similarity in product distribution for ethane (Table III) and ethene (Table V). Table VII indicates that these telomer chains may occur before Br addition on the basis of Markovnikov orientation of C_3H_7Br for the ethane and propane systems.

The low product yields for reaction in solid ethene (Table V) may not reflect low reactivity of the nascent bromine but rather failure of the intermediate radical (following Br addition) to abstract hydrogen from neighboring C_2H_4 molecules. The mechanism for C_3H_7Br production probably involves direct recoil dissociation of ethane ($C_2H_4 = 2CH_2$, $\Delta H = 9.06$ eV), which may be assisted through the charge neutralization process. Such single-carbon radical addition to ethene would produce a secondary C_3H_7 radical which could react with Br to give the virtually complete i-C_3H_7Br results shown in Table VII.

The product yields for reaction of decay-produced bromine with cyclopropane probably involve rearrangement of the substrate to allene rather than fragmentation of the parent compound. The activation energy for the formation of alkyl radical from c-C_3H_6 is $\sim$0.8 eV,[33] so we can expect that rearrangement of c-C_3H_6 to form C_3H_6 should be possible for both ^{76}Br and ^{77}Br. However, the complete yield of i-C_3H_7Br (Table VII) indicates that it is the rearranged allyl radical which reacts with bromine rather than the anti-Markovinikov addition of Br to allene. The substantial yield of C_2H_5Br may be related to the thermodynamic ease for cyclopropane decomposition to ethene ($2c\text{-}C_3H_6 = 3C_2H_4$, $\Delta H_R° = -2.72 \pm 0.02$ eV), which may further telomerize to give the higher homologues of Table VII.

Conclusion

A method to study the chemical effects of nulear transformations which produce bromine atoms has been described. This method involves the generation of ^{76}Br and ^{77}Br which are formed by the decay of ^{76}Kr and ^{77}Kr, respectively. It was interesting to compare these two bromine isotopes since the energetics and decay modes of each are different, and therefore differences would be expected in their reactivities. The reactions of both bromine isotopes can be studied simultaneously with the use of γ-ray spectrometer since each emits characteristic gamma rays. High-pressure liquid chromatography was applied to the study of these isotopes as an analytical procedure since this method possesses some advantages over the more conventional method of gas chromatography.

In the solid phase at 77 K very different product distributions were observed for the two isotopes. These differences were interpreted in terms of variations in charge states and recoil energy for ^{76}Br and ^{77}Br. Bromine-76 reactions involve combination with unsaturated compounds which result from rearrangement of carbonium ions produced during charge neutralization of bromonium cations. Contrasting are the reactions of ^{77}Br, which result primarily from radicals produced by dissipation of recoil energy in the solid substrate. The differences in the product distributions for the two isotopes are due to the fact that the nature of the reactive cage environment is different when produced as the result of charge neutralization or recoil energy dissipation.

Acknowledgment. We thank the staff of the Washington University who operated the 52-in. cyclotron for their assistance. J. J. F. was supported by NIH MSIP Grant No 5-T05-GM02016.

---

(33) Kerr, J. A.; Smith, A.; Trotman-Dickenson, A. F. *J. Chem. Soc.* **1969**, 1400.

Reactions of Recoil Bromine Formed by the $^{76,77}\mathrm{Kr} \rightarrow {}^{76,77}\mathrm{Br}$ Systems with Simple Hydrocarbons. Pressure and Additive Effects on Gas-Phase Reactivity[1]

James J. Frost, Stephen M. Moerlein, and Michael J. Welch*[2]

Contribution from the Mallinckrodt Institute of Radiology, Washington University School of Medicine, St. Louis, Missouri 63110. *Received July 31, 1980*

Abstract: Recoil bromine species produced by the systems $^{76,77}\mathrm{Kr} \rightarrow {}^{76,77}\mathrm{Br}$ were reacted with a series of hydrocarbons in the gas phase over the density range 2×10^{-5} to 0.5 g/cm^3. In the region below 100 atm differences in reactivity are related to differences in decay modes and recoil energies. In the low-density methane system an ion–molecule mechanism involving excited CH_4Br^+ is suggested. At higher pressures, the yields are explained in terms of the onset of "caging" reactions due to autoradiation effects. At high percent "inert" moderator, yields increased for CH_4, above those of the pure methane system. Brominating complexes such as $KrBr^+$ and $ArBr^+$ are hypothesized to explain the results.

The influence of charge and kinetic energy on the reactions of bromine atoms produced by nuclear recoil methods have been studied intensively for several decades.[3] The large variety of nuclear processes which are available for the production of bromine atoms often result in bromine atoms with different initial kinetic energies, initial charges, and initial degrees of electronic excitation. On the basis of these differences in the initial state of the bromine atom, in most cases one can expect differences in its chemical reactivity. By correlating such differences with knowledge of the charge, kinetic energy, and electronic state at the time the atom reacts, one can hope to gain insight into the manner in which these variables influence chemical reactions.

This work represents a study of the reactions of two isotopes of bromine, ^{76}Br and ^{77}Br, which are produced by the method of decay-induced activation. The ^{76}Br and ^{77}Br produced in this manner have different kinetic energies and charges and will be shown to display significant differences in chemical reactivity in the gas phase, as has been done for the solid phase.[4]

Experimental Section

The method used in this work for the production and purification of ^{76}Kr and ^{77}Kr has been described previously.[4] The purified, carrier-free ^{76}Kr and ^{77}Kr are Toepler-pumped into reaction vessels, and the other

---

(1) This work was supported in part by NIH Grants HL13851 and HL14147.

(2) To whom correspondence should be addressed.

(3) For review articles and books see: (a) Campbell, I. G. *Adv. Inorg. Chem. Radiochem.* **1963**, *5*, 135. (b) Wolfgang, R. *Prog. React. Kinet.* **1965**, *3*, 97. (c) *Chem. Eff. Nucl. Transform., Proc. Symp.* **1965**. (d) Stocklin, G. "Chemie Heisser Atome"; Verlag Chemie: Weinheim, West Germany, 1969. (e) Urch, D. S. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1972**, *8*, 149.

