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Infrared and Raman Spectra of the TeF_5O^- Anion and Evidence for Contact-Ion-Pair Formation in the $TeF_5OAg–CH_3CN$ System. Normal-Coordinate Analysis of the TeF_5O^- and SeF_5O^- Ions

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Infrared and Raman spectra of TeF_5OCs and TeF_5OAg in CH_3CN solutions and in the solid state are reported. The vibrations of the TeF_5O^- ion are assigned on the basis of C_{4v} symmetry. Contact-ion-pair formation is observed in concentrated solutions of TeF_5OAg in CH_3CN, giving rise to two new bands which are assigned as the Te–O and the axial Te–F stretching modes in the complex. A normal-coordinate calculation has been carried out. The axial Te–F stretching force constant is found to be significantly smaller than the equatorial. The stretching force constants of SeF_5O^- have been calculated and are compared with the corresponding constants of TeF_5O^- and IOF_5.

Introduction

Pentafluoroorthotelluric acid, TeF_5OH,[1] has been shown by spectrophotometric,[2] conductometric,[3] and ^1H nmr studies[4] to be a strong acid. Interaction with metal fluorides, chlorides, and cyanides thus leads to evolution of the corresponding acid and formation of salts containing the TeF_5O^- anion.[5] Only incomplete infrared data with tentative assignments for this ion were published so far.[6]

Current interest in XY_5Z and related pseudooctahedral species (SF_5O^-,[7] IOF_5,[8] SF_5Cl,[9] SeF_5Cl,[10] $XeOF_4$,[11] $TeOF_4^{2-}$,[12] IOF_4^- [13]) prompted us to report the vibrational spectrum of the TeF_5O^- anion and the results from a normal-coordinate analysis. For comparison force constants were computed for the SeF_5O^- anion as well, employing vibrational data from the literature.[14]

In the course of collecting vibrational data for TeF_5OAg evidence for contact-ion-pair formation in concentrated acetonitrile solutions was obtained. This interesting topic was further followed up and also helped considerably in the vibrational assignment of the isolated TeF_5O^- anion.

Experimental Section

Materials and Sample Handling. Volatile materials used in this work were manipulated in a glass vacuum line. TeF_5OH (mp 39.1°, bp 59.7°) was prepared[1] from BaH_4TeO_6 and $HOSO_2F$. Cesium chloride (Fluka), rubidium chloride (Fluka), and silver(I) cyanide, prepared from $AgNO_3$ and KCN, were dried and powdered prior to use. Acetonitrile was purified by repeated distillation over P_4O_{10}. Solid products were handled in the dry nitrogen atmosphere of a glove box.

Preparation of TeF_5OCs and TeF_5ORb. An approximately tenfold excess of TeF_5OH was condensed upon dry, powdered CsCl or RbCl. Upon warming to room temperature HCl is evolved and a clear solution is formed. Subliming off excess TeF_5OH leaves behind white, crystalline TeF_5OCs or TeF_5ORb in quantitative yield. Both compounds do not melt or decompose up to 300° and slowly hydrolyze in moist air.

Preparation of TeF_5OAg. TeF_5OH dissolved in CH_3CN was slowly added to a suspension of AgCN in CH_3CN. After stirring for 2 hr at room temperature a clear solution was obtained. Upon distillation of excess solvent, HCN and TeF_5OH *in vacuo*, white crystalline TeF_5OAg (mp 92°) is left behind in quantitative yield.

Raman and Infrared Spectra. Raman spectra were recorded on a Coderg PHO spectrometer, using the 488.0-nm line of a Coherent Radiation Model 52G mixed-gas laser for excitation. A spectral slit width of 2 cm^{-1} was used. Polarization orientations were controlled by means of a half wave plate in the laser beam. Infrared spectra were obtained with a Perkin Elmer model 457 spectrometer in the range 4000- to 250 cm^{-1}. Polyethylene cells were used for the solutions in CH_3CN. The infrared spectra of the solids were run as KBr disks. Raman frequencies are believed to be accurate to ±1 cm^{-1}, and infrared frequencies, to ±3 cm^{-1}.

In the Raman spectra of TeF_5OCs and TeF_5OAg a polarized band at 677 cm^{-1} having a counterpart in the ir was suspected to be an impurity and therefore was not included in Table I. The intensity of this band varied strongly in the spectra of samples made by different synthetic routes, and the band was absent in the spectrum of a sample of TeF_5ORb. It appears that the formation of this impurity is favored by high temperatures.

