C_4H_{10} and C_4D_{10}) gives

$$\frac{(C_3D_7^+)_0}{(C_3D_7^+)} = 1 + \frac{[NH_3]}{2[n\text{-}C_4H_{10}]}\left(\frac{k_2}{k_1}\right) \qquad (3)$$

where $(C_3D_7^+)_0$ and $(C_3D_7^+)$ are the yields of the propyl ions (either secondary or normal) undergoing reaction 1 in the absence and presence of added ammonia, respectively. The effect of NH_3 on the yields of CD_3CDHCD_3 and of $CD_3CD_2CD_2H$ gives independent kinetic plots for the *sec*-$C_3D_7^+$ and *n*-$C_3D_7^+$ ions, respectively, which are shown in Figure 2. There is evidence[8] that reaction between a carbonium ion and NH_3 occurs at every collision. Thus assuming that k_2 is the same for both ions, the slopes in Figure 2 represent the relative rates of reaction of the *sec*-$C_3D_7^+$ and *n*-$C_3D_7^+$ ions with *n*-C_4H_{10} and $k_1(n\text{-}C_3D_7^+)/k_1(sec\text{-}C_3D_7^+) \sim 5$. This result is not unexpected in view of the fact that transfer of an H^- to *sec*-$C_3D_7^+$ is only exothermic when a secondary hydrogen of *n*-C_4H_{10} is involved while any hydrogen in *n*-C_4H_{10} can partake in an exothermic hydride ion transfer to *n*-$C_3D_7^+$.

It is of particular interest that cyclopropane is formed (see Figure 1) in the radiolysis of *n*-C_4H_{10}–NH_3 mixtures with a yield which increases as the ammonia concentration, as does that of propylene. In contrast, no cyclopropane is formed in the radiolysis of isobutane–ammonia mixtures. These facts show that, in systems where *n*-propyl ions are formed, reaction 4 occurs.

$$n\text{-}C_3H_7^+ + NH_3 \longrightarrow \text{cyclo-}C_3H_6 + NH_4^+ \qquad (4)$$

Such a reaction has been suggested to occur in liquid-phase studies involving, for instance, the deoxidation of *n*-propyl alcohol and the deamination of *n*-propylamine.[9] It may be added that the cyclopropane formed in a *n*-C_4D_{10}–*n*-C_4H_{10}–NH_3 system consists entirely of cyclo-C_3D_6 and cyclo-C_3H_6, indicating that there is no randomization of the hydrogen atoms in the reaction complex, and that the precursor ion is not a smaller fragment ion such as $C_3H_5^+$ or $C_3H_4^+$.

On the basis of appearance potential measurements of propyl ions formed in the fragmentation of isobutane and *n*-butane parent ions (as well as of other normal and branched alkane parent ions), it has been suggested[10] in the past that there is only *one* structure for a propyl ion. This structure has been suggested to be the *sec*-propyl configuration[10b] or a protonated cyclopropane configuration.[11] Experimental evidence for the existence of a protonated cyclopropane ion in liquid-phase deamination studies[12] is particularly convincing. The results obtained in the present study demonstrate that propyl ions having *two* distinct structures undergo reaction 1. Although the results of the experiments reported here do not provide any definite conclusions regarding the existence of the protonated cyclopropane ion in these systems, the formation of cyclopropane as a product in reaction 4 suggests but does not prove that the *n*-propyl ion may conceivably acquire that structure prior to or during reaction. By the same token, the data indicate that propyl ions originating from isobutane do not go through a protonated cyclopropane configuration.

An extensive study of the structure and reactivity of propyl ions produced in the radiolysis and photoionization of alkanes is forthcoming.

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Radical Cations. I. Direct Electron Paramagnetic Resonance Observation of the Chlorine Molecule Cation Cl_2^+, a Stable Diatomic Radical Cation, in SbF_5, FSO_3H–SbF_5, and HF–SbF_5 Solutions of ClF

Sir:

We wish to report the direct epr observation of the chlorine molecule cation Cl_2^+.

The ion Cl_2^+ has long been known in the gas phase, and its emission spectrum has been observed.[1] All attempts to prepare it and Br_2^+ in strongly acidic media have, however, failed in the past.[2] No epr absorption was detected for I_2^+ by either Symons[2] or Gillespie,[3] although its existence is known from conductivity and susceptibility studies.

In view of our previous success in ionizing organic halides in SbF_5, FSO_3H–SbF_5, and HF–SbF_5 solutions to the corresponding stable carbonium ions,[4] it was a logical extension of our work to study the behavior of halogen fluorides in the same highly acidic solvent systems in the expectation that ionization would lead to stable halogen cations.

When chlorine monofluoride is dissolved at room temperature in antimony pentafluoride, a stable solution of paramagnetic species ($g = 1.998$) is formed which has the well-resolved epr spectrum shown in Figure 1. We believe this species to be Cl_2^+ (I).[5] The hyperfine pattern shows seven equally spaced (2.5 G) lines with intensities of 1, 2, 3, 4, 3, 2, 1. A hyperfine pattern of this type is typical of two equivalent nuclei of spin $^3/_2$. Chlorine consists of two isotopes: Cl^{35} (75.4%) and Cl^{37} (24.6%) with similar magnetic moments ($0.82\beta_N$ and $0.68\beta_N$, respectively), both of which have spin $^3/_2$. Cl_2^+ therefore consists of three isotopic species: $Cl^{35}Cl^{35+}$ (0.57 of the total), $Cl^{35}Cl^{37+}$ (0.37 of the total), and $Cl^{37}Cl^{37+}$ (0.06 of the total). Comparison of Figure 1 with the theoretically calculated spectrum (Figure 2) clearly indicates that the $Cl^{35}Cl^{35+}$ ion dominates the spectrum and with a finite line width obscures the other isotopic species.

