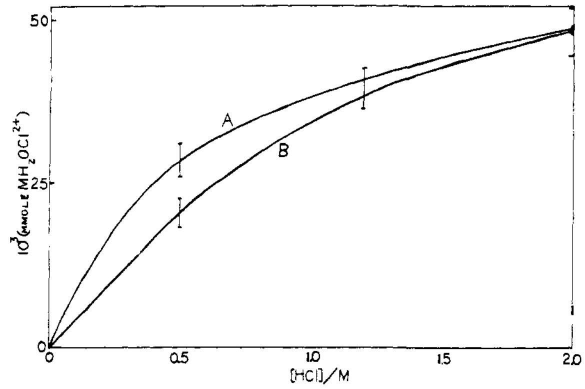

Figure 1. Millimoles of $Co(en)_2H_2OCl^{2+}$ formed as a function of HCl concentration: curve A, ionic strength equal to HCl concentration; curve B, $HClO_4$ added to maintain 2.00 *M* ionic strength.

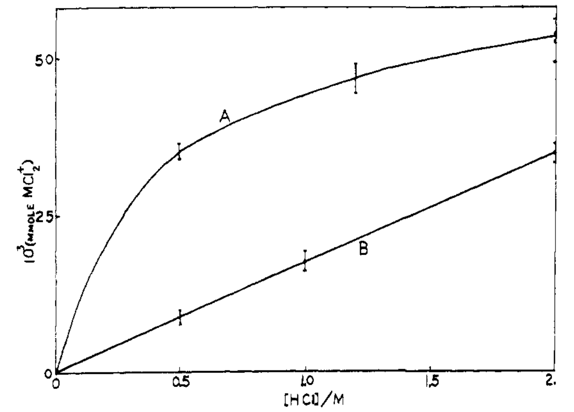

Figure 2. Millimoles of $Co(en)_2Cl_2^{+}$ formed as a function of HCl concentration: curve A, *trans*-$Co(en)_2Cl_2^{+}$ formation (variable ionic strength); curve B, *cis*-$Coen_2Cl_2^{+}$ formation (2.00 *M* ionic strength).

MOH_2^{3+} moieties do not significantly approach a common configuration as Cl^- concentration is decreased because the *trans*-MH_2OCl^{2+}/*cis*-MH_2OCl^{2+} product ratios do not begin to approach one another as Cl^- concentration is decreased.

Fact 4 indicates that the same *c*-MCl^{2+} moiety is formed in the *cis*-$M(DMSO)Cl^{2+}$ + MnO_4^- reaction as in the *cis*-MN_3Cl^+ + NO^+ and *cis*-MCl_2^+ + Hg^{2+} reactions.

Fact 5 (analogous to fact 1) indicates the *c*-MCl^{2+} is not changing rapidly toward an equilibrium configuration common to *c*-MCl^{2+} and *t*-MCl^{2+}.

Facts 1-5 fit the first explanation if Cl^- ions as well as H_2O molecules were in the solvation shell of the activated complex. The entering group could replace the leaving group during deactivation of the activated complex (facts 1, 3, and 5) or the entering group could go in cis and trans to the directing group (facts 2 and 4) as dictated by the energetics of the activated complex. These facts also fit the third explanation if Cl^- ions as well as water molecules occupy positions in the solvent cage of the very short-lived intermediates. Likewise these facts fit the fourth explanation with the five-coordinate intermediates having sufficient stability to establish ion-pair equilibria and to finally react in preferred orientations with different nucleophiles without significantly approaching a common equilibrium nuclear configuration. If the first or third explanation were correct, the entering Cl^- ions must be in the solvation shell of the five-coordinate cobalt(III) moieties so that the Cl^- ion can occupy the sixth coordination site as well as water; these Cl^- ions are there as a result of ion-pair formation with the reactant(s). These three explanations can be tentatively distinguished by further facts given below.