Results and Discussion

Vibrational Spectra and Assignment. Table I contains infrared and Raman data for the cesium and the silver salts of the TeF_5O^- anion in the solid state and in acetonitrile solution. The Raman spectra are depicted in Figure 1. No further bands could be found in the Raman spectra under high gain conditions down to 100 cm^{-1}, and no splitting of the reported bands could be observed using 1-cm^{-1} resolution. The solid-state and solution spectra shown in Figure 1 are very similar for the cesium and the silver salt, with the exception of two extra bands at 852 and 588 cm^{-1} found in concentrated solutions of TeF_5OAg in CH_3CN. These were found to be due to contact-ion-pair formation and will be discussed in the following section. Therefore the spectra can be assigned considering only the internal vibrational modes of the TeF_5O^- anion.

For TeF_5O^- no structural data are yet available. The ^{19}F nmr spectrum of the ion consisting of an AB_4 pattern suggests, however, C_{4v} symmetry.[15] The isoelectronic molecule IOF_5 has been shown by microwave studies to belong to the point group C_{4v} with 90° angles.[16] The same structure has been assumed for SF_5O^-.[7] Therefore the assignment will be given for C_{4v} symmetry, this giving rise to the vibrational representation

$$\Gamma_{vib} = 4\ A_1(ir, R) + 2\ B_1(R) + B_2(R) + 4\ E(ir, R)$$

The infrared and Raman activities are shown in parentheses. Of the four expected polarized bands of A_1 symmetry, three should occur in the Te–O and Te–F stretching region. The highest polarized band at 863 cm^{-1} is assigned to the Te–O stretching vibration, analogous to the assignments of the X–O stretching modes in IOF_5[8] and SF_5O^-.[7] The most intense polarized band in the Raman spectrum at 650 cm^{-1} is assigned as the symmetrical stretching vibration of the four equatorial fluorine atoms, and the other polarized band at 580 cm^{-1}, as the stretching mode of the axial fluorine atom. The assignment in this order is based first on intensity considerations because symmetric TeF_4 stretching mode should result in the most intense Raman line; second, and more important, is the behavior of the band at 580 cm^{-1} in concentrated solutions of TeF_5OAg (discussed in the following section). The fourth polarized band, the symmetric TeF_4 out-of-plane deformation, would be expected between 300 and 350 cm^{-1} in analogy to IOF_5.[8] However, the Raman bands found in this region are

Table I. Observed Infrared and Raman Bands of TeF_5OCs and TeF_5OAg as Solids and in Acetonitrile Solutions (in cm^{-1})^d

Cesium salt				Silver salt		
Ir		Raman		Ir	Raman	
Solid	Soln	Solid	Soln^a	Soln^b	Soln^b	Assignment
280 sh	280 w	286 w	289 w, dp	280 w	282 w, dp	$\nu_{11}(e)$
315 vs	330 vs	312 } m	328 m, dp	330 vs	327 m, dp	$\nu_{10}(e)$
330 sh	345 sh	331 }	*c*	345 sh	347 w, dp	$\nu_9(e)$
~580 sh	585 w	578 m	581 m, p	~585 sh	580 } m, p	$\nu_3(a_1)$
					588 }	
			624 w		627 w	
635 vs	640 vs			637 vs		$\nu_8(e)$
650 sh	650 sh	650 vs	650 vs, p	650 sh	650 vs, p	$\nu_2(a_1)$
			663 sh		664 sh	$\nu_5(b_1)$
				850 } s	852 } s, p	
873 s	861 s	871 s	863 s, p	861 }	863 }	$\nu_1(a_1)$
1215 vw						$\nu_3 + \nu_8 = 1215$
1740 vw						$2\nu_1 = 1746$

^{a} Saturated solution ~0.6 *M*. ^{b} 3 *M* solution. ^{c} Area covered by CH_3CN band. ^{d} Key: s, strong; m, medium; w, weak; v, very; sh, shoulder; p, polarized; dp, depolarized.