(4) Frost, J. J.; Moerlein, S. M.; Welch, M. J. *J. Am. Chem. Soc.*, preceding article in this issue.

components are then added by using standard vacuum-line techniques. For the pressure range 0–40 atm, thick-walled glass vessels fitted with a Teflon needle valve were used and for pressures from 50 to 400 atm stainless-steel vessels and valves were used. Both vessel types were of approximate volume 1.5 mL. All glass vessels were filled to a known pressure by freezing from a known volume (the vacuum line). Pressures were measured by using a Statham pressure transducer, and pressures were displayed to the nearest 0.5mmHg by using a digital voltmeter which had been directly calibrated in millimeters of Hg. Stainless-steel vessels were filled to an approximate pressure by freezing out of a volume of approximately 550 mL. The vessels were weighed before and after filling so that the exact mass of gas added could be determined. From this and the known volume of the vessel, the density could be determined. Studies of identical substrate systems in glass and stainless-steel vessels at the same denisty gave the same results within experimental error. All gases used were of research purity purchased from Matheson Gas Co. with the following composition: methane (99.99% min), 20 ppm N_2, 12 ppm C_2H_6, 10 ppm H_2, 4 ppm O_2; ethane (99.96% min), C_3H_8 0.02%, C_3H_6 0.01%; argon (99.9995% min), $N_2 < 0.1$ ppm, $O_2 < 0.1$ ppm, $H_2 < 0.1$ ppm, $CO_2 < 0.1$ ppm, hydrocarbons as $CH_4 < 0.1$ ppm; krypton (99.995% min), Xe < 25 ppm, $N_2 < 25$ ppm, hydrocarbons as $CH_4 < 10$ ppm, $H_2 < 5$ ppm, $O_2 < 4$ ppm, Ar < 4 ppm; xenon (99.995% min), Kr 50 ppm, N_2 10 ppm, hydrocarbons as CH_4 10 ppm, O_2 5 ppm, Ar 5 ppm, H_2 5 ppm.

The vessels were allowed to stand in the dark for about 24 h, after which the gaseous contents of the reaction vessel were frozen down with liquid nitrogen, and a small amount (approximately 0.25 mL) of 90% CH_3OH–10% H_2O saturated with Na_2SO_3 was added. The unreacted gaseous substrate was then removed as previously described,[4] and the remaining solution of carrier-free quantities of bromide reaction products and unreacted bromide was injected onto three 2-ft Waters Associates Corasil C-18 liquid chromatographic columns ($^3/_8$-in. i.d.) in series. The chromatograph was used in conjunction with a 2 in. × 2 in. NaI(Tl) scintillation detector which counted each separated component consisting of both ^{76}Br and ^{77}Br activity. Data was recorded on-line by using a classic LINC computer.[5] Fractions of the eluant were collected so that each peak could be counted on a Ge (Li) γ-ray spectrometer (Ortec Corp., Oak Ridge, TN) to determine for each component the ratio of ^{77}Br to ^{76}Br activity. From this ratio the percent ^{76}Br of total ^{76}Br activity and percent ^{77}Br of total ^{77}Br activity could be calculated for each component.[4] Errors in the data can result from several sources including the composition of the gas and the peak areas obtained from the NaI detector counting. The major errors result from counting of two or more samples from each experiment on the Ge (Li) detector. The errors here depend on the size of the peak and range from $\simeq$5% for large (>15% radiochemical yield) peaks to $\simeq$15% for small (1–2% radiochemical yield) peaks.

Results and Discussion

Results were obtained for the reaction of ^{76}Br and ^{77}Br with CH_4 and C_2H_6 over a range of pressures spanning 4 orders of magnitude in the presence of various additives. All results were obtained at room temperature except for the high-pressure C_2H_6 yields. At pressures greater than approximately 50 atm the ethane experiments were carried out at a temperature slightly above the critical temperature of ethane (33 °C) to ensure gas-phase reaction. In order to accomplish this, we placed stainless-steel vessels in an incubator at about 34 °C.

Although complete moderator experiments were done only with Kr and Ar, the yield of CH_3Br for the system 99.5% Xe + 0.5% CH_4 at 25 atm was determined to be zero within experimental error.

The yields from CH_4 at 25 atm were also obtained by the technique of organic–aqueous extraction and were identical within experimental error to those obtained by the chromatographic method. In the chromatographic method yields are expressed as a percent of the total activity which is in organic and inorganic forms. The inorganic fraction consists predominantly of Br$^-$ (90%–99%), but a second, and as yet unidentified, polar peak is also observed. That this peak is inorganic is shown by the fact that in an organic–aqueous partition experiment all the activity remains in the aqueous phase. In addition, the yields were determined for CH_4 experiments at 25 atm at temperatures of 100 and −78 °C and were found to be the same within experimental error to those at room temperature. Also, blank samples were done in which the CH_4 was added *after* the 24-h decay period. In this case no labeled CH_3Br was observed.

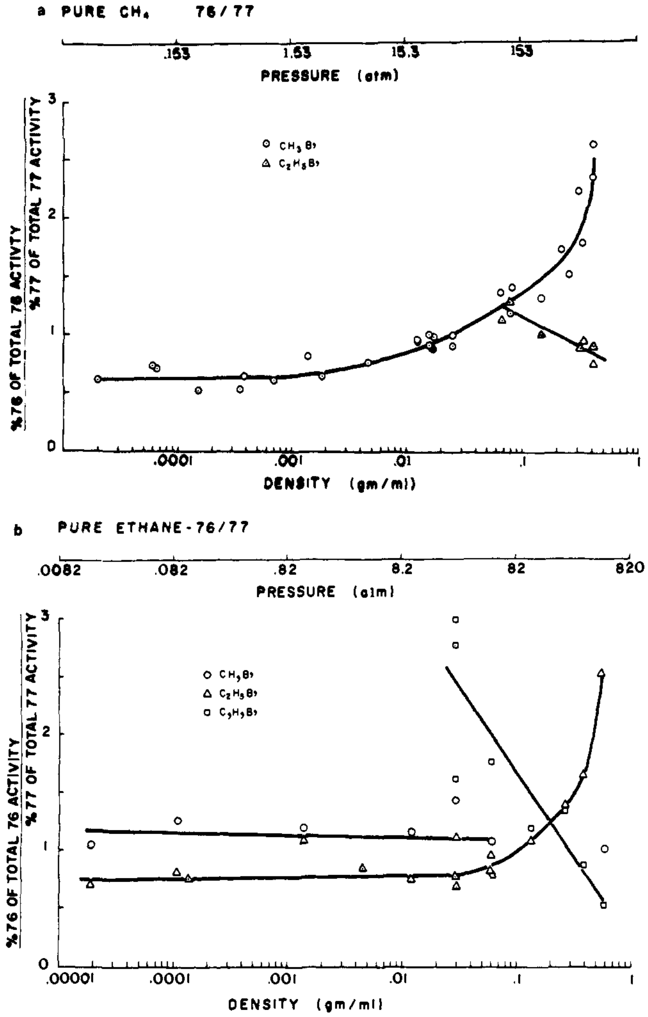


Figure 1. Ratio for the ^{76}Br yield to the ^{77}Br yield for the reaction with (a) CH_4 and (b) C_2H_6. Far right-hand points represent solid-phase values.

For each set of data, except that in Figure 3, the ^{76}Br and ^{77}Br yields are presented and the ratio of the ^{76}Br yield to the ^{77}Br yield for each product is given in a separate figure. Since the major thrust of this work is a comparison of the chemical consequences of two decay processes, it is important to present the data as both absolute and relative yields.

