An Additional Formation of $CH_2{}^{80}BrBr$ *via* a Kinetic-energy-independent Process in the Highly Moderated ^{80m}Br-CH_4 Systems

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(Received July 21, 1971)

The moderator effect of Kr on the reaction of (I.T.)-activated ^{80}Br with CH_4 has been examined, keeping the ratio of Br_2/CH_4 at 0.02 or 0.05. The yield of $CH_2{}^{80}BrBr$ shows a slight decrease at the beginning of moderation and then tends to increase with further moderation. These facts suggest an additional formation of $CH_2{}^{80}BrBr$ *via* a thermal ionic process in highly-moderated systems. When the concentration of Br_2 is varied in the system containing 10 cmHg of CH_4 and from 40 to 36 cmHg of Kr, the yield of $CH_2{}^{80}BrBr$ first increases and then decreases, showing a broad maximum. This dependence not only partly explains the inconsistence of the present results with those previously reported, but also suggests the competition of two types of reaction in its formation. One must be the reaction of a radioactive radical with Br_2, leading to the formation of $CH_2{}^{80}BrBr$:

$$\cdot CH_2{}^{80}Br + Br_2 \longrightarrow CH_2{}^{80}BrBr.$$

The other type of reaction is a scavenging reaction of Br_2 for the reacting ^{80}Br atom.

The determination of the relative importance of the kinetic energy and the positive charge in reactions of the recoil Br atom is a current subject in the recoil Br chemistry. So far, many extensive investigations of the subject have been carried out, particularly on the reactions of ^{80}Br with CH_4.[1-4]

While the (n,γ)-activated ^{80}Br reacts with CH_4 to yield $CH_3{}^{80}Br$, mainly as a result of the recoil kinetic energy acquired by the ^{80}Br atom,[5] the (I.T.)-activated ^{80}Br reacts by two processes, one involving excess kinetic energy, and the other, a thermal process.

Following the determination of the total organic yield by Spicer and Gordus,[6] Tachikawa and Kahara[3] examined the molecular distribution of the products under a high concentration of bromine and reached the conclusion that $CH_2{}^{80}BrBr$ is formed principally *via* the kinetic energy-independent process, while $CH_3{}^{80}Br$ is formed *via* both kinetic-energy and kinetic energy-independent (thermal ionic) processes. Since the Br_2 additive is an efficient moderator of the ^{80}Br atom, it is rather desirable to use the smallest pressure of Br_2. Recently Yagi *et al.*[4] reexamined the above reactions in a Kr-moderated system, keeping $Br_2/CH_4=0.029$; they reached the different conclusions that $CH_3{}^{80}Br$ is principally formed *via* the kinetic-energy process and that $CH_2{}^{80}BrBr$ is formed *via* both processes.

These experiments were all carried out in the total pressure range from 50 cmHg to 76 cmHg. It has been reported that the yields of individual organic products increase with an increase in the total pressure, but tend to level off around 50 cmHg.[3] Thus, one of the possible factors which are responsible for the inconsistency among the results previously reported was the variation in the Br_2 added as a scavenger in the systems.

In the current set of experiments, we carefully studied the reactions, particularly in highly-moderated systems. The results obtained showed a characteristic in $CH_2{}^{80}BrBr$ with the Br_2 concentration. A qualitative explanation of the above contradiction has been attempted.

Experimental

The experimental procedure was the routine one for the study of ^{80}Br activated by the isomeric transition of ^{80m}Br; it involved the irradiation of Br_2 in a quartz ampoule, mixture with reactants and analysis of the products by means of radio-gas chromatography. The details can be found elsewhere.[3]

Materials. Bromine came from the Kanto Chemical Co., and was used after simple purification by vacuum distillation. Methane and krypton, the nominal purities of which were both 99.995%, were supplied by the Takachiho Chemical Co., and were used directly from the vessel.

Measurement of Br_2-pressure. In our previous experiments,[2,3] we used an oil manometer to measure the pressure of irradiated Br_2 added to reaction ampoules. However, it was rather difficult to measure a pressure of less than 1.0 cmHg by means of this apparatus. In the present set of experiments, therefore we used a digital precision pressure gauge, model 145 (Texas Instruments), which involves a quartz buldon gauge. This apparatus allows us to measure pressures down to 0.1 mmHg with precision of better than ±5%.

