have been presented<sup>8</sup> for the  $e_{\text{aq}}^-$ , instead of the H atom, as the main precursor of molecular  $\text{H}_2$ . Assume the  $e_{\text{aq}}^-$  to be the intermediate which reacts with  $\text{NO}_3^-$ . Then, eq. I would yield a lifetime for the  $e_{\text{aq}}^-$  in the spur of  $5 \times 10^{-10}$  sec., based on a rate constant<sup>9</sup> for reaction of  $\text{NO}_3^-$  with  $e_{\text{aq}}^-$  of  $8.15 \times 10^9 M^{-1} \text{sec.}^{-1}$ . This is much longer than the lifetime of  $6 \times 10^{-11}$  sec. to be expected for the  $e_{\text{aq}}^-$  in 0.8  $N$  sulfuric acid owing to reaction with  $\text{H}_{\text{aq}}^+$  alone, based on a rate constant<sup>9</sup> of  $2.06 \times 10^{10} M^{-1} \text{sec.}^{-1}$ . This, together with absence of any marked influence of pH, forces the conclusion that the  $\text{NO}_3^-$  effect is not attributable to reaction of  $\text{NO}_3^-$  with  $e_{\text{aq}}^-$ . This is consistent with the observation of Mahlman<sup>10</sup> that there is no effect of  $\text{H}_{\text{aq}}^+$  on the dependence of  $G_{\text{H}_2}$  on  $\text{NO}_3^-$  concentration.

Magee<sup>11</sup> proposed that three consecutive elementary processes yield OH and  $\text{H}_3\text{O}$  as the primary chemical intermediates in the radiolysis of water.



We suggest that  $\text{H}_3\text{O}$  is the main precursor of molecular  $\text{H}_2$  and disappears by three processes



Assume that  $\text{H}_3\text{O}$  disappears by a first-order process,  $k_7[\text{H}_3\text{O}]$ , in competition with reaction with  $\text{NO}_3^-$ ,  $k_8[\text{H}_3\text{O}][\text{NO}_3^-]$ . Then, eq. I yields a lifetime for  $\text{H}_3\text{O}$  in the spur of  $2.30/k_8$  or about  $4 \times 10^{-10}$  sec., assuming reaction with  $\text{NO}_3^-$  to be diffusion controlled. The pseudo-unimolecular rate constant,  $k_7$ , in this model is taken to be  $k_4[\text{H}_2\text{O}] + k_5[\text{H}_3\text{O}] + k_6[\text{OH}]$ .

In the decomposition of water by fission recoils,<sup>3</sup>  $G_{\text{H}_2}$  is independent of  $\text{UO}_2\text{SO}_4$  concentration up to about 0.01  $M$ , and then it decreases approximately linearly with the square root of the  $\text{UO}_2\text{SO}_4$  concentration.  $G_{\text{H}_2}$ , previously approximated<sup>3</sup> as a square-root dependency, is quantitatively expressed by eq. II.

$$1/G_{\text{H}_2} = 0.571 + 0.645[\text{UO}_2\text{SO}_4] \quad (\text{II})$$

This dependency is consistent with the assumptions that  $\text{H}_3\text{O}$  is the sole precursor of  $\text{H}_2$  and that it disappears by a first-order process in competition with reaction with uranyl sulfate,  $k_8[\text{H}_3\text{O}][\text{UO}_2\text{SO}_4]$ . Equa-

(7) M. V. Smoluchowski, *Z. Physik. Chem.* (Leipzig), **92**, 129 (1918).

(8) H. A. Schwarz, *Radiation Res. Suppl.*, **4**, 89 (1964).

(9) J. H. Baxendale, et al., *Nature*, **201**, 468 (1964).

(10) H. A. Mahlman, Chemistry Division Annual Progress Report, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1963, ORNL-3488.

(11) J. L. Magee, *Radiation Res. Suppl.*, **4**, 20 (1964).

tion II yields a lifetime for  $H_3O$  in the fission recoil track of  $1.13/k_9$  or about  $10^{-9}$  sec.

The dependence of  $G_{H_2}$  on the concentration of  $NO_3^-$  for the decomposition of water by  $^{60}Co$   $\gamma$ -radiation, previously approximated<sup>12,13</sup> as a cube-root dependency, is quantitatively expressed by eq. III, but only for

$$1/G_{H_2} = 2.93 + 7.53[NO_3^-] \quad (III)$$

concentrations from 0.01 to 1.0  $M$ . Equation III yields a lifetime for  $H_3O$  in the spur of  $2.57/k_8$ , in excellent agreement with eq. I. The failure of eq. III to apply at concentrations less than 0.01  $M$  leads us to propose that  $H_2$  formation by  $^{60}Co$   $\gamma$ -radiation results from two processes: intraspur and interspur processes with  $G_{H_2} = 0.34$  for the former. In interspur processes, intermediates from one spur interact with intermediates from an adjacent spur before they escape into the bulk of the solution. The dependence of  $G_{H_2}$  on  $NO_3^-$  at concentrations less than 0.01  $M$  is consistent with both  $G_{H_2} = 0.11$  and a lifetime for  $H_3O$  of approximately  $300/k_8$  for interspur processes.