Although the yields from ^{76}Br and ^{77}Br reacting with methane and ethane are similar, there is a difference, as can be seen from Figure 1. For most of the low-pressure region the primary yield from ^{77}Br is greater than that from ^{76}Br, even though 46.8% of ^{77}Br is formed in the very unreactive state of Br$^-$.[6] It appears that the higher reactivity of ^{77}Br in the low-pressure region must be due to the higher average recoil energy of ^{77}Br atoms. The only fraction of ^{77}Br atoms which have a higher average recoil energy than the ^{76}Br atoms are those formed by EC decay of ^{77}Kr, which is not followed by IC decay via long-lived (>10^{-11} s) states of ^{77}Br; this fraction comprises 13.3% of all ^{77}Br atoms.[4]

The importance of kinetic energy in the formation of CH_3Br is also indicated by moderator experiments (see Figure 2). The fact that the CH_3Br yields for both isotopes are reduced by the addition of Kr or Ar indicates that reactions which give rise to

---

(5) Loberg, M. D.; Coble, C.; Mullani, N.; Straatmann, M.; Welch, M. J. presented at the 6th International Hot Atom Chemistry Symposium; Brookhaven National Laboratory: New York, 1971.

(6) Kashihara, N.; Vietzke, E.; Zellerman, G. *Chem. Phys. Lett.* **1976**, *39*, 316.

(7) Field, F. H.; Franklin, J. L. In "Electronic Impact Phenomena"; Academic Press: New York, 1970; p 163.

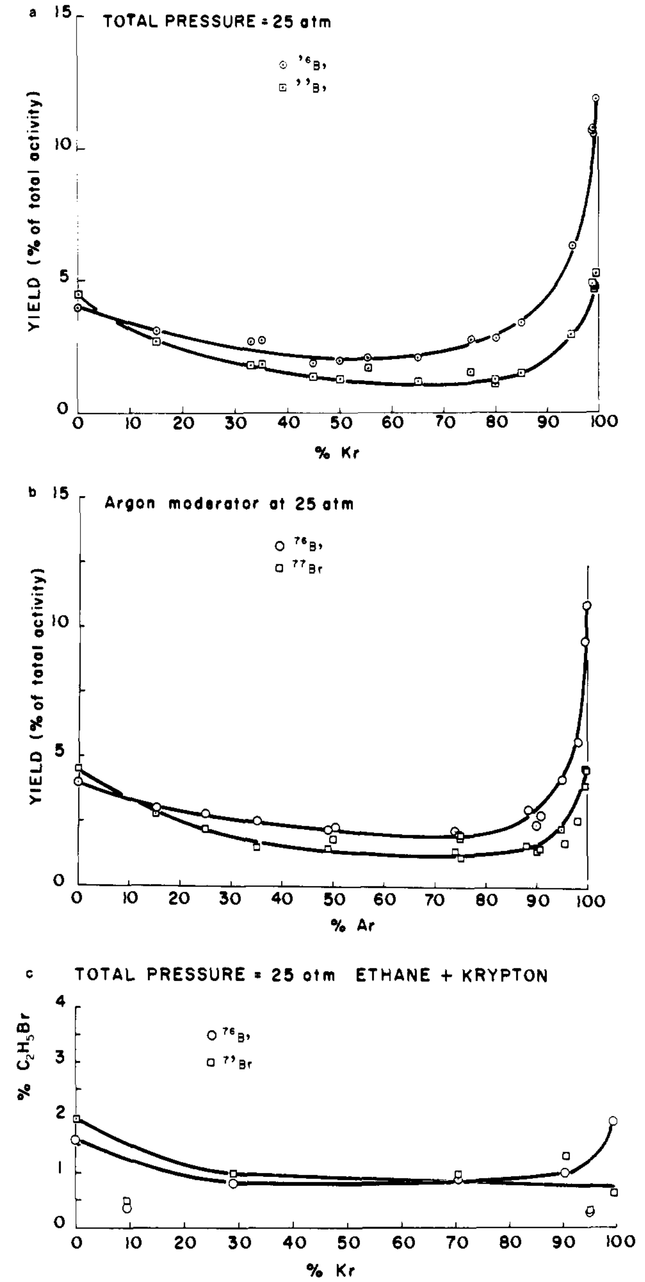


Figure 2. Primary yields as a function of added inert moderator at a total pressure of 25 atm: (a) $CH_3{}^{76}Br$ and $CH_3{}^{77}Br$ in added Kr; (b) $CH_3{}^{76}Br$ and $CH_3{}^{77}Br$ in added Ar; (c) $C_2H_5{}^{76}Br$ and $C_2H_5{}^{77}Br$ in added Kr.

CH_3Br are kinetic energy dependent. In addition, the fact that the $CH_3{}^{77}Br$ yield is reduced more than the $CH_3{}^{76}Br$ yield indicates that the $CH_3{}^{77}Br$ yield is more dependent on kinetic energy than is the $CH_3{}^{76}Br$ yield.

Since ^{76}Br atoms are all charged initially and we are attributing the ^{77}Br yield to the EC function of ^{77}Kr decays, it seems that charged species may be important. By comparing the ionization potential of CH_4 with the electronic recombination energies of various excited states of Br^+, we can predict which excited states of Br^+ can be supported in a CH_4 environment. Only if ΔH for the reaction $Br^+ + CH_4 = CH_4{}^+ + Br\cdot$ is less than or equal to zero will charge exchange take place,[5] assuming that the reactants are at low relative velocity and that any exothermicity can be taken up by the vibrational modes of CH_4.[8] Comparing the recombination energies for various excited states of Br^+ with the ionization potential of CH_4 using the above criteria, we see that only the $^3P_1$ and $^3P_0$ states can exist in CH_4.[9] The ΔH for the above reaction involving $Br\cdot$ is 1.15 eV,[10] and this endothermicity must be overcome by the kinetic energy of the Br ion. However, only 17.3% of the bromine ion's kinetic energy can be transferred into the reaction coordinate,[11] so a threshold energy of 1.48 eV/0.173 or 6.65 eV is needed. For the case of ^{77}Br, sufficient kinetic energy is available either from the EC decays (67.5 eV) or some fraction of the positron decays (37.8 eV maximum), but for ^{76}Br the recoil energy (7.5 eV) is barely over the threshold energy required.[4] In addition, this recoil energy is for a bromine atom which is initially formed with a charge of ~5+ and will probably undergo at least one collision with methane before being neutralized by charge exchange. From an average logarithmic energy loss parameter $\alpha_{CH_4} = 0.3 \pm 0.1$,[12] as measured in other systems,[13] the average kinetic energy after one collision is about 74% of the initial kinetic energy. Therefore, the energy of ^{76}Br atoms after one collision is about 5.45 eV, which is below the threshold energy. Thus, whereas some ^{77}Br may react via the above mechanism, ^{76}Br probably does not.