(6) For the *trans*-$MN_3OH_2^{2+}$ + NO^+ reaction, the number of millimoles of MH_2OCl^{2+} formed shows (see Figure 1) a saturation effect with increasing Cl^- concentration both for varying and constant ionic strength conditions while the value of the product ratio r_1 defined by eq 1 decreases from 0.48 ± 0.06 at 0.50 *M* HCl to 0.28 ± 0.04 at 2.00 *M* HCL.

$$r_1 = \frac{(\text{total mmol of } MH_2OCl^{2+})}{[Cl^-](\text{total mmol of } M(H_2O)_2^{3+})} \qquad (1)$$

(7) For the *trans*-MN_3Cl^+ + NO^+ reaction, the number of millimoles of *trans*-MCl_2^+ formed shows (see Figure 2) a strong saturation effect at variable ionic strength while the value of the product ratio r_2 defined by eq 2 decreases from 0.95 ± 0.05 at 0.50 *M* HCl to 0.34 ± 0.04 at 2.00 *M* HCl. (Insolubility of [*trans*-MN_3Cl]ClO_4 prevented use of $HClO_4$ to maintain constant ionic strength.)

$$r_2 = \frac{(\text{total mmol of } Co(en)_2Cl_2^{+})}{[Cl^-](\text{total mmol of } MH_2OCl^{2+})} \qquad (2)$$

(8) For the *cis*-$M(DMSO)Cl^{2+}$ + MnO_4^- reaction, the number of millimoles of *cis*-MCl_2^+ formed does not show (see Figure 2) a saturation effect at constant ionic strength and the product ratio r_2 is constant at 0.14 ± 0.02.

Fact 6 is more consistent with production of the *t*-MOH_2^{3+} intermediate and saturation with respect to *t*-$MOH_2^{3+}\cdot Cl^-$ ion-pairs with increasing Cl^- concentration than with the first and third explanations because +3 cations are known to be better ion-pair formers than +2 cations. Fact 7 virtually excludes the first and third explanations because saturation with respect to *trans*-$MN_3Cl^+\cdot Cl^-$ ion pairs in the Cl^- concentration range used is not a very acceptable explanation. Facts 7 and 8 are consistent if *t*-MCl^{2+} forms more ion pairs with Cl^- corrected positioned for reaction trans to the Cl^- directing group than *c*-MCl^{2+} forms for reaction cis to the Cl^- directing group.

Acknowledgment. We wish to thank Professor J. F. Endicott and a referee for helpful suggestions concerning intermediate lifetimes.

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Electron Spin Resonance Spectrum of F_3NO^-. A Hypervalent Radical from First-Row Elements[1]

Sir:

We wish to report the ESR detection and identification of the trifluoramine oxide radical anion, F_3NO^-. This radical is of particular interest because it represents the first example of a 33 valence electron species derived solely from first-row elements, although the related phosphoranyl radicals PF_4[2] and Cl_3PO^-[3] are well established. Perhaps the discovery of this novel radical is not entirely unexpected in the light of previous work showing that the electronic structure of phosphoranyl radicals does not require extensive d-orbital participation.[3]