Sample Processing. All relative products distributions were determined by radio-gas chromatography, employing a side window-type gas-flow counter. The inorganic bromides were isolated from the organic bromides by the insertion of a short glass column packed with potassium ferrocyanide into the gas stream ahead of the organic separation column. The separation column consisted of a celite base (60—80 mesh) coated with dioctyl sebacate (15% by weight) packed in a glass tube 4 mm in inside diameter and 5 m long. The major products observed were, in all cases, $CH_3{}^{80}Br$ and $CH_2{}^{80}BrBr$, although several minor products, such as $C_2H_5{}^{80}Br$ and $CH_2{}^{80}BrBr_2$, were also observed.

In the determination of the total organic yields, the products were frozen by dipping an ampoule into a liquid-nitrogen bath. The tip of the ampoule was cut in order to pour a mixture of 5 ml of 0.5M Na_2SO_3 and 3 ml of CCl_4. After sealing-off the tip, the ampoule was vigorously shaken. The organic phase was then separated from the inorganic one. Each phase contained in a vessel specially designed for count-

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

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

3) E. Tachikawa and T. Kahara, *ibid.*, **43**, 1293 (1970).

4) M. Yagi, K. Kondo, and T. Kobayashi, *ibid.*, **44**, 580 (1971).

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

6) L. D. Spicer and A. A. Gordus, "Chemical Effects of Nuclear Transformations," Vol. 1, IAEA, Vienna (1965), p. 185.

ing was measured by an end window-type gas-flow counter. The activity of ^{80}Br in each phase was corrected for ^{80m}Br and ^{82}Br using the decay curves of the activities. No correction for freezing, shaking, or separation was applied in the calculations of the total organic yield, since the decay correction based on the time spent for these processes was less than a few percent and could be disregarded. The percentage yields reported in this paper were the percentage of individual activities relative to the total organic activities observed, multiplied by the total organic yield.

Results

The effects of the moderator gas, Kr, on the individual product yields are graphically depicted in Fig. 1. The plots include all the results obtained from systems where the concentrations of Br_2 as a scavenger, relative to CH_4, were 0.02 and 0.05. In all cases, the total pressure was kept constant at 50 ± 1 cmHg. At zero m.f. of Kr, the yields were $4.3\pm0.4\%$ $CH_3{}^{80}Br$, $2.1\pm0.2\%$ $CH_2{}^{80}BrBr$, and $6.4\pm0.6\%$ total organic.

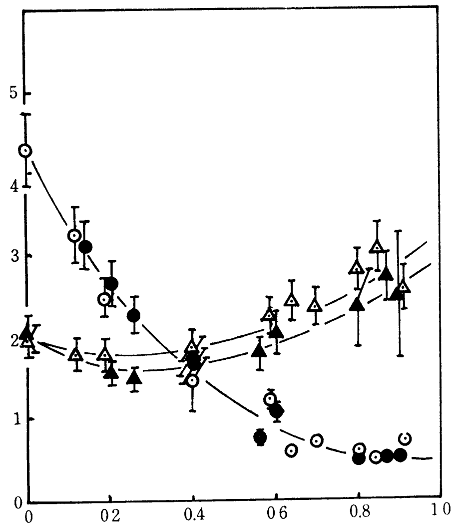

Fig. 1. The Kr-moderator effects on the individual products. The ratio, Br_2/CH_4 was 0.02 and 0.05
Br_2/CH_4: 0.02 ●: $CH_3{}^{80}Br$ ▲: $CH_2{}^{80}BrBr$
Br_2/CH_4: 0.05 ⊙: $CH_3{}^{80}Br$ △: $CH_2{}^{80}BrBr$

As the dilution of the reaction system with Kr proceeded, the yield of $CH_3{}^{80}Br$ decreased and could be extrapolated to $0.6\pm0.1\%$ at 1.0 m.f. of Kr in either case. However, the yield of $CH_2{}^{80}BrBr$ showed a slight decrease at the beginning of dilution, but it tended to increase when the m.f. of Kr exceeded 0.5. At 1.0 m.f. of Kr, the limiting yield of $CH_2{}^{80}BrBr$ was $2.9\pm0.3\%$ or $3.2\pm0.3\%$; depending upon the value of Br_2/CH_4.