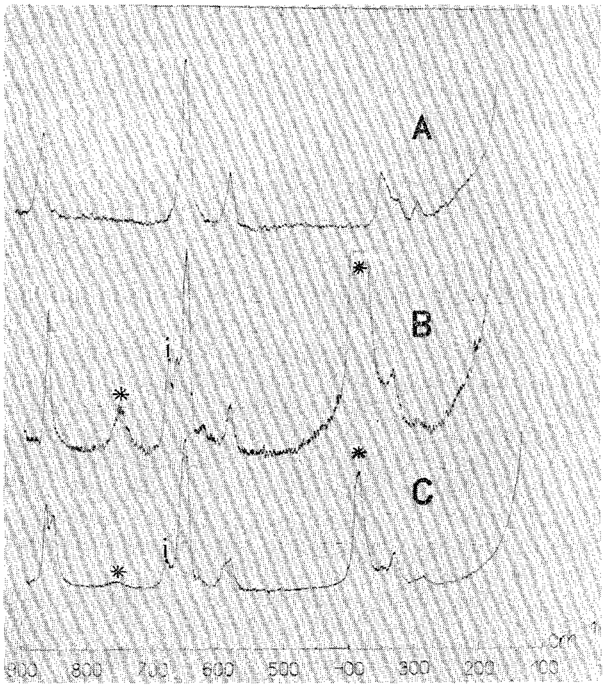


Figure 1. Raman spectra of the TeF_5O^- anion: (A) the cesium salt as a solid; (B) the cesium salt in CH_3CN solution (0.6 *M*); (C) the silver salt in CH_3CN solution (3 *M*); *, CH_3CN bands; i, impurity.

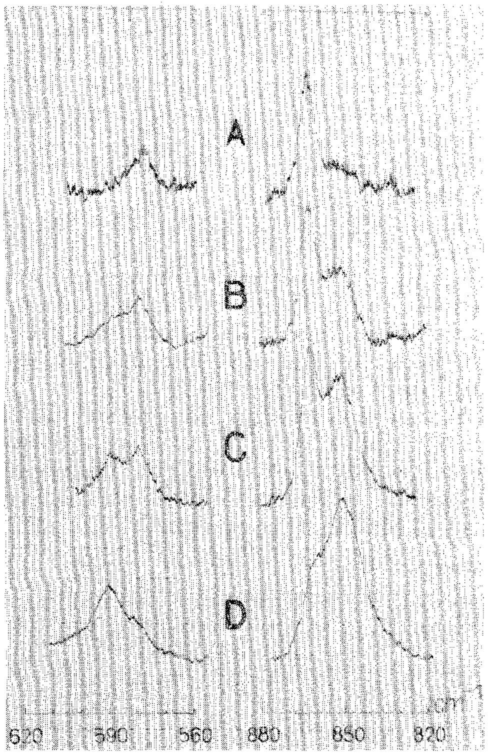


Figure 2. Changes in the Raman spectrum of a solution of TeF_5O-Ag in CH_3CN with increasing silver salt concentration: (A) 0.1 *M*; (B) 1.0 *M*; (C) 2.5 *M*; (D) 5.0 *M*.

all depolarized within experimental error. Therefore this band of A_1 symmetry either is of very low intensity or has a depolarization ratio approaching 6:7. Since all the bands in the deformation region can be assigned satisfactorily as degenerate modes, we prefer not to assign the A_1 deformation to any of the other bands observed.

The strongest band in the infrared spectrum of TeF_5OCs at 640 cm^{-1} is certainly the TeF_4 antisymmetric stretch. The corresponding Raman band is probably obscured by the strong band at 650 cm^{-1}. The weak Raman band at 624 cm^{-1} seems to be too low to be a counterpart of the 640-cm^{-1} infrared band and is more likely due to an overtone or a combination of bands appearing around 300 cm^{-1}. The other three bands in the infrared spectrum at 345, 330, and 280 cm^{-1} all have counterparts in the Raman spectrum and are therefore assigned to the remaining three deformation modes of E symmetry.

Of the remaining three fundamentals of B_1 and B_2 symmetry, only one can be found in the Raman spectrum at 663 cm^{-1} which is assigned to the TeF_4 symmetric out-of-phase stretching vibration. No evidence could be found in the Raman spectra for the other two vibrations of B_1 and B_2 symmetry in the region of the deformation modes. The combination bands and overtones found in the infrared spectrum can be accounted for satisfactorily on the basis of the assigned fundamentals.

