Isotope Effects on the Reactions of ^{82}Br Activated by Isomeric Transition between CH_4 and CD_4

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^{82}Br activated by the isomeric transition originally has a high charge and a high energy resulting from the Auger process following the internal conversion.[1] Thus, it can react with a reactant *via* the energetic process and also *via* the thermal ionic process.

Spicer and Gordus[2] studied the reaction of ^{80}Br activated by the (I.T.) process with CH_4 and CD_4 and found that the total organic yield in the reaction with CH_4 is higher than in that with CD_4 by a factor of 1.5. On the other hand, Nicholas and Rack[3] attempted to prove that equal organic yields result from both the ^{82m}Br-CH_4 and ^{82m}Br-CD_4 systems. However, these measurements do not offer any information concerning the isotope effects in the individual reaction processes, energetic and thermal ionic.

This paper will described the study of the influence of the moderator gas on the individual products from both the ^{82m}Br-CH_4 and the ^{82m}Br-CD_4 systems; this study was undertaken in order to ascertain the isotope effects on each reaction process separately. The details of the experimental methods may be found elsewhere.[4] In all samples the ratio of Br_2 as a scavenger relative to CH_4 or CD_4 was kept constant, 0.11 ± 0.01, and the total pressure was 51 ± 1 cmHg.

Figure 1 shows the moderator effects on the products. $CH_3{}^{82}Br$ and $CD_3{}^{82}Br$ are $5.0\%\pm0.5\%$ and $2.1\%\pm0.2\%$ respectively at zero mole fraction of the moderator, and both can be extrapolated to $0.5\%\pm0.2\%$ at a 1.0 mol fraction of the moderator. On the other hand, $CH_2{}^{82}BrBr$ and $CD_2{}^{82}BrBr$ are constant at $1.1\%\pm0.2\%$ at any mole fraction of the moderator. This indicates that the $CH_3{}^{82}Br$ and $CD_3{}^{82}Br$ formed *via* the energetic process are $4.5\%\pm0.5\%$ and $1.6\%\pm0.2\%$ respectively. It may, then, be concluded that there is an isotope effect between CH_4 and CD_4 in the energetic reaction but not in the thermal ionic reactions.

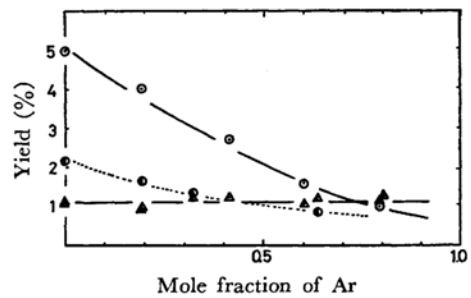

Fig. 1. Moderator effects on the yields of CH_3Br and CH_2Br_2.
system: ^{80m}Br-CH_4 ◐ $CH_3{}^{80}Br$ ◭ $CH_2{}^{80}BrBr$
system: ^{82m}Br-CH_4 ⊙ $CH_3{}^{82}Br$ △ $CH_2{}^{82}BrBr$

Several possible sources for the observed isotope effect in the energetic reaction can be considered, such as in the case of the reaction of the recoil tritium atom[5]: the moderator isotope effect, the probability-integral isotope effect, and the average-energy isotope effect. The present results demonstrate that the yeild of $CH_3{}^{82}Br$ is consistently higher than that of $CD_3{}^{82}Br$ at any mole fraction of the moderator and that the $CH_3{}^{82}Br/CD_3{}^{82}Br$ ratio for the energetic reaction is rather constant (3.0 ± 1.0). These findings are consistent with the moderator isotope effect and /or the probability-integral isotope effect. However, the moderator isotope effect is particularly important in the low mole fraction of the moderator; it becomes less important with an increase in the mole fraction of the moderator, since the energy loss through the nonbonding collisions with the moderator then become predominant. Thus, it would appear that the probability integral isotope effect is more important than the moderator isotope effect.

At this moment, it is not clear why the isotope effect was not found for the total organic yields in the work by Rack et al.[3] One possible reason is the inclusion of a polymer tagged with ^{82}Br in their analytical results.

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

4) J. Okamoto and E. Tachikawa, This Bulletin, **42**, 1504 (1969).

5) E. K. C. Lee, G. Miller and F. S. Rowland, *J. Am. Chem. Soc.*, **87**, 190 (1965).