spectrum. On warming the sample a 20-line spectrum ~170 G wide appeared which included lines attributable to C_2H_3 and C_2H_5. These results imply that the 185-nm photolysis of c-CH_2N_2 in CH_4 produces CH_2, some of which abstracts from CH_4 (as translationally hot CH_2 or as the singlet before relaxation to the stable triplet ground state), and some of which is stabilized until the sample is warmed allowing $^3CH_2$ + $^3CH_2$ and $^3CH_2$ + CH_3 encounters which result in reactions 1 and 2 and/or 4. No CH_2 ESR signal was observable in the CH_4 matrix.

Photolysis of CH_2CO in Xe and in CH_4. The photolysis of (CH_2CO) has been extensively used as a source of CH_2 radicals in gas-phase studies.[13a] By contrast to the results in the gas phase, CH_2CO does not yield CH_2 when photolyzed in an N_2 matrix.[14] This was attributed to a prompt back-reaction of CH_2 with CO, or reaction of the CH_2 with the N_2 matrix to form CH_2N_2. We have sought evidence for CH_2 formation from the photolysis of CH_2CO in the inert matrix Xe and also in CH_4, and have looked for evidence of CH_2CO decomposition to form species other than CH_2 and CO.

When either Xe or CH_4 containing 0.1 mol % CH_2CO was photolyzed with the full light of the Suprasil low-pressure Hg lamp for 30 min at 5 K no CH_2 signal was detectable in the sample even at very high sensitivity. In both matrices a broad (120 G) ESR line centered at 3200 G, with a peak-to-peak line width of ~30 G appeared with some superimposed, partially resolved line structure. This signal did not change significantly on warming to 35 K, in either matrix. The concentrations achieved were of the order of 10^{-3} M. The identity of the species responsible for the signal remains in question.

Summary

The results of the experiments described above in which CH_3 and c-CH_2N_2 were photolyzed are summarized in Table I. Photolysis of either CH_3 or c-CH_2N_2 in either CH_4 or Xe at 5 K by 185-nm light produced a trapped species which reacted to form C_2H_3 (and C_2H_5 if CH_3 was present) when the matrix was warmed to a temperature where CH_2 can diffuse. Even though the ESR signal of CH_2 was only observable in the c-CH_2N_2–Xe system, there seems to be no other possible precursor for the C_2H_3 and C_2H_5 observed in the other systems.[15] The results imply that in the solid phase the $CH_2 + CH_2 \rightarrow C_2H_3 + H$ and $CH_2 + CH_3 \rightarrow C_2H_5$ reactions are important relative to the $CH_2 + CH_2 \rightarrow C_2H_2 + H_2$ (or 2H) and $CH_2 + CH_3 \rightarrow C_2H_4 + H$ reactions commonly postulated to explain the products found in gas phase studies of CH_2. Other features of particular interest in the data include the evidence for (1) stabilization of activated c-CH_2N_2 without decomposition in CH_4 following 290- and 254-nm photon absorption, in contrast to the decomposition in Xe; (2) the $CH_2N_2 + h\nu$ (185 nm) $\rightarrow$ H + CHN_2 reaction in Xe. Similar to the latter is the evidence, not in the table, that 185-nm absorption by ketene in CH_4 or Xe yields H atoms and radicals.

Acknowledgment. This work was supported, in part, by the U.S. Department of Energy under contract DE-AC02-76ER01715-A005.

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(13) (a) See for examples and references: Okabe, H. "Photochemistry of Small Molecules"; Wiley-Interscience: New York, 1978. (b) Laufer, A. H.; Keller, R. A. *J. Am. Chem. Soc.* **1971**, *93*, 61. (c) Braun, W.; Bass, A. M.; Pilling, M. J. *Chem. Phys.* **1970**, *52*, 5131.

(14) Moore, B. C.; Pimentel, G. C. *J. Chem. Phys.* **1964**, *41*, 3504.