These experiments indicate that charged species are important in the reactions leading to CH_3Br formation. A possible ionic mechanism is $Br^+ + CH_4 = CH_3Br + H^+$, $\Delta H(^3P_1) = 2.76$ eV and $\Delta H(^3P_0) = 3.26$ eV.[14] Reaction involving $Br^+(^3P_1)$ requires at least 2.76 eV/0.173 = 15.95 eV of kinetic energy, so although ^{77}Br could react via the above mechanism, ^{76}Br could not.

An alteration of the above mechanism involves the reaction $H^+ + CH_4 = CH_5{}^+$, $\Delta H = -5.51$ eV.[15] If CH_4 accepts the proton which is ejected, the overall reactions above become endothermic: $Br^+ + 2CH_4 = CH_3Br + CH_5{}^+$, $\Delta H(^3P_1) = -2.75$ eV. Although some reactions have been postulated to explain the results for the reaction of I^+ with CH_4 in a similar system,[16] this mechanism conflicts with the deduction from the moderator experiments that the mechanism probably occurs in endothermic steps.

The compromise solution to this problem is to assume that the actual mechanism lies somewhere between the latter two mechanisms so that the overall mechanism is only slightly endothermic. Such a mechanism may well involve the formation of the intermediate CH_4Br^+ through the following two steps: $Br^+ + CH_4 = CH_4Br^+$ and $CH_4Br^+ + CH_4 = CH_3Br + CH_5{}^+$. The one problem in the evaluation of this type mechanism is that ΔH for the first step is not known, although it is expected to be exothermic. If, in addition, the second reaction is slightly endothermic, then one could explain the observed behavior in the moderator experiments. This idea is supported by the fact that in similar systems involving I^+, the reaction $CH_4I^+ + CH_4 = CH_3I + CH_5{}^+$ was suspected to be endothermic by 0.26–2.0 eV.[16] Thus the interpretation would be that some of the 17.2% of the bromine atom's kinetic energy which is transferred into the internal energy of the CH_4Br^+ complex is available in the second encounter with a CH_4 molecule to effect the endothermic transfer of a proton from CH_4Br^+ to CH_4.

An observation which relates to the above mechanistic considerations concerns the change in the CH_3Br yields with increasing pressure. In these experiments the yields increase only slightly with increasing pressure; a factor of 10^3 increase in pressure results in only an approximately 25% increase in the yields. The two-step mechanism is only operative if the complex possesses internal excitation, so that energy-transferring nonreactive collisions would tend to reduce the probability that the complex would react to form CH_3Br even though they would tend to stabilize it. Pressure stabilization could still operate on the final product,

---

[8] Lindholm, E. In "Ion-Molecule Reactions in the Gas Phase"; American Chemical Society: Washington, DC, 1966; pp 1–19.

[9] Gurnie, E. F.; Magee, J. L. *J. Chem. Phys.* **1957**, *26*, 1237.

[10] Calculated from bond energies In Vedeneyev, V. I.; Gurvich, L. V.; Kondratyev, V. N.; Medvedev, V. A.; Frankevich, Y. L. "Bond Energies, Ionization Potentials and Electron Affinities"; (English Translation); Edward Arnold: London, 1966.

[11] Stocklin, G. "Chemie Heisser Atome"; Verlag Chemie: Weinheim, West Germany, 1969.

[12] Estrup, P. J.; Wolfgang, R. L. *J. Am. Chem. Soc.* **1960**, *82*, 2665.

[13] Sacki, M.; Tachikawa, E. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 839.

[14] Calculated from thermochemical data in ref. 6 and 8.

[15] Beauchamp, J. L. *Am. Rev. Phys. Chem.* **1971**, *22*, 527.

[16] Loberg, M. D.; Krohn, K. A.; Welch, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 5496.

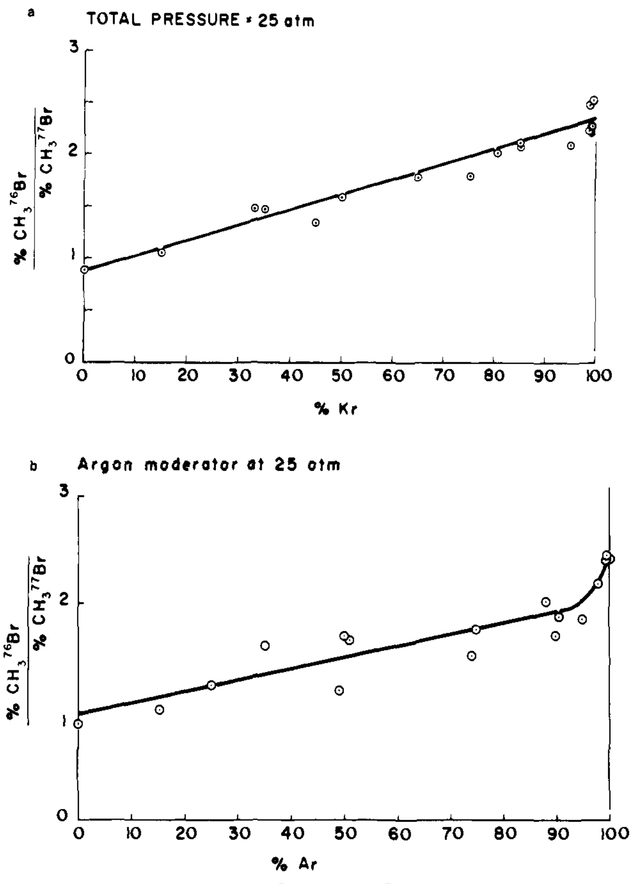


Figure 3. Yield ratios for $CH_3{}^{76}Br$ to $CH_3{}^{77}Br$ from reaction of CH_4 in (a) added Kr and (b) added Ar.

CH_3Br, if it were formed in an excited state, and the slight increase in the yields may be a result of this effect.

Consideration of the moderator experiments (Figures 2 and 3) indicates that at low percent moderator the yield is decreased but at higher percent Kr or Ar the yield increases to values greater than those for pure methane. The initial decrease is due to moderation of kinetic energy, since this is the normal effect of the addition of noble gases and since the yield is reduced more for $CH_3{}^{77}Br$ than for $CH_3{}^{76}Br$.

The approximate linearity of the $^{76}Br/^{77}Br$ yield ratio vs. percent Kr involves two explanations, since there are two processes responsible for the observed yield behavior: kinetic energy moderation in the region below 60% moderator and other mechanisms (to be discussed) at greater than 60% moderator. At the present time we do not have an explanation for the observed linearity in terms of the kinetic energy distribution functions which describe the moderation of kinetic energy in this region.