The chlorine molecule cation I is also obtained when ClF is dissolved in FSO_3–SbF_5 or HF–SbF_5 solutions at room temperature. When these solutions are cooled

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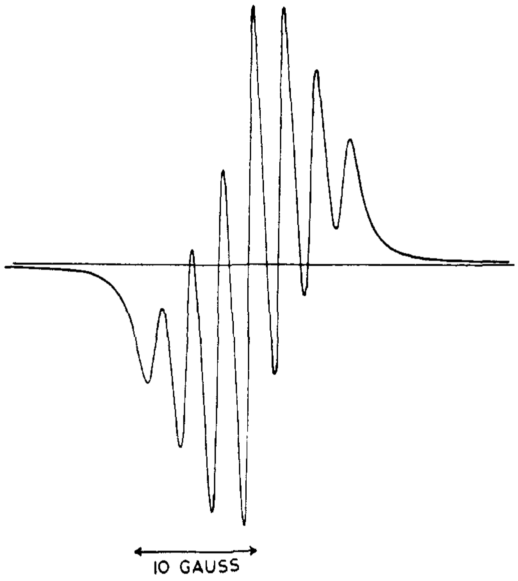

Figure 1. Epr spectrum of Cl_2^+.

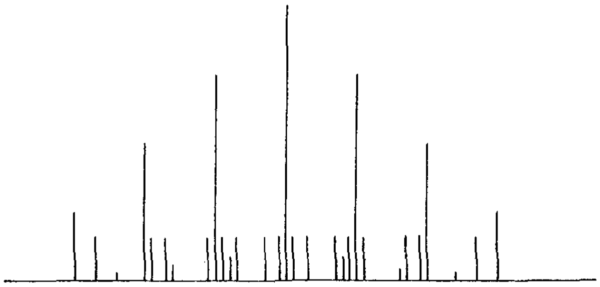

Figure 2. Theoretical spectrum for Cl_2^+ with natural isotopic abundances (see text).

to −60°, no change in the spectra is observed except that the hyperfine pattern disappears as viscosity broadening of the signal takes place. The same behavior of the antimony pentafluoride solution is observed, except that the viscosity broadening sets in at around 0° instead of −60°.

The stoichiometry of the formation of Cl_2^+ from ClF is not yet known with certainty, but the following reaction is the most plausible.

$$5ClF + 3SbF_5 \longrightarrow 2Cl_2^+ + ClF_2^+ + 3SbF_6^-$$

To our knowledge, Cl_2^+ is the first simple diatomic radical ion observed by epr in solution. Other diatomic radical ions, like Cl_2^-, O_2^+, and O_2^-, have been observed in rigid media.[5,6]

When the solutions of Cl_2^+ are heated to 60°, a second paramagnetic species (II) is formed ($g = 2.006$) which is in equilibrium with Cl_2^+. When a solution containing I and II is cooled from 60° to lower temperatures, the relative amounts of I and II change reversibly, with I predominating at lower temperatures. Investigation of the system is still in progress, and at the present time we cannot yet unequivocally state the nature of species II, although it may be the radical cation ClF_3^+.

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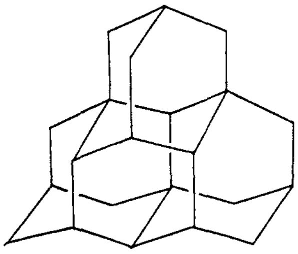
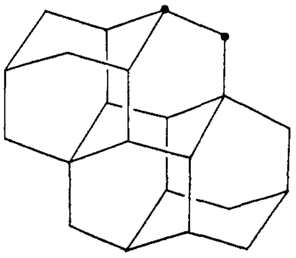
Nonacyclo[11.7.1.1^{2,18}.0^{3,16}.0^{4,13}.0^{5,10}.0^{6,14}.0^{7,11}.0^{15,20}]docosane,[1] a Bastard[2] Tetramantane

Sir:

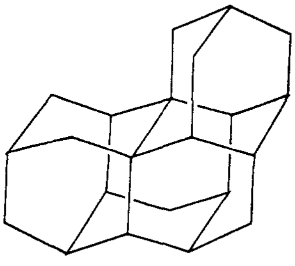
There exists a close formal similarity between the simple aliphatic hydrocarbons and the homologous series of adamantane compounds based on the diamond structure. Methane, ethane, and propane correspond to adamantane,[3] diamantane ("congressane"),[4] and triamantane.[5] Just as ethane can be thought of as two tetrahedral methane units joined together, so can diamantane be regarded as a similar combination of two tetrahedral adamantane units. Propane and triamantane bear the same relationship. The point groups of corresponding alkane and diamondoid hydrocarbons are the same, provided the alkanes adopt staggered conformations. A further analogy exists in the number of possible isomeric forms of corresponding members of the two homologous series. Such isomers first appear with the fourth member of each series. Two structural isomers of C_4H_{10} are possible, isobutane and *n*-butane, and the latter can exist in two minimum energy conformations, *anti* and *skew*. The carbon skeletons of these three forms correspond in arrange-



I



II



III

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