(15) The susceptibility of the signal to broadening by small changes in the matrix environment is illustrated by the reversible disappearance of the signal when CH_2 in Xe is warmed from 5 to 30 K and returned to 5 K, as observed both in the present and previous work.[6]

Temperature Effect on Ion–Molecule Reaction of Hydrogen Transfer in γ-Irradiated 2,3-Dimethylbutane at 4 and 77 K As Studied by Electron Spin Resonance Spectroscopy

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(Received: August 17, 1981; In Final Form: October 22, 1981)

Drastic temperature effects on an ion–molecule reaction of H_2 transfer in solid hydrocarbon systems were studied at 4 and 77 K by ESR spectroscopy. When a 2,3-dimethylbutane (DMB)–SF_6 (0.55 mol %)–*i*-C_4H_8 (0.55 mol %) mixture is γ-irradiated at 4 K, the DMB^+ ion in addition to the DMB radical is formed. The tetramethylethylene (TME) cation is produced by warming the irradiated DMB–SF_6–*i*-C_4H_8 mixture from 4 to 77 K. The formation of the TME^+ ion observed at 77 K is interpreted in terms of the H_2 transfer reaction between the DMB^+ ion and *i*-C_4H_8. This ion–molecule reaction is completely suppressed at 4 K. The suppression of the ion–molecule reaction is explained by failure of the formation of a reaction complex in the rigid matrix at 4 K. The amounts of TME^+ ions in the DMB–SF_6–*i*-C_4H_8 mixture increase gradually upon storage of the irradiated mixture at 77 K. This result indicates that the H_2 transfer reaction occurs slowly at 77 K.

Introduction

Extensive studies on ion–molecule reactions have been undertaken in the gas phase and have shown that most of the reactions occur quite rapidly. For example, the rate constant for the H_2 transfer reaction between c-$C_6H_{12}^+$ and 1-C_4H_8 is 2.1×10^{-9} cm^3 $molecule^{-1}$ s^{-1},[1] which is much larger than a collision frequency.

The H_2 transfer reaction in the solid phase at 77 K has been studied previously by analysis of final products[2] and ESR spectroscopy.[3] When 2,3-dimethylbutane (DMB)

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(1) Sieck, L. W.; Searls, S. K. *J. Am. Chem. Soc.* **1970**, *20*, 2937.

(2) (a) Scala, A. A.; Lias, S. G.; Ausloos, P. *J. Am. Chem. Soc.* **1966**, *88*, 5701. (b) Ausloos, P.; Scala, A. A.; Lias, S. G. *Ibid.* **1967**, *89*, 3677.

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containing a small amount of SF_6 is γ-irradiated at 77 K, the yields of tetramethylethylene (TME) cations increase upon the addition of ethylene, propylene, cyclopropane, or isobutene. The increase of the yields of the TME^+ ion is due to the H_2 transfer from the DMB^+ ion to the olefin or cyclopropane.[3]

In this work we have studied the H_2 transfer reaction in solid DMB–i-C_4H_8 systems at 4 and 77 K.

Experimental Section

The 2,3-dimethylbutane (DMB), isobutene, and sulfur hexafluoride were the same as used before.[3] The tetramethylethylene (TME) supplied by Tokyo Kagaku Seiki Co. was more than 99.0 mol % pure.

γ irradiations at 4 K were done by Cobalt-60 γ-rays to a total dose of 0.1 Mrd. In order to completely cool a sample, we kept the sealed sample in liquid helium for 1 h before the irradiation at 4 K. The γ irradiation of a CCl_3F–DMB mixture at 77 K was done to a total dose of 1.5 Mrd.

The free radicals and cations produced were measured at 4 and 77 K with a JES-3BX ESR spectrometer at a microwave power level of 0.1 mW, which does not result in saturation of the signals of the free radicals and cations.

Results

Figure 1A shows the ESR spectrum of pure 2,3-dimethylbutane (DMB) γ-irradiated at 4 K and measured at 4 K after exposure to light from a tungsten lamp. Since ionic species, such as trapped electrons, are bleached with the light illumination, the spectrum is ascribed to the DMB radical. When the irradiated sample was warmed to 77 K, the spectrum was changed to a well-resolved quintet spectrum (cf. Figure 1a of ref 3).