Solvent–Solute Interactions. The vibrational spectra of TeF_5OCs show only minor variations in going from the solid state to solutions in CH_3CN. Some solvent–anion interaction of a hydrogen-bonded nature does appear to be present as evidenced by the decrease of the Te–O stretching frequency from 871 cm^{-1} in the solid state to 863 cm^{-1} in solution. This is further supported by a wave number shift of the corresponding deformation modes from 312 and 331 cm^{-1} in the solid state to 330 and 345 cm^{-1} in solution. For the silver salt, however, with increasing concentration more drastic changes occur which are best explained by the formation of contact ion pairs. In the following the argument for the formation of contact ion pairs will be developed in analogy to the

$AgNO_3$–CH_3CN system where this type of interaction has been investigated extensively by Janz.[17] With respect to the TeF_5O^- vibrations these changes only involve the bands at 863 and 580 cm^{-1} and are depicted in Figure 2. At the lowest concentration experimentally accessible (0.1 *M*) only one band is present at 863 cm^{-1} with a broad hump at the low wave number side. With increasing concentration of TeF_5OAg a second band appears at 852 cm^{-1} which becomes dominant at the highest concentration investigated (5 *M*). Simultaneously a band appears at 588 cm^{-1} at the high wave number side of the 580 cm^{-1} band (Figure 2) with a similar concentration dependence. The position of the 863 cm^{-1} band is not concentration dependent within the concentration range 0.1–2.5 *M*. At higher concentrations the center of this band appearing as a shoulder is difficult to locate.

These changes are best interpreted as cation–anion pairing in the form of a contact ion pairing similar to the $AgNO_3$–CH_3CN system.[17] The extra band at 852 cm^{-1} is assigned to a Te–O stretching mode with oxygen coordinated directly to the silver ion. The decrease of the Te–O stretching frequency from the "free" ion to the complex is similar to the change observed for $AgNO_3$ in CH_3CN (for "free" NO_3^-, ν_{sym} 1041 cm^{-1}; for complexed NO_3^- as $Ag^+NO_3^-$, ν_{sym} 1036 cm^{-1}).[17]

The other band found in concentrated solutions at 588 cm^{-1} (Figure 2) we prefer to assign to an axial Te–F stretching mode in a $TeF_5O^-Ag^+$ complex, thus fixing the band at 580 cm^{-1} as the axial Te–F stretching mode in "free" TeF_5O^-. This assignment is based first on experimental evidence from ^{19}F nmr spectra where mainly the axial fluorine atom is influenced by solvent effects.[15] Second, it has been demonstrated by *ab initio* calculations on a series of iodine–oxygen–fluorine compounds that the bonding in these compounds is dominated by the p functions of the central atom iodine.[18] If one assumes this to apply for tellurium compounds as well, it becomes obvious from symmetry considerations alone that in TeF_5O^- coordination at the oxygen atom should affect the fluorine atom in the trans position at least by an order of magnitude more than the fluorine atoms in equatorial positions.

No other changes were observed for the internal vibrations of the silver salt of the TeF_5O^- ion with increasing concentration such as loss of degeneracy causing splitting of vibrational modes. Apparently C_{4v} symmetry is retained in the ion pair $TeF_5O^-Ag^+$. Even the half-bandwidth of the strongest band in the Raman, the symmetric TeF_4 stretching vibration at 650 cm^{-1}, is about the same in TeF_5OCs–CH_3CN and TeF_5OAg–CH_3CN solutions. This is quite different from the situation found in the $AgNO_3$–CH_3CN system where loss of degeneracy of several modes is taken as evidence for contact-ion-pair formation.

Further support for the proposition of contact-ion-pair formation in TeF_5OAg comes from some changes observed in the Raman spectrum of the solvent CH_3CN: in addition to the bands of pure CH_3CN two polarized bands are found at 2272 and 928 cm^{-1} which become more intense with increasing TeF_5OAg concentration. No splitting of degenerate modes of CH_3CN was noticed. This again parallels the results found for the $AgNO_3$–CH_3CN system.[17] Two additional solvent bands at 2272 and 928–931 cm^{-1} were assigned as C–N and C–C stretching vibrations of CH_3CN which is bound to the cationic species of the solute (in pure CH_3CN: C–N stretch, 2252 cm^{-1}; C–C stretch, 919 cm^{-1}). The structure of the complex formed is assumed to be $Ag^+\cdots N\equiv CCH_3$ with C_{3v} symmetry (on the basis of vibrational selection rules).

No bands were found in the low wave number region of concentrated solutions of TeF_5OAg in CH_3CN which could be assigned as Ag–O or Ag–N stretching vibrations.