The more remarkable observation concerning the moderator experiments is the fact that in the region of high percentage moderator the yields increase with increasing percent moderator. It is believed that the reactions are due to Br^+, possible in various excited states. As evidence for this, we note that the ratio of the yields extrapolated to 100% moderator, about 2.4, is approximately the same as the expected ratio of the number of atoms initially formed with a 1+ charge or greater; this value from our calculations is 100/38.9, or 2.6.[4]

There are two effects which can explain the increased yields at high percent moderator: (1) a greater number of reactive bromine atoms or ions are present and/or (2) the reactivity of the reactive species originally present is increased. The first of these explanations involves the fact that krypton can only neutralize the $^1S_2$ state of Br^+ and argon cannot neutralize any states of Br^+.[10] Thus in the case of krypton moderation the $^1D_2$ may be reacting and in the case of argon both the $^1D_2$ and $^1S_2$ may be reacting. As the percent of inert gas increases, the number of nonreactive, quenching collisions between bromine and methane would decrease, leading to an increase in the number of excited Br species.

The second explanation involves the formation of $KrBr^+$ and $ArBr^+$ complexes in the region of high percent moderator and their influence on the reactivity of methane. It may be that reactions in the region of high percent moderation are proceeding via the brominating complexes $KrBr^+$ and $ArBr^+$ since it is known that the isoelectronic molecules Br^2 and BrCl are stable and that the iodine analogs can iodinate various compounds under some conditions.[17] This hypothesis is further supported by the recent isolation of the $KrBr^+$ ion using tandem mass spectrometry.[18] This ion was stable enough for measurements of its enthalpy of formation to be made.

Because reactions taking place in the region of high moderation occur without excess kinetic energy, the mechanism by which they proceed is different from the endothermic mechanism discussed for the low percent end of the moderator curve. It is probable that the general mechanism $Br^+ + CH_4 = CH_3Br + H^+$ is operative and can be exothermic overall if Kr or Ar accepts the proton; the gas-proton affinities for Kr and Ar are 4.51 and 3.53 eV, respectively.[15] Although the proton affinity of CH_4 is greater than that of Kr or Ar, the mechanism probably does not involve formation of $CH_4{}^+$ because increased yield would result at low percent moderator (high CH_4 fraction) rather than at increased moderator concentration. It is also possible that the reaction in this region is proceeding via the one-step reaction: $KrBr^+$ ($ArBr^+$) + $CH_4 = CH_3Br + KrH^+$ (ArH^+). The energetics of the argon reaction is difficult to evaluate because the heat of formation of $ArBr^+$ is not known, but using $\Delta H = 11.47$ for the heat of formation of $KrBr^+$ [18] allows a calculated $\Delta H = -8.71$ eV for the reaction $KrBr^+ + CH_4 = CH_3Br + Kr + H^+$. If proton abstraction to form KrH^+ is assumed to be involved in a one-step reaction mechanism, the ΔH is even greater ($\Delta H = -13.22$ eV). In addition to the $^3P_1$ and $^3P_0$ states, other excited states of Br^+ may be reacting to some extent because of the changing relationship of ionization potentials in the system as Kr or Ar is added. In this case the $^1S_2$ and $^1D_2$ may be reactive, and ΔH for their reactions via the mechanism $Br^+ + CH_4 = CH_3Br + H^+$ are −0.245 and 1.825 eV, respectively.[12] The $^1S_2$ state reacts exothermically with methane and so might provide the needed pathway to CH_3Br. Although krypton can undergo exothermic charge exchange with $Br^+(^1S_2)$, it is expected that the cross section for exchange is low since the energy deficit is so large.[9] Thus it may be that $^1S_2$ states are responsible for the reactivity in both moderator systems.

The yields for the system 99.5% Xe + 0.5% CH_4 at 25 atm were determined since xenon can undergo exothermic charge exchange with all charge states of Br^+ except the ground state. No CH_3Br was formed from either isotope. Although the energy deficit is large, charge exchange may be occurring fast enough to suppress all reactions. Alternatively, perhaps near resonant charge exchange occurs with the $^3P_1$ state with large cross section and reaction by the $^1S_2$ and $^1D_2$ does not occur. The increased yields at high krypton or argon moderation would then be due to increased reactivity of the $^3P_1$ state rather than because more ionic states of Br^+ are available for reaction. A third explanation might involve the fact that the $XeBr^+$ complex is expected to be more stable than the $KrBr^+$ and $ArBr^+$ complexes. This is expected because the gas-phase proton affinities increase in the order Ne < Ar < Kr < Xe,[19] and one would expect a similar order for the Br^+ affinities. If the $XeBr^+$ heat of formation is large enough, reactions of $XeBr^+$ with CH_4 may not be exothermic. However, since the thermochemical data are not available to evaluate this possibility, we tend to support the above interpretation that reactions are due only to $Br^+(^3P_1)$. Although $Br^+(^3P_0)$ cannot be neutralized by Xe, the reaction of $^3P_0$ with CH_4 is more endothermic than that of $^3P_1$, so no CH_3Br is expected to form.

---

(17) Sambols, E.; Williams, H. J. *Nature (London)* **1961**, *190*, 1221.

(18) Watkins, H. P.; Koski, W. S., submitted for publication in *Chem. Phys. Lett.*

(19) Wexler, S. *J. Chem. Phys.* **1962**, *36*, 1992.

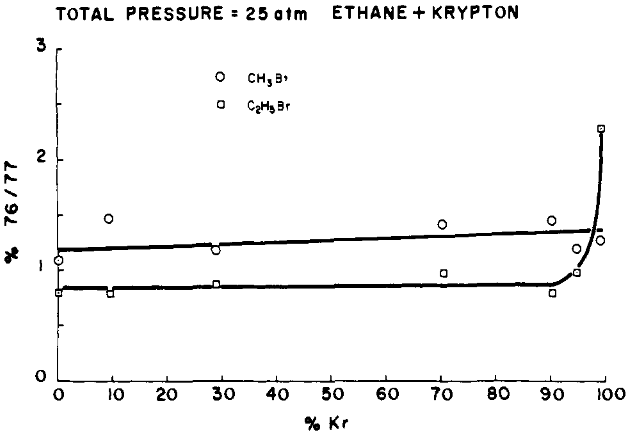


Figure 4. Yield ratios for ^{76}Br to ^{77}Br from reaction of C_2H_6 in added Kr.