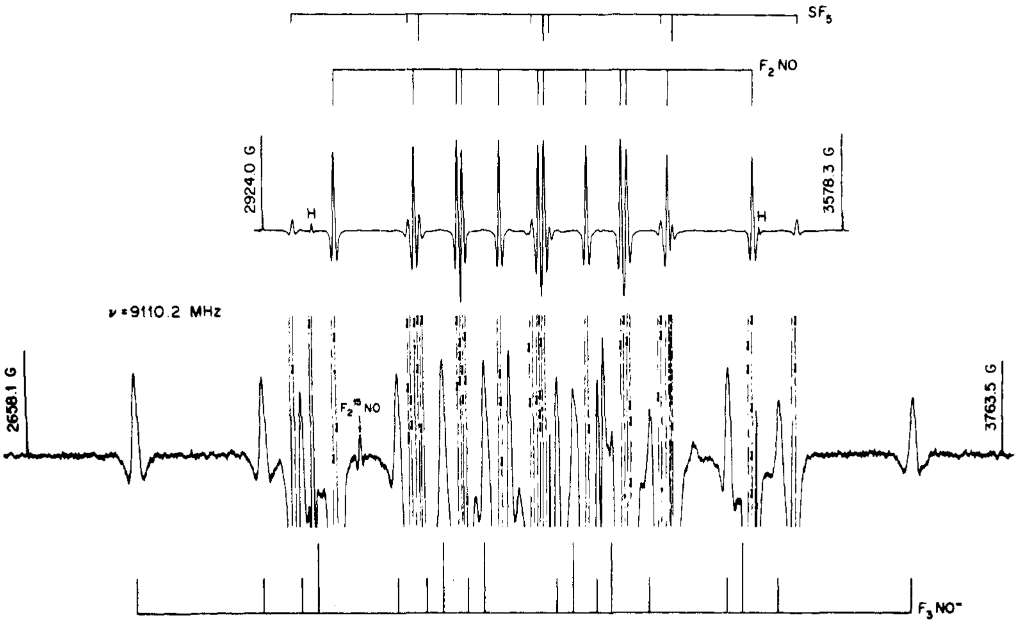

Figure 1. Second-derivative ESR spectra of a γ-irradiated solid solution of 5 mol % F_3NO in SF_6. The sample was irradiated at −196°, and the spectra were recorded at −170° immediately after irradiation. The lower spectrum was recorded at high gain to reveal the hyperfine components of the F_3NO^- radical anion which are much weaker than those of the SF_5 and F_2NO radicals shown in the upper spectrum. The stick diagram for F_3NO^- was calculated according to simple second-order theory.

Recent work[4-7] has exploited the usefulness of the SF_6 matrix for isotropic ESR studies of trapped inorganic radicals, a technique first employed by Fessenden and Schuler.[2] In the present study, solid solutions containing 1-10 mol % trifluoramine oxide[8] in SF_6 were γ irradiated at −196° and the ESR spectra recorded at −170°. Optimum signal intensities for the F_2NO and F_3NO^- radicals relative to those of the SF_5 radical[2,9] were obtained from a 5 mol % solution irradiated for 0.3 Mrad.

The ESR spectrum shown in Figure 1 is dominated by a pattern consisting of a 1:2:1 triplet of 1:1:1 triplets with the central lines of the 1:2:1 triplets resolved into their two second-order components of equal intensity. This hyperfine structure is attributable to the interaction of the unpaired electron with two equivalent ^{19}F ($I = \frac{1}{2}$) nuclei and one ^{14}N ($I = 1$) nucleus, the corrected ESR parameters being a_F (2) = 143.8 G, a_N = 93.3 G, and $g = 2.0058 \pm 0.0002$. These *isotropic* parameters are quite similar to those previously ascribed to the F_2NO radical produced by photolysis of presumably polycrystalline F_3NO at −196°.[8a,10] This assignment is certainly supported by the similarity of the ^{19}F coupling to the corresponding value of 142.4 G for the isoelectronic CF_3 radical in a xenon matrix,[11] and by the large ^{14}N coupling which is diagnostic of a pyramidal nitrogen-centered radical analogous to CF_3.[11] Moreover, confirmation of the F_2NO identification was obtained through the detection of an identical ESR spectrum from a γ-irradiated solution of FNO in SF_6,[12] fluorine atom addition to the solute being expected on the basis of previous results.[2,4,6,7]

In addition to the lines from SF_5 and F_2NO, a family of weaker spectral components can be seen in Figure 1 under conditions of high gain. Starting from the wings, the well-resolved outer lines are easily grouped into two sets of 1:1:1 triplets whose individual spacings are in accord with the second-order shifts attributable to a ^{14}N interaction. Although some inner components of the spectrum are overlapped by the strong lines from the spectra of H, SF_5, and F_2NO, sufficient structural detail is present to analyze the pattern into a 1:3:3:1 quartet of ^{14}N triplets, each of the central lines from the quartets being resolved into two 1:2 second-order components,[13] as shown in the stick diagram. The quartet hyperfine structure is interpreted in terms of coupling to three equivalent fluorines, and the corrected ESR parameters are a_F (3) = 195 G, a_N = 147 G, and g = 2.014.

The identification of this second radical as F_3NO^- is strongly supported by the large value of a_N which corresponds to an unprecedented spin density of 0.27 in the nitrogen 2s orbital.[14] This is quite comparable to the spin densities in the central atom 3s orbitals of phosphoranyl and related radicals possessing fluorine ligands.[3,15] However, in order for the equivalence of the three fluorines in the ESR spectrum of F_3NO^- to be consistent with a trigonal bipyramidal (C_s) structure characteristic of phosphoranyl radicals, there must be a rapid exchange of the fluorine ligands between the axial and equatorial sites on the ESR time scale.[16] Alternatively, if F_3NO^- retains the C_{3v} symmetry of the parent molecule, the fluorines are always isotropically equivalent since the unpaired electron occupies an a_1 orbital composed largely from the antibonding combination of the nitrogen 2s and fluorine $2p_\sigma$ orbitals. Despite this ambiguity, it is reassuring that INDO calculations for each of these geometries[17] predict nitrogen 2s spin densities of 0.20 (C_s) and 0.30 (C_{3v}) which are reasonably close to the experimental value (0.27) and they are also able to reproduce the approximate magnitude of the fluorine 2s spin density (0.011).[14] In contrast, the calculations for the radical cation F_3NO^+ with the expected C_{3v} symmetry indicate that most of the spin density now resides in an oxygen 2p orbital perpendicular to the C_{3v} axis, and the symmetry of the half-occupied MO excludes the direct participation of the nitrogen 2s orbital. Considering other possible species, the isotropic parameters derived recently for NF_3^+ [18] are quite different from those obtained here for F_3NO^-.