Table II. Stretching Vibrations of Several XF_5O Molecules (Assuming C_{4v} Symmetry) (cm^{-1})

Normal mode	Symmetry	TeF_5O^-	SeF_5O^-	IOF_5
$\nu(X\text{–}O)$	A_1	863	919	927
$\nu(X\text{–}F_{ax})$	A_1	581	559	680
$\nu_{sym}(XF_4)$	A_1	650	649	640
ν_{sym}(out-of-phase XF_4)	B_1	663	556	640
$\nu_{asym}(XF_4)$	E	637	639	710

Table III. Comparison of the TeF_5O^- Stretching Force Constants and Stretch–Stretch Interaction Constants with those of SeF_5O^- and IOF_5 (mdyn Å^{-1})

Molecule	f_o	f_r	f_R	f_{rr}	$f_{rr'}$
TeF_5O^-	6.16	4.16	3.38	−0.05	0.66
SeF_5O^-	6.49	3.59	2.98	0.31	0.49
IOF_5	6.99	4.42	4.60	0	0.18

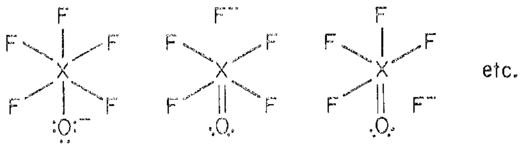
[a] Key: f_0, X–O stretch; f_r, X–F_{eq} stretch; f_R, X–F_{ax} stretch; f_{rr}, interaction between adjacent X–F_{eq}'s; $f_{rr'}$, interaction between opposite X–F_{eq}'s.

Force Constant Calculations and Comparison with Other XF_5O Molecules. In Table II the stretching frequencies of TeF_5O^- are compared with the corresponding frequencies of IOF_5 as assigned by Smith and Begun[8] and of SeF_5O^- with the assignment given by Seppelt.[14] The assignments for both molecules have been based on C_{4v} symmetry, and the frequencies listed were recorded in the gas phase for IOF_5 and in CH_3CN solution for SeF_5O^- with potassium as cation. The stretching modes of SF_5O^- assigned only recently have not been included in this table because the spectra were run in the solid state and therefore no polarization data are available.[7]

For all three molecules the highest frequency has been assigned as the X–O stretching vibration, in accordance with the partial double-bond character of this type of bond found in similar molecules. Differences in the assignment are found, however, for the other two polarized bands. For TeF_5O^- and SeF_5O^- the higher wave number band of the two is assigned as the symmetric XF_4 stretching vibration, the lower as the axial X–F stretching vibration, and *vice versa* for IOF_5. Although this reversed assignment will lead to differences in the X–F stretching force constants, it appears to be correct. The band at 680 cm^{-1} in IOF_5 was assigned as the axial I–F stretching mode because it displays in the gas-phase infrared spectrum a sharp Q branch, indicating a dipole moment change parallel to the C_{4v} axis.

For IOF_5 the valence force constants have been calculated using a general valence force field.[8] Results of similar calculations on TeF_5O^- and SeF_5O^- are not as meaningful because for both ions three of the six deformation modes have not been observed yet. However, in view of the heavy central atom in these ions, it is acceptable to separate the stretching motions from the bending motions. This approximation holds less well for SeF_5O^- than for TeF_5O^- because the interaction constants are expected to become more significant. We have calculated a set of stretching force constants from the five stretching frequencies observed for TeF_5O^- and SeF_5O^- assuming the following geometries: $r_{Te\text{–}F} = R_{Te\text{–}F'} = 1.84$ Å, $D_{Te\text{–}O} = 1.70$ Å, $r_{Se\text{–}F} = R_{Se\text{–}F'} = 1.72$ Å, and $D_{Se\text{–}O} = 1.58$ Å, where F' refers to the axial (unique) fluorine ligand; 90° angles were used throughout.[19] The bond lengths were estimated by comparison with similar molecules. A perfect fit between calculated and observed frequencies was obtained only if the two interaction constants f_{rr} (interaction between adjacent X–F_{eq}) and $f_{rr'}$ (interaction between opposite X–F_{eq}) were included in the iteration. The resulting force constants are shown in Table III together with the stretching force constants of IOF_5 taken from the literature.[8]

Table III allows the following conclusions. (i) The values of f_0 indicate for XF_5O^- XO bond orders somewhat smaller than 2 (f_0 in SeO_2F_2 = 8.00 mdyn/Å). This can be rationalized by contributions from the resonance structures