In order to examine the yield variation with the concentration of Br_2 in highly-moderated systems, the Br_2/CH_4 ratio was varied from 0.01 to 0.4, while keeping the pressure of CH_4 constant at 10 cmHg. Consequently, the pressure of Kr (40 to 36 cmHg) was adjusted to attain a total pressure of 50 ± 1 cmHg. In view of the relative efficiency of Br_2 and Kr as kinetic-energy moderators for an energetic ^{80}Br, the change in moderator efficiency accompanied by the small variation in composition, cannot be important. The results obtained are plotted in Fig. 2. The variation in $CH_3{}^{80}Br$ did not exceed the experimental fluctuation from the value of $0.6\pm0.1\%$ over the range studied. On the other hand, the yield of $CH_2{}^{80}BrBr$ increased with the increase in the ratio of Br_2/CH_4 at the beginning, and then decreased when the ratio exceeded around 0.15, showing a broad maximum in the range from 0.05 to 0.10 of Br_2/CH_4.

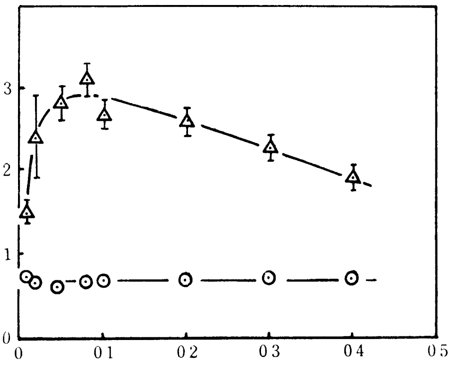

Fig. 2. The effects of the variation of the ratio, Br_2/CH_4 on the yields of $CH_3{}^{80}Br$ and $CH_2{}^{80}BrBr$ in the highly moderated systems (CH_4: 10 cmHg, Br_2: 0.1—4.0 cmHg, and the total pressure was kept constant at 50 ± 1 cmHg by adjusting Kr-pressure).
⊙: $CH_3{}^{80}Br$ △: $CH_2{}^{80}BrBr$

Discussion

Comparisons with Reported Results. The total organic yield ($6.4\pm0.6\%$) with no additive agreed reasonably well with those reported by Spicer and Gordus ($6.8\pm0.8\%$)[6] and by Yagi *et al.* ($7.0\pm0.3\%$).[4] However, when the limiting yields of the individual products at 1.0 m.f. of Kr are compared, a significant difference can be noticed between the present results and the Yagi *et al.* results. They reported the limiting yield of zero percent for $CH_3{}^{80}Br$ and 1.4% for $CH_2{}^{80}BrBr$. In their series of moderator experiments, the smallest m.f. of CH_4 reached was 0.25, and their extrapolation of the yields of products to 1.0 m.f. of Kr relied on results covering the range from zero to 0.75 m.f. of Kr. According to the present results, however, their extrapolated curves do not necessarily represent the real moderator curves under highly moderated conditions. For example, when the variations in $CH_3{}^{80}Br$ from zero to 0.7 m.f. of a moderator in the present results are taken into account, the extrapolation of $CH_3{}^{80}Br$ to zero percent at 1.0 m.f. of moderator is rather probable. Thus, their results can be understood to show the moderator effects of the products up to around 0.75 m.f. of moderator, but can not be extented to much further moderation.

The most significant difference between the present results and the reported ones, however, can be seen in the yield of $CH_2{}^{80}BrBr$ at a higher moderation, and consequently in its limiting yield at 1.0 m.f. of Kr. When the Br_2/CH_4 ratio was varied while keeping the pressure of CH_4 constant, at 5.0 cmHg (the pressure of Kr was also varied from 45 to 41 cmHg to attain the total pressure of 51 cmHg), a dependence of the yield of $CH_2{}^{80}BrBr$ as the Br_2/CH_4 ratio similar to that shown in Fig. 2 was observed. This suggests that this kind of variation in the yield curve of $CH_2{}^{80}BrBr$ with the ratio can always be expected at high moderations and that a small variation in the ratio sometimes leads to a large difference in the yield of $CH_2{}^{80}BrBr$. Consequently, the limiting yields of $CH_2{}^{80}BrBr$ and of the total organic at 1.0 m.f. of Kr may vary considerably depending upon the amount of Br_2 added in highly moderated systems. Thus, if the Br_2/CH_4 ratio is varied little from 0.02 in such a high moderation, the difference in the yield of $CH_2{}^{80}BrBr$ between the two experiments, the present and the previous ones, can be easily accounted for.

