BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2877—2878 (1973)

Reactions of ^{82}Br Activated by Isomeric Transition in CH_4: A Re-Evaluation*

Richard W. Helton, David W. Oates, and Edward P. Rack
University of Nebraska, Lincoln, Nebraska 68508 U.S.A.

(Received September 18, 1972)

In the first experiments utilizing rare-gas moderators in reactions of ^{82}Br activated by isomeric transition, Nicholas and Rack$^{1)}$ found that in the $^{82}Br+CH_4$ system, the total organic product yield, extrapolated to zero mole fraction moderator, was 7.4±0.5%. The organic yield data appeared to extrapolate to 3.7±0.5% at zero mole fraction CH_4 for the various rare-gas moderators, suggesting that 7.4% minus 3.7% was formed by excess kinetic energy processes and that 3.7% of the organic ^{82}Br was formed by thermal (kinetic energy independent) processes.

Tachikawa$^{2,3)}$ studied the effect of argon moderator on the individual product yields of (I.T.)-activated ^{82}Br in CH_4. The extrapolation to zero mole fraction argon (6.1±0.7%) agreed well with that of Nicholas and Rack, considering the larger amount of Br_2 scavenger used by Tachikawa (0.11 mol fraction Br_2), compared to a constant 15 Torr Br_2 at 700 Torr total pressure used by Nicholas and Rack. However, Tachikawa found that extrapolation to zero mole fraction CH_4 gave a total organic yield of 1.6±0.4%. Since this difference is much too large for experimental error, and the value at this extrapolation is necessary for determining the relative importances of kinetic energy dependent and thermal reactions, it was decided that a re-evaluation of the system was in order, to determine the nature of this discrepancy.

A description of our sample making techniques, irradiation procedures, and extraction techniques can be found elsewhere.$^{4-7)}$ At least six samples were made for each condition, each containing 5 Torr of Br_2, and varying amounts of CH_4 and argon, for a total system pressure of 700 Torr. Neutron irradiations were for 30 sec in the Omaha, Nebraska, V. A. Hospital reactor, employing the "in-reactor technique" described by Nicholas and Rack.$^{1)}$ All relative product distributions were determined by radiogas chromatography$^{8)}$ employing a modified flow-through proportional counter of the type described by Wolf *et al.*$^{9)}$ Only two organic products were observed in each case, $CH_3{}^{82}Br$ and $CH_2Br^{82}Br$.

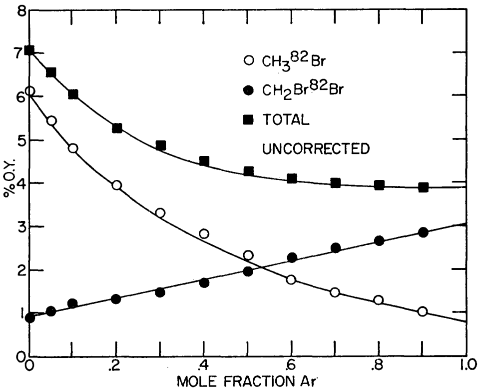

Fig. 1. Effect of Ar moderator on the product distribution in the reaction of (I.T.)-activated ^{82}Br with CH_4.

Depicted in Fig. 1 are the total organic product and individual organic product yields as a function of mole fraction argon. It can be seen that the extrapolations to zero mole fraction argon are in good agreement with both Nicholas and Rack, and Tachikawa. The $CH_3{}^{82}Br$ curve, also, strongly resembles that of Tachikawa. However, the $CH_2Br^{82}Br$ product increases linearly with increasing mole fraction argon, so that the total organic product yield resembles that of Nicholas and Rack, extrapolating to 3.8±0.4% at zero mole fraction CH_4.

This linear dependence of organic yield upon concentration of moderator has been previously reported$^{10)}$ and determined to be due to rare-gas sensitized radiation damage.

Figure 2 represents the total and individual organic product yields as a function of argon concentration, corrected for radiation damage.$^{10)}$ Mixtures of CH_4

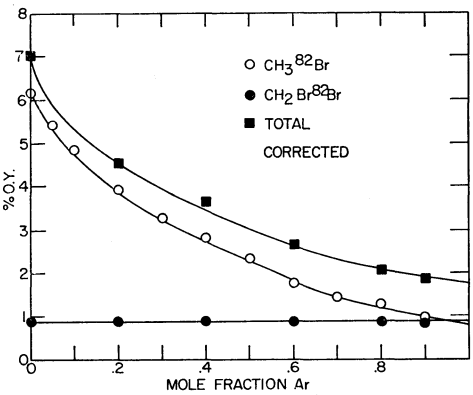

Fig. 2. Effect of Ar moderator on the reaction of (I.T.)-activated ^{82}Br with CH_4, corrected for radiation damage.

---

* This work was supported by the U.S. Atomic Energy Commission under Contract No. AT(11-1)-1617. This is AEC Document No. COO-1617-34.

1) J. B. Nicholas and E. P. Rack, *J. Chem. Phys.*, **48**, 9, 4085 (1968).

2) E. Tachikawa, This Bulletin, **42**, 2404 (1969).

3) E. Tachikawa, *ibid.*, **43**, 63 (1970).

4) J. A. Merrigan, W. K. Ellgren, Jr., and E. P. Rack, *J. Chem. Phys.*, **44**, 174 (1966).

5) J. A. Merrigan, J. B. Nicholas, and E. P. Rack, *Radiochim. Acta*, **6**, 94 (1966).

6) E. P. Rack and A. A. Gordus, *J. Phys. Chem.*, **65**, 944 (1961).

7) J. A. Merrigan and E. P. Rack, *ibid.*, **69**, 2795 (1965).

8) R. M. Lambrecht and E. P. Rack, *J. Chem. Phys.*, **48**, 3735 (1963).

9) M. Welch, R. Withnell, and A. P. Wolf, *Anal. Chem.*, **39**, 275 (1967).

10) E. P. Rack and A. A. Gordus, *J. Chem. Phys.*, **34**, 1855 (1961).

and argon containing 5 Torr of Br_2 and 0.1 Torr of ^{131}I labeled molecular I_2 were irradiated for 30 sec in the nuclear reactor. The percent of ^{131}I as total organic product yield was plotted as a function of argon concentration. Gas chromatographic analysis of the ^{131}I-labeled organic products was also performed. No $CH_3{}^{131}I$ product was detected at the various argon concentrations. Extrapolation of the corrected individual product yields to zero mole fraction CH_4 gives $0.9\pm0.2\%$ and $0.8\pm0.2\%$ for $CH_2Br^{82}Br$ and $CH_3{}^{82}Br$, respectively. This compares very well with the data of Tachikawa for the Br_2–CH_4–Ar system ($CH_2Br^{82}Br$, $1.1\pm0.2\%$ and $CH_3{}^{82}Br$, $0.5\pm0.2\%$), and, also, with other moderator studies.[11]

An important observation from inspection of Figs. 1 and 2 is that the only ^{82}Br labeled product affected by the argon-sensitized radiation damage is $CH_2Br^{82}Br$, which is formed exclusively by thermal (non-kinetic energy activated) ion-molecule reactions. No radiation damage is associated with the $CH_3{}^{82}Br$ product.

The apparent reason that this laboratory observes moderator-sensitized radiation damage while Tachikawa does not, is that we irradiated the premixed sample, containing all system components, and Tachikawa mixes the components after making the Br_2 radioactive.[3,11]

---

11) E. Tachikawa and J. Okamoto, *Radiochim. Acta*, **13**, 159 (1970).