SHORT COMMUNICATIONS

The Effect of the Krypton Moderator on the Isomeric Transition-induced Reactions of ^{80}Br with CH_4

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(Received October 22, 1970)

In a previous paper[1] we studied the reactions of isomeric transition-activated ^{80}Br in the CH_4-$^{80m}BrBr$ system and found that the $CH_3{}^{80}Br$ yields were much higher than the $CH_2{}^{80}BrBr$ yields over the whole range of mole fractions of the $^{80m}BrBr$ additive. In this paper, we will report on our investigation of the effect of the Kr moderator in the same system in order to elucidate further the chemical behavior of the isomeric transition-activated ^{80}Br.

Nicholas and Rack[2] studied the effects of rare gas moderators on the total organic yields in the CH_4-$^{82m}BrBr$ system and suggested that one-half of the organic products are formed *via* the excess kinetic-energy processes, while the others are formed *via* the thermal ionic (kinetic-energy-independent) processes. Tachikawa[3] and his co-workers[4,5] also studied the influence of the moderator gases, such as He, Ar, and Xe, on the individual product yields in the CH_4-$^{80m}BrBr$ and the CH_4-$^{82m}BrBr$ systems, they concluded that the radioactive $CH_3{}^*Br$ is formed *via* both the excess kinetic-energy and the thermal ionic processes, while the radioactive $CH_2{}^*BrBr$ is formed *via* only the thermal ionic processes.

Since the Br_2 additive is an efficient moderator of the bromine hot atoms, it is necessary to use the smallest pressure of Br_2. Therefore, in our experiments, the mole fraction of the $^{80m}BrBr$ additive to CH_4 was kept constant at 0.029 and the individual product yields were determined in the presence of pressures of Kr gas sufficient to remove the excess kinetic-energy of the ^{80}Br atoms. The experimental methods may be found elsewhere.[1]

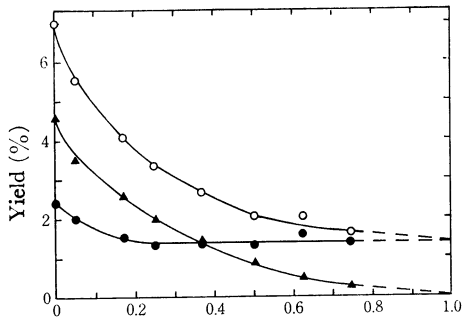

Fig. 1. Effect of the Kr moderator on the product distribution in the reaction of (I.T.)-activated ^{80}Br with CH_4. ($^{80m}BrBr/CH_4=0.029$, total pressure: 400—700 mmHg)
○: ^{80}Br as organic, ▲: $CH_3{}^{80}Br$, ●: $CH_2{}^{80}BrBr$

The effects of the Kr moderator on the total organic and the individual product yields are shown in Fig. 1. Extrapolations of the presented values to the zero mole fraction of the Kr moderator gave the limiting $CH_3{}^{80}Br$ yield of $4.6\pm0.2\%$ and the $CH_2{}^{80}BrBr$ yield of $2.4\pm0.1\%$ respectively. On the other hand, at one mole fraction of the Kr moderator, the data are $0.0\pm0.1\%$ for the $CH_3{}^{80}Br$ and $1.4\pm0.1\%$ for the $CH_2{}^{80}$ BrBr respectively. Our value of 1.4% for the total organic yield at one mole fraction of the Kr moderator was agreed very well with that of 1.6% reported by Tachikawa[3] and his co-workers[4,5] for the ^{80}Br and ^{82}Br systems. However, it was significantly lower than that of 3.7% reported by Nicholas and Rack[2] for the ^{82}Br. It is not immediately obvious why our value is lower than their value.

Under our experimental conditions, $CH_3{}^{80}Br$ may be seen to be formed *via* only the excess kinetic-energy processes. On the contrary, it is clear that the $CH_2{}^{80}BrBr$ yield of 2.4% minus 1.4% is derived from the excess kinetic-energy processes and that of 1.4% is derived from the thermal ionic processes. These facts indicate that about 80% of the organic products are formed principally *via* the excess kinetic-energy processes, while the rest are formed principally *via* the thermal ionic processes under the present conditions.

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