Figure 1B shows the ESR spectrum of the DMB–SF_6 (0.55 mol %)–i-C_4H_8 (0.55 mol %) mixture γ-irradiated at 4 K and measured at 4 K. The spectrum was not changed by light illumination.

Figure 1C shows the ESR spectrum of the DMB–SF_6 (0.55 mol %)–i-C_4H_8 (0.55 mol %) mixture measured at 77 K after γ irradiation at 4 K. The spectrum consists of 11 equally spaced lines separated by 16.9 G and coincides well with the reported spectra[3-5] of the TME^+ ion where each CH_3 group rotates freely. The splitting constant of 16.9 G is approximately equal to the reported values (16.7[4] and 16.6[3,5] G). Thus, the TME^+ ion is formed by warming the irradiated sample from 4 to 77 K.

Figure 1D shows the ESR spectrum of the DMB–SF_6 (0.55 mol %)–i-C_4H_8 (0.55 mol %) mixture measured at 4 K after γ irradiation at 4 K and annealing at 77 K. The spectrum is quite different from those of Figure 1, B and C. If all CH_3 groups of the TME^+ ion undergo a tunneling rotation[6] at 4 K, the ESR spectrum of the TME^+ ion shows 25 lines, separated by 8.3 G. The spectrum of Figure 1D consists of 23 equally spaced lines separated by 8.3 G and coincides roughly with the TME^+ ion, produced by charge transfer from the irradiated DMB to the TME solute at 4 K (cf. Figure 1E).

Figure 1E shows the spectrum of the DMB–SF_6 (0.55 mol %)–TME (0.55 mol %) mixture γ-irradiated at 4 K and measured at 4 K. The spectrum is ascribed to the TME^+ ion, produced by charge transfer from the irradiated DMB to the TME solute.

Figure 1F shows the spectrum of the CCl_3F–DMB (0.2 mol %) mixture measured at 4 K after γ irradiation at 77 K. It has been reported recently that the γ irradiation of CCl_3F or a Freon mixture containing a small amount of alkane gives the ESR spectrum of the solute cation.[7,8] The spectrum in the former matrix is free from superimposing background signals. Thus, the spectrum of Figure 1F may be ascribed to the DMB^+ ion.