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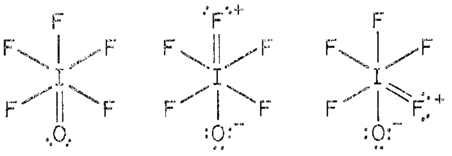
with II and III being more dominant than I as expected from the higher electronegativity of F when compared to that of O. The polarization of the X–F bond also explains the strong drop of f_{XF} from XF_6 to XF_5O^- (f_{Te-F} in TeF_6, 5.07 mdyn/Å;[20] f_{Se-F} in SeF_6, 4.99 mdyn/Å).[21] (ii) Molecular orbital arguments favor II over III, causing f_R to become smaller than f_r in XF_5O^-. (iii) In IF_5O, however, argument (ii) combined with the resonance structures



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causes f_R to become slightly larger than f_r. (iv) The XF_5 part of XF_5O^- is less electronegative in TeF_5O^- than in SeF_5O^-, thus giving in TeF_5O^- more weight to resonance structure I. This causes f_0 to increase and f_r and f_R to decrease when going from TeF_5O^- to SeF_5O^-.

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Registry No. TeF_5OCs, 19610-48-1; TeF_5OAg, 50700-88-4; TeF_5O^-, 42503-56-0; SeF_5O^-, 42310-69-0; IOF_5, 16056-61-4.

Supplementary Material Available. A detailed description of the normal-coordinate analysis of the TeF_5O^- ion will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number AIC403713.

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Polar and Free-Radical Additions of Fluorinated Species to Unsaturated Carbon–Nitrogen Systems

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Polar and free-radical addition reactions to halo nitriles and imines are examined and compared. The new compounds $CF_3C(OSO_2F)_2N(OSO_2F)_2$, $ClC(OSO_2F)_2N(OSO_2F)_2$, $(CF_3)_2C{=}NCF_3$, $(CF_3)_3CN(CF_3)_2$, $(CF_3)_3CNNCF_3$, $(CF_3)_2CFN(CF_3)Cl$, $(CF_3)_2CFN(CF_3)H$, and $ClCCF_3{=}NCF_3$ were prepared and characterized. While polar addition reactions are discussed in terms of the polarization of the reaction site, radical addition products are explained *via* the formation of a nitrene intermediate. The radical additions to halo nitriles are shown to be synthetically useful, giving yields of up to 80%.

Introduction

In the literature, examples of free-radical addition to carbon–nitrogen unsaturated moieties are rare. In fact, various nitriles have been used as solvents in studies which involve radical reactions. In the presence of methyl radicals, cyanogen reacts to give acetonitrile as well as solid products[1] which were not identified. Hydrogen atoms have been reported to react with RCN (R = alkyl) to yield the intermediate $RC(H){=}N\cdot$.[2] However, the final products were not identified. The additions of H atoms to cyanogen at 25° and to azomethane as well as the addition of CN radicals to CH_3CN to yield the intermediate $CH_3C(CN){=}N\cdot$[3] demonstrate the ease with which radical additions to carbon–nitrogen unsaturated systems may take place. Unfortunately, none of the final products was isolated and identified.

Only a few radical additions of synthetic utility have been reported, *e.g.*, the fluorination with elemental fluorine of materials such as trifluoroacetonitrile gave $CF_3CF_2NF_2$, $C_2F_5N{=}NC_2F_5$, and $CF_3C(F){=}NF$.[4,5] Photolysis of mixtures of SF_5Cl and ClCN or of SF_5Cl and CF_3CN yielded $SF_5N{=}CCl_2$ or $SF_5N{=}CClCF_3$, respectively.[6] The reaction of the phosphazene, $Ph_3P{=}N{-}N{=}CPh_2$, and CF_3CN at 25° to yield $Ph_3P{=}N(CF_3)C{=}NN{=}CPh_2$ was reported to occur *via* radical addition.[7] When photolyzed with $(CN)_2$, tetrafluorohydrazine, a good source of difluoramine and fluorine radicals, produced NF_2CF_2CN, $(NF_2CF_2)_2$, and $C_2F_5NF_2$.[8]

The paucity of radical additions to carbon–nitrogen double and triple bonds suggested that such a study should be undertaken and the results compared with similar polar interactions. Investigation of the reaction of radicals and polar