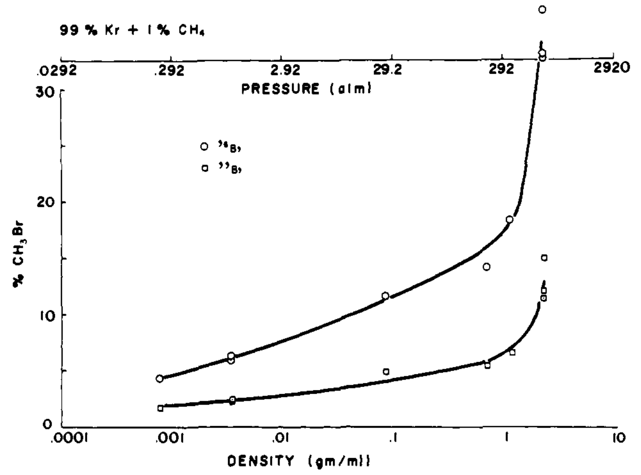


Figure 5. Yields of CH^{76}Br and $CH_3{}^{77}$Br as a function of pressure in the system 99% Kr + 1% CH_4. Far right-hand points are solid-phase values.

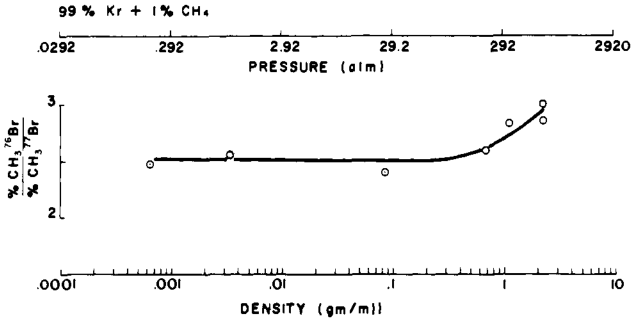


Figure 6. Ratio of $CH_3{}^{76}$Br yield to that of $CH_3{}^{77}$Br from Figure 5.

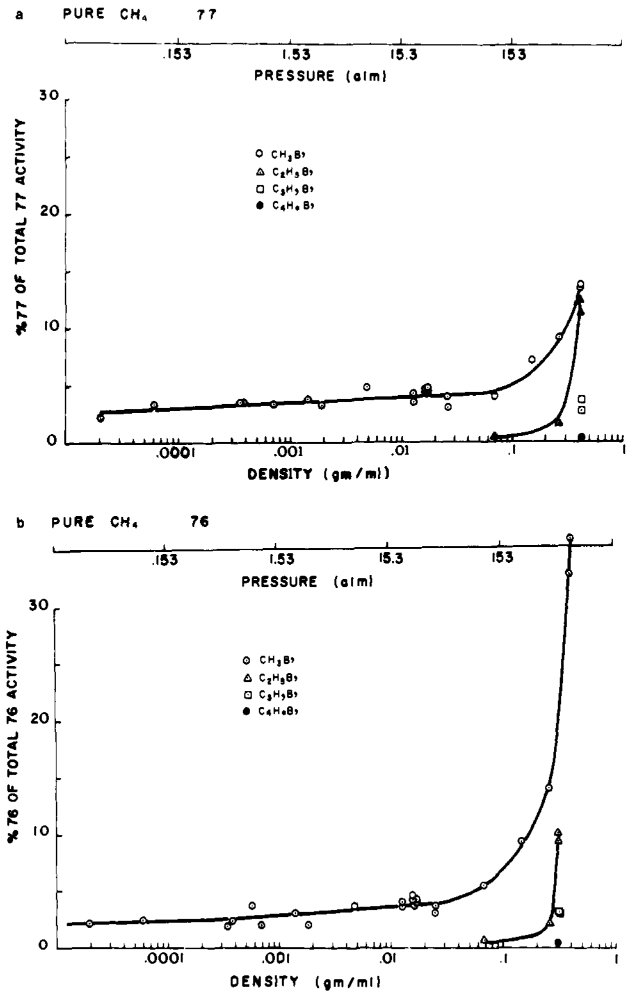


Figure 7. Yield of bromine products from reactions with CH_4 as a function of density (the far right-hand points are solid-phase values): (a) ^{76}Br; (b) ^{77}Br.

It can be seen in Figure 2 that the increase in yield begins at a lower percent moderator for argon than for krypton and that for both moderators the yield of $CH_3{}^{76}$Br increases faster than the $CH_3{}^{77}$Br yield with increasing moderator (see Figure 3). Since ^{77}Br has a higher initial kinetic energy than ^{76}Br,[4] it undergoes more nonreactive collisions with methane before it thermalizes and becomes incorporated into a KrBr$^+$ complex. This results in more quenching of the bromine atom to a less reactive state so that a lower yield of $CH_3{}^{77}$Br results. In addition, since argon is a poorer moderator than krypton, both isotopes undergo more nonreactive collisions before thermalization in argon, so a higher concentration of argon is needed to prevent quenching by CH_4. This explanation also predicts the linear increases in the ^{76}Br/^{77}Br yield ratio with increasing percent moderator (Figure 3) since the fraction of collisions during moderation to thermal energies which occur with CH_4 should be inversely proportional to the percent moderator so that the yield ratio should be directly proportional to the percent moderator.

An alternative explanation would involve the fact that the ArBr$^+$ complex is expected to be less stable than the KrBr$^+$ complex in analogue with the relative stabilities of the KrH$^+$ and ArH$^+$ complexes.[19] Therefore, in the argon system the Br$^+$ ion spends less time combined in the metastable complex than in the krypton system. This means that more collisions occur between CH_4 and the Br$^+$ ion in the argon system and a higher concentration of argon is required to keep the same fraction of Br$^+$ ions complexed.

This type of explanation also accounts for the marked increase in CH_3Br yields with increasing pressure for the system 99% Kr + 1% CH_4 (see Figures 5 and 6) than for similar experiments with pure CH_4 (Figure 7). As the pressure is increased, the fraction of bromine atoms which are present as KrBr$^+$ increases and the excited $^3P_1$ state has a greater chance to react. This also explains the general constancy of the ^{76}Br/^{77}Br yield ratio in Figure 6 because in the limit of 100% Kr the effect on both isotopes would be the same.

In the ethane system (Figures 1 and 8) CH_3Br and C_2H_5Br are formed, although in much lower yields than in the methane system. In ethane, Br$^+$ ions will not exist due to its low ionization potential[10] and so the reactions must occur via the free radical reactions $Br\cdot + C_2H_6 = C_2H_5Br + H$ ($\Delta H = 1.25$ eV)[10] and $Br\cdot + C_2H_6 = CH_3Br + CH_3\cdot$ ($\Delta H = 0.78$ eV).[10] Bromine can transfer 28.2% of its kinetic energy into the reaction coordinate[11] so 7.5 eV × 0.282 = 2.1 eV of kinetic energy is available in the case of ^{76}Br and 67.5 eV × 0.282 = 19.0 eV for the case of ^{77}Br. Both of the above reactions are therefore possible due to the kinetic energy of the recoiling bromine atoms.

