

Reaction of excess 1,1-dimethylallene (Iib), 3-chloro-3-methylbutyne, and potassium *t*-butoxide at -40° resulted in formation of 1-isopropylidene-2-(2-methylpropenylidene)cyclopropane (Vb), b.p. $39-41^\circ$ (2 mm.), of fair purity in 19% yield. Considerable polymerization occurs during addition, and 1,1-dimethyl-2-methylene-3-(2-methylpropenylidene)-cyclopropane (Vc), the product anticipated by capture of dimethylvinylidene carbene (IV) by the internal double bond of Iib, has as yet not been isolated. The structure of Vb was assigned on the basis of its analysis, its infrared absorption at 5.03 and 5.72 μ for allenic and *exo* unsaturation, and its n.m.r. peaks for cyclopropyl hydrogens (multiplet) at τ 8.63, olefinic methyls (multiplet) at 8.26, and allenic methyls (multiplet) at 8.15.⁹ Adducts Va and Vb are affected rapidly by heat, acids, and oxygen; studies of their transformation products are in process.^{10,11}

(9) The distillation product does not exhibit n.m.r. absorption for vinyl protons as anticipated if Vc were present.

(10) Product Va rearranges almost quantitatively to an isomeric hydrocarbon when heated under nitrogen at $90-150^\circ$ or when gas chromatographed at 150° on Carbowax 20M or SE-30. Vb rearranges into other products under such conditions.

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Differences in the Behavior of Bromine Isotopes Activated by Neutron Capture in Bromoethane

Sir:

Several recent papers¹⁻³ have reported differences in the isotopic yields of organic radiobromine formed by neutron capture in organic bromides. Some of these effects, for example, in bromoform,¹ were shown to be due to thermal exchange reactions. Longer lived isotopes may then show a greater degree of exchange, and yields are dependent upon the time of irradiation.⁴ The other isotope effects reported for liquid systems^{2,3} are found in chloro- or fluorobromomethanes, and are discussed extensively by Filatov.⁵

The effects reported in the bromopropanes^{6,7} have been in dispute for some years, and Willard has reported⁸ several unsuccessful attempts to reproduce the results of Capron and his co-workers, who claimed to have found a greater total organic yield for ^{82}Br than for ^{80}mBr .

We wish to report isotopic effects in mixtures of bromoethane and bromine irradiated in the thermal column of British Experimental Pile O., at A.E.R.E., Harwell (slow neutron flux $4 \times 10^9 \text{ cm}^{-2} \text{ sec}^{-1}$; γ -ray flux less than 10^4 r./hr.). Inorganic bromine, as Br_2 or HBr , was first removed with an aqueous wash, and after addition

of carriers, separations were made by gas chromatography using a 3-m. silicone grease column with temperature programming. Fractions were trapped at the end of the column, and after dissolving in ethanol, they were counted in a liquid-sheath Geiger counter. Two measurements were made: the first, 4 hr. after collection, to establish transient equilibrium between ^{80}mBr and its daughter, and the second after 20 hr., so that ^{80}mBr (4.5 hr.) and ^{82}Br (36 hr.) were both determined in the same experiment.

The total activity obtained from the column was normalized to the over-all organic yield determined independently from a small portion of the irradiated material taken before analysis. Table I shows values for the isotope ratios, established on the basis of several experiments, of the seven major products from neutron-irradiated bromoethane. Variation of the time of irradiation from 1 to 24 hr. did not alter the observed ratios, so that the effects cannot be ascribed to thermal exchange or slow reactions of the inorganic bromine with small amounts of impurities in the irradiated mixtures.