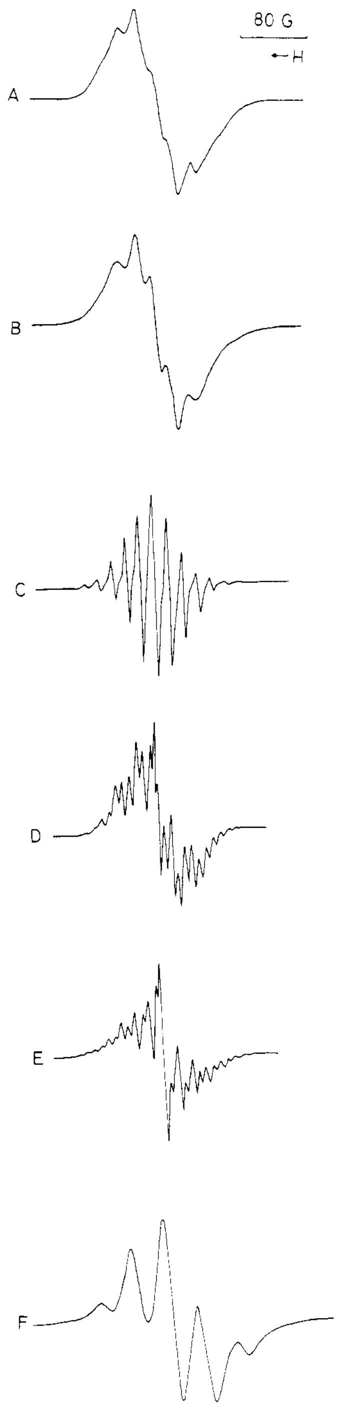

Figure 1. (A) ESR spectrum of DMB measured at 4 K after γ irradiation at 4 K and then illumination with tungsten lamp at 4 K; (B) ESR spectrum of DMB–SF_6 (0.55 mol %)–i-C_4H_8 (0.55 mol %) measured at 4 K after γ irradiation at 4 K; (C) ESR spectrum of DMB–SF_6 (0.55 mol %)–i-C_4H_8 (0.55 mol %) measured at 77 K after γ irradiation at 4 K; (D) ESR spectrum of DMB–SF_6 (0.55 mol %)–i-C_4H_8 (0.55 mol %) measured at 4 K after γ irradiation at 4 K and then annealing at 77 K; (E) ESR spectrum of DMB–SF_6 (0.55 mol %)–TME (0.55 mol %) measured at 4 K after γ irradiation at 4 K; (F) ESR spectrum of CCl_3F–DMB (0.2 mol %) measured at 4 K after γ irradiation at 77 K.

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When the DMB–SF_6 (0.55 mol %) mixture was γ-irradiated at 4 K, the ESR spectrum like Figure 1B was obtained. The annealing of the irradiated sample at 77 K gives the ESR spectra similar to Figure 1, C and D, indicating the formation of the TME cation by annealing. The amounts of the TME^+ ion in the DMB–SF_6 (0.55 mol %) system are about 65% of those in the DMB–SF_6 (0.55 mol %)–i-C_4H_8 (0.55 mol %) system.

Discussion

Temperature Effect on the Formation of TME^+ Ion. When the DMB–SF_6 (0.55 mol %)–i-C_4H_8 (0.55 mol %) mixture is γ-irradiated at 4 K and then warmed to 77 K, the TME^+ ion is formed by the H_2 transfer reaction between the DMB cation and i-C_4H_8 (cf. Figure 1, B–D)

$$\mathrm{DMB} \overset{\mathrm{SF_6}}{\rightsquigarrow} \mathrm{DMB_t}^+ + \mathrm{SF_6}^- \tag{1}$$

$$\mathrm{DMB_t}^+ + i\text{-}\mathrm{C_4H_8} \rightarrow \mathrm{TME}^+ + \mathrm{C_4H_{10}} \tag{2}$$

where DMB_t^+ represents a DMB cation trapped near the i-C_4H_8 solute. Since the TME^+ ion is not formed by γ irradiation at 4 K, reaction 2 is suppressed at 4 K. The H_2 transfer reaction proceeds by way of a reaction complex between DMB_t^+ and i-C_4H_8.[9] The conformation suitable for the reaction between the cation and isobutene may be hindered by rigidity of the matrix at 4 K, resulting in suppression of the H_2 transfer reaction. Since the methyl groups in the molecules rotate freely at 77 K, the reaction complex may be formed easily and thus the H_2 transfer reaction takes place.

When the DMB–SF_6 (0.55 mol %)–TME (0.55 mol %) mixture is γ-irradiated at 4 K, the TME cation is formed at 4 K by the positive charge transfer from the solvent to TME (cf. Figure 1E). Since any significant change of the conformation of the molecules is not necessary in the charge transfer reaction, the reaction can proceed even at 4 K.

Clear evidence for the existence of the DMB^+ ion, which is expected in reaction 1, was not obtained in the present work because of the possible broadening of the ESR spectrum of the ion at 4 K. The ESR spectrum in Figure 1B may consist of the spectrum of the DMB radical (cf. Figure 1A) and that of the DMB^+ ion (cf. Figure 1F).

It is concluded that the H_2 transfer reaction is suppressed in the solid phase at such a low temperature as 4 K, though in some cases this ion–molecule reaction takes place quite rapidly in the gas phase without any activation energy.