The new model for  $H_2$  formation leads us to propose an alternative viewpoint concerning the influence of pH on  $G_{e_{aq}^-}$ .  $H_{aq}^+$  reacts with those electrons,  $k_{10}[H_{aq}^+][e_{aq}^-]$ , which would otherwise disappear in spur processes. The lifetime for the  $e_{aq}^-$  in the spur is  $130/k_{10}$  or  $6 \times 10^{-9}$  sec. (originally reported<sup>14</sup> as  $0.01/k_{10}$  and attributed to  $H_2O^*$ ).

(12) H. A. Mahlman and J. W. Boyle, *J. Chem. Phys.*, **27**, 1434 (1957).

(13) H. A. Mahlman, *ibid.*, **32**, 601 (1960).

(14) F. S. Dainton and D. B. Peterson, *Proc. Roy. Soc. (London)*, **A267**, 443 (1962).

CHEMISTRY DIVISION  
OAK RIDGE NATIONAL LABORATORY  
OAK RIDGE, TENNESSEE

THOMAS J. SWORSKI

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### The Polar Addition of Hydrogen Bromide to Cyclohexene<sup>1</sup>

Sir:

In recent years a variety of examples of polar *cis* additions of acids and alcohols to olefins has been reported.<sup>2-5</sup> These include the addition of deuterium bromide to cyclohexene, which has been reported<sup>2</sup> to give 26, 31.5, 63, and 74% of *cis* adduct at 10, 25, 45, and 60°, respectively. This variation in stereochemistry with temperature seemed unusual to us and prompted us to re-examine this reaction. Our results are in substantial disagreement with the earlier findings. When cyclohexene-2,6,6- $d_3$  is allowed to react with hydrogen bromide in acetic acid, addition of acetic acid as well as hydrogen bromide occurs, and the addition is very predominantly *trans* at temperatures from 15 to 60°.

The stereochemistry of addition to cyclohexene-2,6,6- $d_3$  can be established from the n.m.r. spectra of

(1) This research was presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1964.

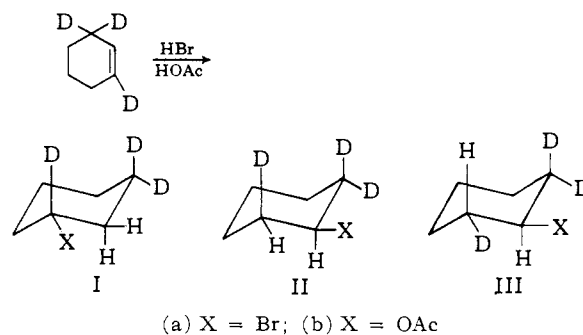
(2) J. V. Smirnov-Zamkov and G. A. Piskovitchina, *Ukr. Khim. Zh.*, **28**, 531 (1962).

(3) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 2245, 2248, 3645 (1963).

(4) S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Letters*, 185 (1963).

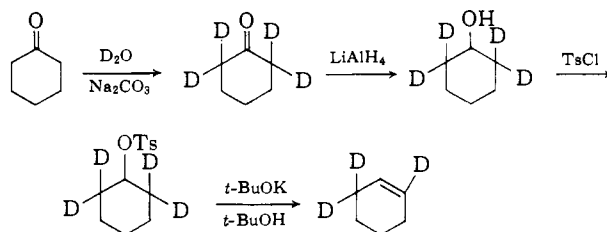
(5) H. Kwart and J. L. Nyce, *J. Am. Chem. Soc.*, **86**, 2601 (1964).

the products. The bromides Ia-IIIa and the acetates Ib-IIIb are possible products depending on the direction and stereochemistry of the addition. No low-



field resonance is expected for Ia or Ib, whereas IIa and IIb (from *trans* addition) and IIIa and IIIb (from *cis* addition) should give low-field doublets for the  $C_1$ -H resonance with expected splittings of 2-4 and 8-10 c.p.s., respectively. Complications due to coupling involving deuterium can be averted through the use of deuterium double irradiation.<sup>6</sup>

Cyclohexene-2,6,6- $d_3$  was prepared according to the following reaction sequence



In a typical addition experiment, 20 ml. of 0.5  $M$  hydrogen bromide in dry acetic acid, 0.5 ml. of cyclohexene-2,6,6- $d_3$ , and 10 mg. of 2,6-di-*t*-butyl-*p*-cresol (used to inhibit free-radical addition) were sealed in an ampoule and placed in a thermostated bath for 1-4 hr. The reaction was worked up in water by extracting with pentane. The pentane fraction was washed with dilute bicarbonate, dried over anhydrous sodium carbonate, and filtered. Evaporation of the pentane gave 75-95% crude yields of product. The polar character of the reaction was demonstrated by showing that addition of hydrogen bromide to 1-hexene in the presence of cyclohexene gave 2-bromohexane and cyclohexyl bromide, with no 1-bromohexane (the free-radical addition product) being formed.

Analysis of the reaction products, both by n.m.r. and by v.p.c., demonstrated the presence of both acetate and bromide. In control experiments it was shown that, under the reaction conditions, cyclohexyl bromide is not converted to cyclohexyl acetate, whereas cyclohexyl acetate is very slowly converted to the bromide. The n.m.r. spectrum of the addition product mixture showed broad signals at 4.67 (acetate) and 4.13 p.p.m. (bromide) downfield from TMS, which sharpened into doublets with 3.3 and 3.5 c.p.s. spacings, respectively, when the samples were simultaneously irradiated at the deuterium resonance frequency. The ob-

(6) A Nuclear Magnetic Resonance Specialties, Inc., Model SD-60 spin decoupler was used in conjunction with a Varian HR-60 spectrometer in these studies.