TABLE I

RATIOS OF ISOTOPIC YIELDS OF PRODUCTS FROM NEUTRON-IRRADIATED BROMOETHANE

Product	Yield for ^{80}mBr /yield for ^{82}Br				
	Molar fraction of Br_2 present during irradiation 10^{-3}	0.1	0.2	0.5	0.75
$\text{C}_2\text{H}_5\text{Br}$	0.96	1.03	1.47	1.47	1.58
CH_3Br	2.40	2.15	2.40	2.50	3.05
CH_2Br_2	1.82	1.76	2.02	2.15	2.28
CHBr_3	1.06	1.08	1.30	1.47	1.53
$\text{CH}_2\text{Br} \cdot \text{CH}_2\text{Br}$	0.74	0.72	0.74	0.70	0.61
$\text{CH}_3 \cdot \text{CHBr}_2$	0.77	0.80	0.86	0.93	0.89
$\text{CH}_2\text{BrCHBr}_2$	0.45	0.46	0.52	0.53	0.61
Total organic	0.96	0.98	1.08	1.13	1.09

The root-mean-square deviation of yields from repeated runs was $\pm 5\%$, except in the case of the methyl bromide fractions, where larger errors ($\pm 20\%$) were obtained; apart from this fraction, the errors only slightly exceeded those expected from the statistics of counting ($\pm 3\%$).

Wexler and Davies have shown⁹ that the percentage of charged atoms formed by neutron capture is different for each bromine isotope, and Nesmeyanov and others (see ref. 5) have attempted to explain isotopic differences on the basis of ion-molecule reactions. The recent discovery¹⁰ that most ^{82}Br is produced through an isomer $^{82\text{m}}\text{Br}$ (6.2-min. half-life) suggests that the products from this isotope may arise predominantly from processes associated with internal conversion, for example, the formation of highly charged atoms¹¹ by emission of Auger electrons. Reactions could then proceed by charge transfer from neighboring molecules, or through interaction with localized radiolysis products formed by the Auger electrons.¹² Differences in the isotopic yields would then be expected if the activation of ^{80}mBr was predominantly through recoil.

(9) S. Wexler and T. H. Davies, *J. Chem. Phys.*, **20**, 1688 (1952).

(10) (a) J. F. Emery, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1964, Abstract R26; (b) O. U. Anders, *ibid.*, Abstract R25.

(11) (a) S. Wexler and T. H. Davies, *J. Chem. Phys.*, **18**, 376 (1950); (b) S. Wexler, *Phys. Rev.*, **93**, 182 (1954).

(12) P. R. Geissler and J. E. Willard, *J. Phys. Chem.*, **67**, 1675 (1963).

(1) A. N. Nesmeyanov, A. E. Borisov, and I. Zvara, *Radiokhimiya*, **1**, 325 (1959).

(2) A. N. Nesmeyanov, A. E. Borisov, E. S. Filatov, V. I. Kondratenko, C.-H. Chang, K. Panek, and B. M. Shukla, *ibid.*, **1**, 712 (1959).

(3) A. N. Nesmeyanov and E. S. Filatov, *ibid.*, **3**, 501 (1961).

(4) M. Milman and P. F. D. Shaw, *J. Chem. Soc.*, 2101 (1956).

(5) E. S. Filatov, *Usp. Khim.*, **3**, 752 (1962).

(6) P. C. Capron and E. Crevecoeur, *J. Chem. Phys.*, **21**, 1843 (1953).

(7) D. J. Apers, P. C. Capron, and L. Gilly, *J. chim. phys.*, **54**, 314 (1957).

(8) J. E. Willard, "Chemical Effects of Nuclear Transformations," International Atomic Energy Agency, Vienna, 1961, p. 215.

With these assumptions, the results in Table I indicate that di- and tribromoethanes are more often formed with ^{82}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,¹³ 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).

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Kinetic Evidence for H_3O as the Precursor of Molecular Hydrogen in the Radiolysis of Water¹

Sir:

$G_{\text{H}_2\text{O}_2}$ ^{2a} and G_{H_2} ^{2b} for the decomposition of water by ^{60}Co γ -radiation and G_{H_2} ³ 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 H_2O_2 .^{2a} Attempts to derive the observed dependence from the "diffusion-kinetic" model have resulted⁴ in a quantitative inconsistency. We have found that the precursor of molecular H_2 disappears by a first-order process. Therefore, homogeneous kinetics can be substituted for diffusion kinetics to express the dependence of G_{H_2} on solute concentration.