In most of the moderator experiments previously reported,[7] the amount of Br_2 relative to that of the reactant was determined from scavenger curves in the unmoderated systems. Once it was determined, the Br_2/reactant ratio was kept constant or nearly constant throughout the m.f. of the moderator. With regard to this conventional selection of the Br_2/reactant ratio the present results are thus very suggestive. In conclusions, in order to identify the yields of the organic products as the kinetic-energy or kinetic-energy-independent yields, the present types of behavior of the products under highly moderated conditions, as well as the physical natures of the moderator[8] must be taken into account.

Kinetic-energy-independent Yields of Products. From the results shown in Fig. 1, it may be concluded that the kinetic-energy-independent yield of $CH_3{}^{80}Br$ was $0.6\pm0.1\%$, which corresponded to *ca.* 14% of the total $CH_3{}^{80}Br$ formed. This conclusion, however, includes the assumption that the moderator curve obtained reflects the true reaction processes involved in the formation of $CH_3{}^{80}Br$. Recent moderator experiments on ^{80m}Br–C_2H_6,[8] however, have indicated that when the reaction system is diluted with inert gases, the distribution of the charged ^{80}Br is modified so that an additional formation of $CH_3{}^{80}Br$ *via* the kinetic-energy-independent process occurs. Furthermore, in the present work the increase in the yield of $CH_2{}^{80}BrBr$ at a high moderation is an indication of the additional formation of the compound *via* the kinetic-energy-independent process. Thus, the present value of 0.6% for the kinetic-energy-independent yield of $CH_3{}^{80}Br$ should be understood to be a maximum value.

On the other hand, it is not possible to identify the observed yield of $CH_2{}^{80}BrBr$ with no additive as kinetic-energy and kinetic-energy-independent yields on the basis of the present results alone. Nevertheless, we preferred to conclude that it was mainly formed *via* the kinetic-energy-independent process and that the formation due to the kinetic-energy process was less important. This is qualitatively consistent with the conclusion reached in the early experiments using a rather high concentration of Br_2.[9] One support for the above prediction is given by the recent experiments in our laboratory.[10] When the $^{82}BrBr$ molecule is irradiated with the light of the wavelength of 2537 Å, an energetic ^{82}Br atom with 1.2 or 1.7 eV, but with no charge is formed. This atom reacts with CH_4 to give $CH_3{}^{80}Br$. The $CH_2{}^{80}BrBr$ was not detected within the limits of experimental uncertainty, and its yield, if it is also formed, must be less than a small percentage of that of $CH_3{}^{82}Br$. The results obtained with the reaction of ^{80}Br activated by the (n,γ) process with CH_4 were also consistent with the above prediction. The ^{80}Br thus activated has a higher energy and less charge than that from the (I.T.) activation, and it reacts with CH_4 to yield a total organic yield of 13.8%, principally *via* the kinetic energy process.[5,11] Spicer and Gordus reported that 89% of the total organic yield was $CH_3{}^{80}Br$, while 11% was $CH_2{}^{80}BrBr$. A further analysis of the results using the Estrup-Wolfgang kinetic theory showed that the yields due to the kinetic-energy processes were 12.3% for $CH_3{}^{80}Br$ and 1.0% for $CH_2{}^{80}BrBr$.[12] These values gave the ratio of 0.08 for $CH_2{}^{80}BrBr/CH_3{}^{80}Br$.

As a crude approximation, we attempt to evaluate the maximum yield of $CH_2{}^{80}BrBr$ due to the kinetic-energy process in the present reaction with the assumption that the value of 0.08 for the $CH_2{}^{80}BrBr/CH_3{}^{80}Br$ ratio also holds in the present reaction system. The maximum yield of the kinetic-energy process to form $CH_2{}^{80}BrBr$ was estimated to be $0.08\times3.9=0.3\%$, this, however, explains only 14% of the total yield of $CH_2{}^{80}BrBr$.

