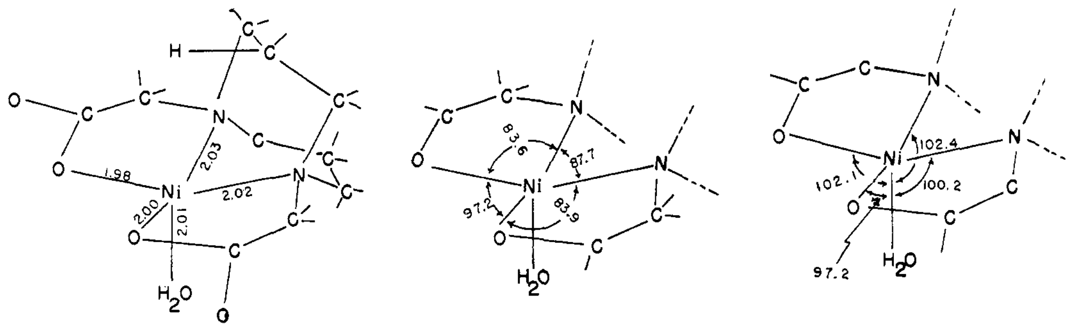

Figure 1. Perspective of Ni(dacoDA)(H_2O). Bond lengths and bond angles in angströms and degrees, respectively.

to form normal octahedral complexes with cobalt(III).[5] The blue complex Ni(EDDA)$(H_2O)_2$ was prepared and its aqueous absorption spectrum found to adhere closely to that expected for a normal six-coordinate complex. The band at 9900 cm^{-1} ($^3A_{2g} \rightarrow {}^3T_{2g}$, O_h symmetry) corresponding to $10Dq$, was used to calculate the energies of the transitions to the $^3T_{1g}$(F) and $^3T_{1g}$(P),[6] and these values were within 3% of the experimental energies. Thus the nickel(II) sees an average environment. On the other hand, the spectrum of Ni(dacoDA)(H_2O) dissolved in water was quite different from that obtained for the octahedral prototype. There was no corresponding band in the region of the $^3T_{2g}$ transition, and the observed bands were considerably more intense than those found for Ni(EDDA)$(H_2O)_2$ as might be expected if the Ni(II) were in a severely distorted octahedral or square-pyramidal field where there is no effective center of symmetry. Furthermore, it was found that the positions of the bands of Ni(dacoDA)(H_2O) in the visible region were the same in the solid state (mull) as in aqueous solution suggesting that the complex has the same stereochemistry in both states.

A very interesting situation has been observed for the Co(II) complex of dacoDA which further substantiates the five-coordinate geometry imposed by this ligand. Whereas the Co(II) complex of EDDA is very easily oxidized to the Co(III) complex (Co(EDDA)$(H_2O)_2$ is most easily prepared in an oxygen-free atmosphere), the dacoDA complex is very stable to oxidation. Oxygen and hydrogen peroxide will not oxidize the cobalt(II) complex even in the presence of carbon as evidenced from the lack of change in the absorption spectrum. Furthermore the reaction of H_2dacoDA with $Na_3[Co(CO_3)_3]$ and $[CoCO_3(NH_3)_4]Cl$ yielded after prolonged heating the cobalt(II) complex of dacoDA as evidenced by absorption spectra. The spectrum of crystalline solid isolated from one of the reaction solutions corresponded quantitatively to that of the Co(II)–dacoDA complex. Since cobalt(III) appears to form exclusively six-coordinate complexes in aqueous solution, it would seem that the ligand is very effective in preventing coordination of the sixth water. It might then be asked how effectively could this ligand stabilize normally very easily oxidized chromium(II) or might it yield a nonoctahedral chromium(III) complex? The answers to these questions are currently being sought.

Both nickel complexes are high-spin with moments of 3.2 BM. Green [Ni(dacoDA)(H_2O)]·$2H_2O$ is easily and reversibly converted to the anhydrous square-planar complex by heating or treating with absolute ethanol. The complex is orange and diamagnetic. The details of the studies of the Co(II), Ni(II), and Cu(II) complexes of dacoDA and EDDA will be reported in the near future. Investigation of the corresponding complexes of other metal ions (*e.g.*, Cr(II), Cr(III), Fe(II), Fe(III), Pd(II), and Pt(II)) is being undertaken.

It is quite clear from our initial studies of the chelating properties of dacoDA that this ligand and its analogs offer a very interesting and unusual system for the investigation of such phenomena as kinetics of ligand exchange at an axial position and electron spin resonance. These studies are planned.

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(5) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).

(6) W. C. E. Higginson, S. C. Nyburg, and J. S. Wood, *ibid.*, **3**, 463 (1964).