Evidence to support this suggestion resulted from further examination of the striking effect⁵ of NO_3^- on Ce^{4+} reduction in sulfuric acid solutions. Tl^+ increases $G(\text{Ce}^{3+})$ from $2G_{\text{H}_2\text{O}_2} + G_{\text{H}} - G_{\text{OH}}$ to $2G_{\text{H}_2\text{O}_2} + G_{\text{H}} + G_{\text{OH}}$. NO_3^- at concentrations greater than 0.01 *M* markedly enhances $G(\text{Ce}^{3+})$ both in the presence and in the absence of Tl^+ , the effect being equal in both cases. The NO_3^- effect is not pH dependent; no significant difference was observed between 0.08 and 0.8 *N* sulfuric acid. The enhancement,⁶ $\Delta G(\text{Ce}^{3+})$, for 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.

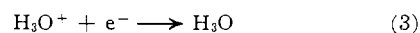
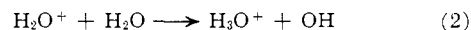
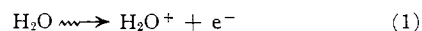
(5) T. J. Sworski, *J. Am. Chem. Soc.*, **77**, 4689 (1955).

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

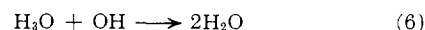
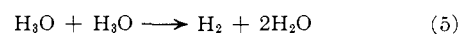
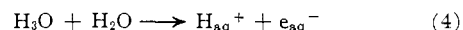
The NO_3^- effect is attributed to a decrease in G_{H_2} with a concomitant increase in $G_{\text{H}_2\text{O}_2}$. Quantitatively, these results are consistent with the assumption that an intermediate in the spur disappears by a first-order process in competition with reaction with NO_3^- . This is a pseudo-unimolecular process since the NO_3^- effect is temperature independent and not proportional⁷ to T/η .

Plausible arguments have been presented⁸ for the e_{aq}^- , instead of the H atom, as the main precursor of molecular H_2 . Assume the e_{aq}^- to be the intermediate which reacts with NO_3^- . Then, eq. I would yield a lifetime for the e_{aq}^- in the spur of 5×10^{-10} sec., based on a rate constant⁹ for reaction of NO_3^- with e_{aq}^- of $8.15 \times 10^9 \text{ M}^{-1} \text{ sec.}^{-1}$. This is much longer than the lifetime of 6×10^{-11} sec. to be expected for the e_{aq}^- in 0.8 *N* sulfuric acid owing to reaction with H_{aq}^+ alone, based on a rate constant⁹ of $2.06 \times 10^{10} \text{ M}^{-1} \text{ sec.}^{-1}$. This, together with absence of any marked influence of pH, forces the conclusion that the NO_3^- effect is not attributable to reaction of NO_3^- with e_{aq}^- . This is consistent with the observation of Mahlman¹⁰ that there is no effect of H_{aq}^+ on the dependence of G_{H_2} on NO_3^- concentration.

Magee¹¹ proposed that three consecutive elementary processes yield OH and H_3O as the primary chemical intermediates in the radiolysis of water.



We suggest that H_3O is the main precursor of molecular H_2 and disappears by three processes



Assume that H_3O disappears by a first-order process, $k_7[\text{H}_3\text{O}]$, in competition with reaction with NO_3^- , $k_8[\text{H}_3\text{O}][\text{NO}_3^-]$. Then, eq. I yields a lifetime for H_3O in the spur of $2.30/k_8$ or about 4×10^{-10} sec., assuming reaction with 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,³ G_{H_2} is independent of UO_2SO_4 concentration up to about 0.01 *M*, and then it decreases approximately linearly with the square root of the UO_2SO_4 concentration. G_{H_2} , previously approximated³ 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 H_3O is the sole precursor of 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).