Effects of the Br_2 Concentration on $CH_2{}^{80}BrBr$ in Highly Moderated Systems. The appearance of the maximum in the yield of $CH_2{}^{80}BrBr$ in Fig. 2 can only be explained in terms of the competition between two types of reaction.[13] If at least a part of the yield is directly dependent on the presence of inactive bromine, the latter contributes to their formation. An example would be the reaction of a radioactive radical with Br_2, leading to the formation of $CH_2{}^{80}BrBr$:

$$\cdot CH_2{}^{80}Br + Br_2 \longrightarrow CH_2{}^{80}BrBr.$$

The other type of reaction involved is a scavenging reaction of Br_2 for the reacting ^{80}Br atom, since Br_2 is the reacting scavenger. At higher concentrations of inactive bromine, the collision of the reacting ^{80}Br with Br_2 becomes important and the yield is progressively

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[7] J.E. Willard, "Chemical Effects of Nuclear Transformations," Vol. 1, IAEA, Vienna (1965), p. 221.

[8] E. Tachikawa and K. Yanai, *Radiochim. Acta*, **17**, 138 (1972).

[9] E. Tachikawa and J. Okamoto, *Radiochim. Acta*, **13**, 159 (1970). In the series of previous experiments, the yield of $CH_2{}^{80}BrBr$ was constantly smaller than those expected from the present works. This is partly due to the experimental method used. In the previous works, the reaction mixture was once transferred into the injection loop for the radio-gas chromatographic analysis. Thus a constant fraction of $CH_2{}^{80}BrBr$ was lost due to the adsorption, mainly on the stopcock involved. Furthermore an addition of Xe or Ar as a moderator may lead to a different behavior of $CH_2{}^{80}BrBr$. However, this does not alter the conclusion previously reached that $CH_2{}^{80}BrBr$ was mainly formed *via* the kinetic-energy-independent process.

[10] K. Hamanoue and E. Tachikawa, unpublished data.

[11] M. Saeki, K. Numakura, and E. Tachikawa, This Bulletin, **45**, 1715 (1972).

[12] M. Saeki and E. Tachikawa, presented at the 26th Annual Meeting of the Chemical Society of Japan, Hiratsuka, Kanagawa (April, 1972), to be appeared in this Bulletin.

[13] Z. Abedinzadeh, R. Radicella, K. Tanaka, and M. Milman, *Radiochim. Acta*, **12**, 4 (1969).

reduced and the usual scavenger curve prevails.

The fact that a small concentration of Br_2 (6×10^{-2} m.f.) brings about such a sharp increase in the yield also means that the radical responsible for it must be reasonably stable and long-lived to be able to react with Br_2. Assuming the Maxwellian distribution of both $CH_2{}^{80}Br$ and Br_2, the life-time of the radical was calculated as $\geq 10^{-7}$ sec.[14]

The formation of the $CH_2{}^{80}Br$ radical must involve the breaking of two C–H bonds. In an energetic reaction, the importance of the double-replacement reaction is already known.[15] However, the foramtion of the $CH_2{}^{80}Br$ radical in the present reaction system is probably initiated mostly *via* the kinetic-energy-independent process of ^{80}Br. The direct application of the double-replacement reaction to the present case, therefore cannot be made. As was suggested in a previous paper,[9] the formation of $(CH_4{}^{80}Br)^+$ is the most realistic primary step involved. However, the details of the reaction pass leading to $CH_2{}^{80}BrBr$ from $(CH_4{}^{80}Br)^+$ must await the carrying-out of further experiment.

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[14] The calculation based on the equation,

$$Z = N_2 \sigma_{12}^2 \left(\frac{8kT}{\pi\mu} \right)^{1/2}$$

for the collision density (see S. W. Benson "The Foundations of Chemical Kinetics," MacGraw-Hill, New York, (1960) p. 153). The molecular diameter used are 4.27 Å for Br_2 and 4.0 Å for CH_2Br in analogy with CH_3Br (ref. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "The Molecular Theory of Gases and Liquid," John Wiley and Sons, Inc., New Yrok, (1960) p. 1110).

[15] R. Wolfgang, "Prog. Reaction Kinetics," Vol. 3 (1965) p. 97.