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Structure and Reactivity of Propyl Ions in Gas-Phase Radiolysis

Sir:

Several years ago, Borkowski and Ausloos[1] irradiated equimolar mixtures of *n*-C_4D_{10} and *n*-C_4H_{10} and examined the isotopic structure of the propane formed in the hydride transfer reaction

$$C_3D_7^+ + C_4H_{10} \xrightarrow{k_1} C_3D_7H + C_4H_9^+ \qquad (1)$$

They noted that most of the C_3D_7H consisted of CD_3CDHCD_3 and that, therefore, *n*-propyl ions, if formed in the primary fragmentation, rearranged before or during the hydride transfer reaction to the secondary structure. As was expected only *sec*-propyl ions were seen to react in the radiolysis of isobutane.[2]

Since the time those studies were carried out, considerable advances in our understanding of the gas-phase radiolysis of hydrocarbons have occurred.[3] We now know, for example, that in the earlier studies the straightforward interpretation of the mass spectra of

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(1) R. P. Borkowski and P. Ausloos, *J. Chem. Phys.*, **39**, 818 (1963).

(2) R. P. Borkowski and P. Ausloos, *ibid.*, **38**, 36 (1963).

(3) (a) P. Ausloos and S. G. Lias, "Actions Chimiques et Biologiques des Radiations," Vol. 11, M. Haissinsky, Ed., Masson & Cie., Editeurs, Paris, 1967, p 1; (b) G. Meisels in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience Publishers, New York, N. Y., 1968.

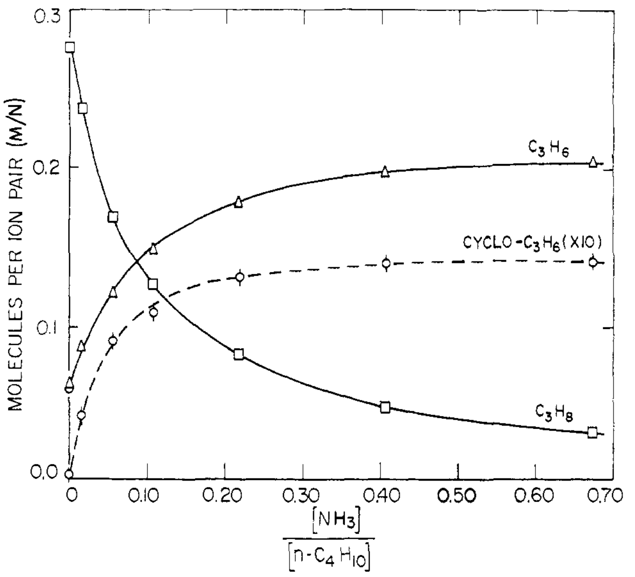

Figure 1. Variations of the yields of propane, propylene, and cyclopropane as a function of the NH_3 concentration in the radiolysis of n-C_4H_{10}-NH_3 mixtures (total pressure, 30 torr).

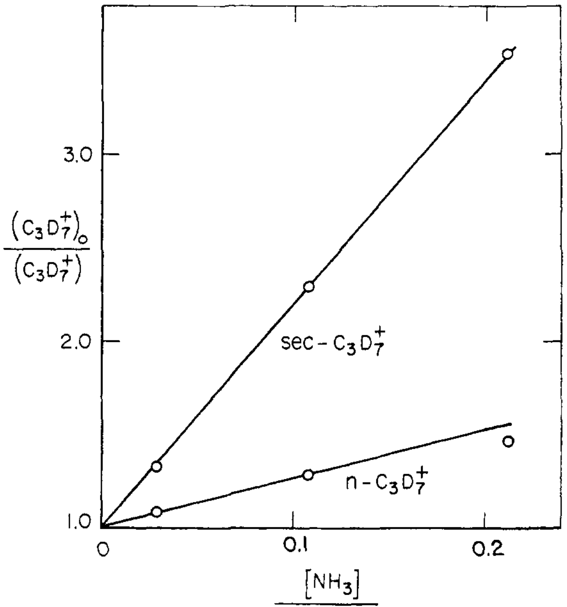

Figure 2. Plots of $(C_3D_7^+)_0/(C_3D_7^+)$ *vs.* NH_3/n-C_4H_{10} derived from the yields of CD_3CDHCD_3 and $CD_3CD_2CD_2H$ measured in the radiolysis of n-C_4H_{10}-n-C_4D_{10}-O_2 (1:1:0.1) mixtures containing various amounts of NH_3.

the propanes was compromised by the presence of propane-d_6 formed in the reaction of the propylene ion with the parent n-butane or isobutane. It has also been possible to obtain more reliable mass spectrometric cracking patterns for CD_3CDHCD_3, $CD_3CD_2CD_2H$, and the d_6-propanes.

In the course of a reexamination of this problem, we see that, in the radiolysis of an iso-C_4D_{10}-iso-C_4H_{10} (1:4)-O_2 mixture at 20 torr, the propane-d_7 formed in reaction 1 is indeed entirely of the structure CD_3CDHCD_3, indicating that only *sec*-propyl ions are involved in its formation. However, in the radiolysis of a n-C_4D_{10}-n-C_4H_{10}-O_2 mixture at a pressure of 40 torr, the propane-d_7 consists of 80% CD_3CDHCD_3 and 20 ± 2% $CD_3CD_2CD_2H$; this result points to the participation of n-propyl ions as well as *sec*-propyl ions in reaction 1.