Even though the endothermicity of the reaction producing CH_3Br is higher, a higher yield of C_2H_5Br is observed. This might be rationalized from statistical considerations since there are three

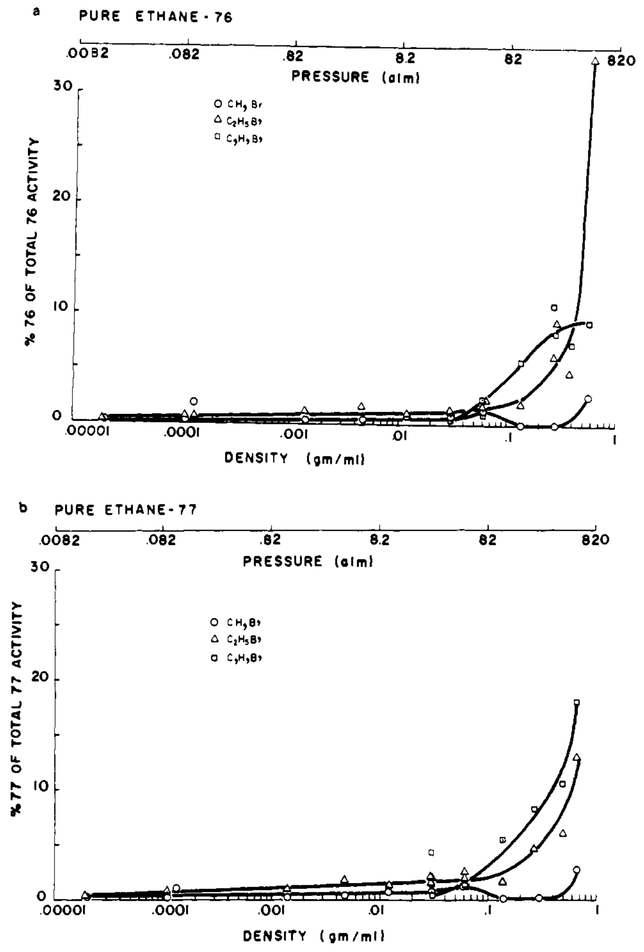


Figure 8. Yield of bromine products from reactions with C_2H_6 as a function of density (the far right-hand points are solid-phase values): (a) ^{76}Br; (b) ^{77}Br.

hydrogen atoms which can be eliminated and only one methyl group. In addition, activation energies may exist and may be greater for the formation of CH_3Br. Whereas the $^{76}Br/^{77}Br$ yield ratio for C_2H_5Br is less than 1, the ratio for CH_3Br is greater than 1 (see Figure 1). The ratio is less than one for C_2H_5Br, which can be explained in terms of the higher kinetic energy of ^{77}Br. Since the reaction leading to the formation of CH_3Br requires less energy, the effects of the differences in kinetic energies between the two isotopes tends to disappear, and a yield closer to that of the total number of Br atoms available for reaction (approximately 100/53.2, or about 2) is seen.[4]

The slight increase in yields with increasing pressure in Figure 8 indicates that the products are not very excited. In addition, the constancy of the $^{76}Br/^{77}Br$ yield ratios in Figure 1 implies that the products are not very excited and hence substitution of a methyl group is probably the only mode of formation of CH_3Br.

The results shown in Figures 2c and 4 demonstrate the importance of kinetic energy in forming C_2H_5Br by both isotopes. At high percent moderator yields are increased, and extrapolation to 100% Kr gives the same yields as in the moderated CH_4 system involving ionic species. The addition of large amounts of moderating gas increases the number of ionic species, some of which react with ethane.

High Density Region

At densities above 0.05 g/mL in both methane and ethane systems one observes a sharp increase in the yields of the primary products (CH_3Br and C_2H_5Br, respectively) as well as the formation of homologous alkyl bromides-C_2H_5Br in the methane case and *n*-C_3H_7Br in the ethane case (see Figures 7 and 8). We believe that at these densities "caging"-type reactions take place as a result of the radiolytic damage which occurs in the environment about the bromine atoms after they are formed.

One problem with this interpretation is that the onset of the yield increases occurs at a density which is fairly low for caging reactions in the usual sense. One commonly thinks of caging reactions occurring at densities where intermolecular densities are on the order of the atomic diameter of the recoiling atom.[11,20] However, the density of 0.05 g/mL corresponds to an intermolecular distance of about 10 Å. Since the atomic diameter of bromine is 1.14 Å and a methane molecule can be considered to be a sphere of radius approximately 1.85 Å,[21] one can see that the density would have to be larger by a factor of 8–10 in order to meet the above requirement for caging.

At lower densities we believe that reaction is occurring due to the formation of radicals from Auger electrons at rather large radii from the initial site of formation of the bromine atoms. As the density is increased the radical environment is compressed about the bromine atoms and the reactivity increases due to the higher concentration of reactive species. Thus, even though the bromine atoms move some distance due to recoil energy imparted to them, at the density of 0.05 g/mL they begin to react to some extent with the radicals formed abut them. In pressure variation experiments using the $^{123}Xe \rightarrow {}^{123}I$ reaction, the onset of the increase is at a density similar to that of the present experiments.[16] This would be expected since the radiolytic mechanisms are expected to be similar.

An important point is that (see Figure 1) the yields of the primary alkyl bromides (CH_3Br in the CH_4 system and C_2H_5Br in the C_2H_6 system) increase faster for ^{76}Br than for ^{77}Br. The interpretation is that ^{77}Br tends to move farther from its site of formation due to its higher average recoil energy and so farther from the center of the radiolytic environment where a higher concentration of reactive species exists; ^{76}Br, with a lower recoil energy, remains closer to the center of the cage and so displays a higher reactivity with increasing density. Even though only 13.3% of all ^{77}Br atoms are formed with a higher recoil energy than ^{76}Br atoms, only 18.8% + 13% = 31.8% of all ^{77}Br atoms undergo Auger charging, so that this 13.3% represents a major fraction of all ^{77}Br reacting due to this mechanism.[7]

Another observation in this density region is that, while the $^{76}Br/^{77}Br$ yield ratio increases with increasing density for CH_3Br and C_2H_5Br (in CH_4 and C_5H_6, respectively), the $^{76}Br/^{77}Br$ yield ratio for the higher alkyl bromides in each system (C_2H_5Br and C_3H_7Br, respectively) decreases with increasing density (see Figure 1). This decrease in the $^{76}Br/^{77}Br$ ratio may indicate the increasing importance of radical formation due to dissipation of recoil energy since ^{77}Br has a higher average recoil energy and therefore may tend to form C_2H_5Br and C_3H_7Br in preference to ^{76}Br. That the slope of the line is greater in the ethane system may indicate that a bromine atom may be more efficient in breaking a C–C bond than a C–H bond.