When the DMB–SF_6 (0.55 mol %) mixture is γ-irradiated at 4 K and then warmed to 77 K, the TME^+ ion is formed remarkably. One possible mechanism for the formation of the TME^+ ion is as follows. The alkenes formed by the irradiation are reacting with DMB^+ ions to form the TME^+ ions. In order to check this possibility, we examined the preirradiation effect on the TME^+ formation. The DMB–SF_6 (0.55 mol %) mixture is γ-irradiated at 77 K at doses from 0.1 to 0.7 Mrd. Then the mixture is melted and γ-irradiated again at 77 K. The yield of the TME^+ ion after the preirradiation was the same as that without the preirradiation, indicating that the irradiation products are not responsible for the formation of the TME^+ ion. Gas-chromatographic analysis showed that the concentration of impurities, which are hydrocarbons of smaller molecular weight than DMB, was less than 0.01 mol %. The concentration of TME as an impurity is less than 2×10^{-5} mol %. These low concentrations of the impurities suggest that the TME^+ formation in the DMB–SF_6 mixture is probably not due to the reaction of the impurity. In fact, if the TME^+ ion is formed by a charge transfer from DMB^+ to TME as an impurity, the TME^+ ion should be formed even at 4 K, since the charge transfer is not suppressed at 4 K (cf. Figure 1E). The formation of the TME^+ ion in the radiolysis of DMB–SF_6 (0.55 mol %) is not suppressed by the addition of 2-methyltetrahydrofuran, which is an efficient charge acceptor.[3] Therefore, the mobile DMB^+ ion does not participate in the formation of the TME^+ ion in the DMB–SF_6 system.

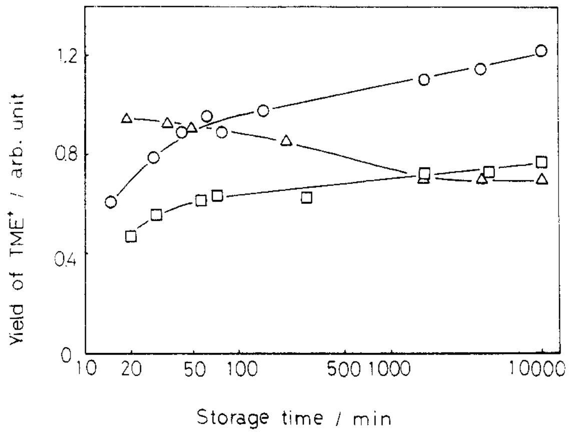

Figure 2. Effect of storage time at 77 K on the yield of TME^+ ion after γ irradiation at 4 K: (○) DMB–SF_6 (0.55 mol %)–i-C_4H_8 (0.55 mol %); (□) DMB–SF_6 (0.55 mol %); (△) DMB–SF_6 (0.55 mol %)–TME (0.55 mol %).

Effect of Storage Time on the Formation of TME^+ Ion at 77 K. Figure 2 shows the effect of storage time on the formation of TME^+ ions in the DMB–solute mixtures, kept at 77 K after γ irradiation at 4 K. The amount of TME^+ ions in the DMB–SF_6 (0.55 mol %)–TME (0.55 mol %) mixture decreases gradually with storage time at 77 K. Such decrease is probably due to neutralization of the TME^+ ion with SF_6^- ion trapped in the matrix.

The amounts of TME^+ ions in the DMB–SF_6 (0.55 mol %)–i-C_4H_8 (0.55 mol %) mixture and the DMB–SF_6 (0.55 mol %) mixture, however, increase gradually with storage time at 77 K. Two mechanisms are conceivable for interpreting these observations. First, the conformation of the DMB^+ ion suitable for the H_2 transfer is gradually formed at 77 K, leading to the slow production of the TME^+ ion. Second, the positive charge migrates slowly through DMB at 77 K to arrive at the i-C_4H_8 solute, resulting in the production of the TME^+ ion. In view of the fact that TME^+ ions do not increase at all in the DMB–SF_6 (0.55 mol %)–TME (0.55 mol %) mixture, the former mechanism is more likely to be operative.[10]

In conclusion, this kind of ion–molecule reaction is suppressed in the solid phase at 4 K, though this reaction takes place quite rapidly in the gas phase. The parent cation of DMB may be stable at 4 K without proton transfer reaction with a neighboring DMB molecule.

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(10) The following recent result also supports the former mechanism. The rate of increase of TME^+ ion in the storage of the irradiated DMB–SF_6 (0.55 mol %)–i-C_4H_8 (0.55, 1.0, and 5.0 mol %) mixtures is independent of the concentrations of i-C_4H_8. Thus, the rate is independent of the distance between the i-C_4H_8 molecules and the positive charges.