It has been suggested that the fragmentation of the n-$C_4H_{10}^+$ ion to form a *sec*-propyl ion requires 11.18 eV and proceeds through a rigid complex[4] or more specifically *via* an isomerization to the iso-$C_4H_{10}^+$ structure,[5] while n-propyl ions are supposed to be formed at about 11.4 eV by a simple C–C cleavage mechanism. Thus it is of interest to determine how the ratio n-$C_3H_7^+$/*sec*-$C_3H_7^+$ in the n-butane system varies with the amount of energy contained in the ion. In order to form parent ions with varying amounts of energy, the xenon- and krypton-sensitized radiolysis of n-C_4D_{10}-n-C_4H_{10} mixtures was carried out in the presence of O_2 as a radical scavenger. These results are given in Table I along with the analogous results for the isobutane systems.

The formation of the *sec*-$C_3D_7^+$ ion is more important in the krypton-sensitized radiolysis where the parent n-$C_4D_{10}^+$ ion is formed with 1–2 eV more energy than in the xenon-sensitized radiolysis. This would seem to indicate that the primary fragmentation is the formation of the n-propyl ion, and that an activation energy is required for the isomerization: $CD_3CD_2CD_2^+ \rightarrow CD_3CDCD_3^+$.

Table I. Structure of Propyl Ions in Rare-Gas-Sensitized Radiolysis of Butanes

Sensitizing gas	$CD_3CDCD_3^+$	$CD_3CD_2CD_2^+$
Xenon (IP = 12.13, 13.44 eV)		
n-Butane	63.3	36.7
Isobutane	100.0	0.0
Krypton (IP = 14.00, 14.67 eV)		
n-Butane	93.4	6.4
Isobutane	100.0	0.0

It is also of interest to see whether a difference in reactivity can be observed between the two propyl ions formed in the n-butane system. For this purpose, n-C_4D_{10}-n-C_4H_{10} (1:1) mixtures were irradiated in the presence of varying amounts of NH_3. Ammonia, because of its high proton affinity, will accept a deuteron from both n-$C_3D_7^+$ and *sec*-$C_3D_7^+$.[6]

$$C_3D_7^+ + NH_3 \xrightarrow{k_2} C_3D_6 + NH_3D^+ \qquad (2)$$

An observed decrease in the yield of propane and increase in the propylene yield as a function of the NH_3 concentration (see Figure 1) is adequately accounted for[7] by the competition between reactions such as 1 and 2. A steady-state treatment of the mechanism represented by reactions 1 and 2 for a C_4H_{10}-C_4D_{10} (1:1) mixture (assuming an equal probability of reaction with

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[4] (a) B. Steiner, C. F. Giese, and M. G. Inghram, *J. Chem. Phys.*, **34**, 189 (1961); (b) W. A. Chupka and J. Berkowitz, *ibid.*, **47**, 2921 (1967).

[5] M. Vestal in ref 3b, p 68.

[6] Accepting a value of 202 kcal/mole for the proton affinity of NH_3 [A. P. Altshuller, *J. Am. Chem. Soc.*, **77**, 3481 (1955)], the ΔH of reaction 2 is 23 kcal when $C_3D_7^+$ has the secondary structure and 40 kcal when it has the primary structure.

[7] (a) T. Miyazaki and S. Shida, *Bull. Chem. Soc. Japan*, **38**, 2114 (1965); (b) T. Miyazaki, *J. Phys. Chem.*, **71**, 4282 (1967).

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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[8] W. Sieck and T. Tiernan, unpublished results.

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[10] (a) F. H. Field and J. L. Franklin, *J. Chem. Phys.*, **22**, 1895 (1954); (b) D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953).

[11] (a) P. H. Rylander and S. Meyerson, *J. Am. Chem. Soc.*, **78**, 5799 (1956); (b) H. M. Grubb and S. Meyerson, "Mass Spectrometry of Organic Ions," Academic Press, New York, N. Y., 1963, p 518.

[12] (a) A. A. Aboderin and R. L. Baird, *J. Am. Chem. Soc.*, **86**, 2300 (1964); (b) C. C. Lee, J. E. Kruger, and E. W. C. Wong, *ibid.*, **87**, 3985 (1965); (c) C. C. Lee and J. E. Kruger *ibid.*, **87**, 3986 (1965); (d) G. J. Karabatsos, C. E. Orzech, and S. Meyerson, *ibid.*, **87**, 4394 (1965); (e) C. C. Lee and J. E. Kruger, *Tetrahedron*, **23**, 2539 (1967).

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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[5] The averaged *g* value for Cl_2^- in single-crystal matrices is 2.03: H. Ueda *J. Chem. Phys.*, **41**, 285 (1964), and references cited therein.