Conclusion

The reactions of decay-produced ^{76}Br and ^{77}Br with a series of hydrocarbons in the gas phase were studied over a range of density of some 4–5 orders of magnitude. In the low-pressure ($\lesssim$100 atm) gas-phase region the difference in the reactivities of the two isotopes was correlated with the difference in their decay modes and recoil energies. A mechanism proceeding via a vibrationally excited CH_4Br^+ complex was suspected to be operative in the methane system. In the presence of large amounts of "inert" gas moderators yields of CH_3Br are greater than those in pure CH_4. Here a different mechanism was thought to be operative which involves bromination complexes such as $KrBr^+$ and $ArBr^+$. Such increases in the yield at high percent moderator have not been demonstrated in other recoil bromine systems, and this may be due to the ever present macroscopic quantities of various bromine-containing compounds in these systems. In our system bromine is produced free of carrier. At pressures above 100 atm "caging" reactions become predominant as the result of radical

---

[20] (20) Bunker, D. L.; Jacobson, B. J. *J. Am. Chem. Soc.* **1972**, *94*, 1843.

[21] (21) Calculated from bond lengths and atomic diameters In Patterson, C. S.; Kuper, H. S.; Nanney, J. R. "Principles of Chemistry"; Meredith Publishing: New York, 1967.

production due to Auger processes and to dissipation of recoil energy. The relative importance of each of these two modes changes as the density is increased.

Future studies using this system should probably concentrate on the high-density gas-phase region. The low-pressure gas-phase region displays interesting behavior, but the processes which take place in it may be more amenable to study with the use of other techniques such as molecular beams, ion cyclotron resonance spectroscopy, etc. In the solid phase, processes can be studied which would be difficult to study by any other means. These processes are microscopic in nature and include the deposition of small (by nuclear physics standards) amounts of recoil energy in a dense medium, production of transient high local charge in the same, microscopic Auger electron radiolysis, etc. As has been demonstrated,[4] the effects of each are quite different, but it is difficult to vary the conditions under which the processes take place since the experiments are conducted at 77 K. It is difficult or impossible to vary the density, use scavengers, do moderator type experiments, or in general study any two compartment systems. In high-pressure gas-phase studies none of these would be a problem, and thus the microscopic radiolytic processes which take place at condensed-phase densities could be more fully explored. One would like to design a pressure vessel which could withstand on the order of 1000 atm, provide for addition of any gases, and allow for easy retrieval of all the bromine activity in the manner described in the experimental section. Using such an experimental technique, one could more completely explore several high-energy processes which are not easily studied by other methods.

Acknowledgment. We thank the staff who operated the Washington University 52-in. cyclotron for their assistance. J.J.F. was supported by NIH MSTP Grant No. 5-T05-GM02016.

Radical Trapping in a Mass Spectrometer Ion Source. 1

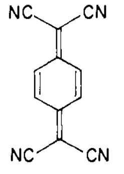
C. N. McEwen* and M. A. Rudat

Contribution from E. I. du Pont de Nemours and Company, Inc., Central Research and Development Department, Experimental Station, Wilmington, Delaware 19898.

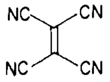
Received November 4, 1980

Abstract: 7,7,8,8-Tetracyanoquinodimethan (TCNQ), tetracyanoethylene (TCNE), and tetracyanopyrazine (TCP) react sufficiently fast with gas-phase carbon-centered radicals that the reaction products dominate the chemical ionization (CI) hydrocarbon reagent gas mass spectrum at high electron emission currents and low partial pressures of TCNQ, TCNE, or TCP. Calculations and radical trapping experiments inside and outside a CI source show that the rate of the TCNQ–radical reaction approaches the diffusion-controlled limit. The radical populations in the CI methane, isobutane, di-*tert*-butyl peroxide, 1-octanol, *n*-octane, and toluene-d_3 plasmas are elucidated, as is the radical population in methane under Townsend discharge conditions. The mechanisms for radical formation under CI conditions are ion fragmentation, hydrogen-atom abstraction from the reagent gas by a radical cation, and ion–electron recombination. Steady-state calculations are given which show the radical concentration under CI conditions can be expected to be much larger than the ion concentration.

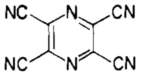
Recently, we reported the first observation of radical addition reactions under chemical ionization (CI) conditions in a mass spectrometer ion source.[1] These gas-phase radical-addition reactions occur between a variety of carbon-centered radicals and 7,7,8,8-tetracyanoquinodimethan (TCNQ), tetracyanoethylene (TCNE), tetracyanopyrazine (TCP), and, to a much lesser extent, hexakis(methoxycarbonyl)trimethylenecyclopropane (**1**) and pentacene (**2**). The measured rate of the TCNE–methyl radical reaction approaches the diffusion-controlled limit and is even faster than methyl radical–radical recombination! The enhanced rate of reaction between carbon-centered radicals and these strong electron acceptors may be the result of charge transfer during a collision or near-collision, leading to gas-phase charge-transfer complexes which rapidly collapse to products.[2] Radical addition to compounds that readily form charge-transfer complexes as electron acceptors are reported to be facile in solution.[3] For example, TCNE[4-7] and TCNQ[5,6] react with radicals by 1,2 or 1,4 and 1,6 addition, respectively.



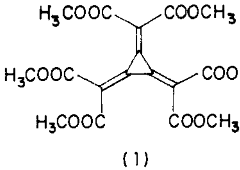
(TCNQ)



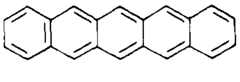
(TCNE)



(TCP)



(1)



(2)

The fast rate of the gas-phase radical-trapping reaction, combined with a higher concentration of radicals than ions in the CI source, as suggested by calculations and experiments, results in radical trapping by TCNQ, TCNE, and TCP being competitive with ionization. Thus, the elemental compositions and the structures[8] of carbon-centered radicals produced in a plasma by ion fragmentation, hydrogen-atom abstraction, and ion–electron recombination can be readily delineated mass spectrometrically.

---

(1) C. N. McEwen and M. A. Rudat, *J. Am. Chem. Soc.*, **101**, 6470 (1979).

(2) S. W. Benson in "Frontiers of Free Radical Chemistry", W. A. Pryor, Ed., Academic Press, New York, 1980, p 16.

(3) A. A. Kuznetsov, S. N. Novikov, and A. N. Pravednikov, *Akad. Nauk SSSR. Ser. Khim., Isv.*, 297 (1979), and reference cited therein.

(4) S. Kukuzumi, K. Mochida, and J. K. Kochi, *J. Am. Chem. Soc.*, **101**, 5961 (1979).

(5) M. Farcasiu and C. S. Russell, *J. Org. Chem.*, **41**, 571 (1976).

(6) D. F. Eaton, *J. Am. Chem. Soc.*, **102**, 3278 (1980).

(7) P. J. Krusic, H. Stoklosa, L. E. Manzer, and P. Meakin, *J. Am. Chem. Soc.*, **97**, 667 (1975).

(8) M. A. Rudat and C. N. McEwen, *J. Am. Chem. Soc.*, following paper in this issue.