In conclusion, we note that the radiation chemistry of this system is consistent with F_2NO and F_3NO^- formation by electron capture reactions. ESR studies with a wide variety of solutes in SF_6 show that the SF_5 radical is generally the most abundant radical produced by radiolysis, and its formation is thought to proceed by dissociative electron capture,[9,19] the undissociated species SF_6^- being produced in much smaller yield.[2,5,9] The present results are remarkable in terms of the large F_2NO-SF_5 intensity ratio indicating therefore that F_3NO competes very favorably with SF_6 for electron capture, although SF_6 is itself known to be an extremely efficient electron scavenger.[19] The high F_2NO-F_3NO^- ratio is explained if the dissociative path is favored, as seems to be the case for SF_6.

Acknowledgment. We thank Professor Gleb Mamantov (University of Tennessee) and Dr. F. Q. Roberto (Edwards AFB, Calif.) for supplying us with samples of FNO and F_3NO. We are also grateful to Drs. A. Hasegawa and C. M. L. Kerr for helpful discussions. Correspondence about the F_2NO radical with Dr. W. B. Fox (Naval Research Laboratory, Washington, D.C.) and Dr. J. R. Morton (National Research Council, Ottawa) is also acknowledged.

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(10) Although the F_2NO spectrum obtained in the previous work[8a] was not published, the close agreement between the F_2NO parameters derived from powder and isotropic spectra is understandable on the basis of our own low-temperature studies. Thus, we find that although radicals do not tumble in the SF_6 matrix below the phase transition at −179°, the spectrum of F_2NO in SF_6 at −196° shows comparatively little anisotropic broadening, even to the extent that the second-order ^{19}F splittings are retained. However, at much lower temperatures (ca. −250°) the pattern becomes typical of a highly anisotropic powder spectrum from a stationary radical. These results suggest that intramolecular motion, probably inversion coupled with rotation, is responsible for the nearly isotropic appearance of the F_2NO spectrum in a randomly oriented sample at −196°. An inversion barrier of only 0.064 kcal mol^{-1} has been calculated theoretically for the H_2NO radical (Y. Ellinger, R. Subra, A. Rassat, J. Douady, and G. Berthier, *J. Am. Chem. Soc.*, **97**, 476 (1975)).

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(12) An unidentified spectrum derived from an irradiated solution of NO in SF_6 was previously analyzed[2] as a ^{19}F doublet ($a_F' = 187$ G) of ^{19}F triplets (a_F (2) = 143 G). The spectrum of F_2NO would fit this description exactly if the central components of the ^{14}N triplets were masked by the usually more intense lines of SF_5 (see Figure 1) thereby converting the ^{14}N triplet interaction to an apparent doublet ($2a_N = a_F'$). Accordingly, a previous tentative assignment[9] to $ONSF_4$ can probably be discounted.

(13) Despite the interference from other spectral lines, it can be deduced from several spectra of F_3NO^- recorded in different experiments that the second-order splitting for line 3 at low field must be less than that for line 10 at high field by about 5 G. Assuming, as expected, that the ^{14}N and ^{19}F coupling constants have the same sign, a calculation of these second-order splittings from the previously determined hyperfine parameters gave values of 14.8 G (line 3) and 19.8 G (line 10). For a comprehensive discussion of the closely related ethyl radical spectrum, see R. W. Fessenden, *J. Magn. Reson.*, **1**, 277 (1969).

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(15) F_3NO^- and the valence-isoelectronic species F_3SO (J. R. Morton and K. F. Preston, *J. Chem. Phys.*, **58**, 2657 (1973) and ref 2) possess the same spin density in the central-atom ns orbital and the sums of the fluorine couplings are 585 G (F_3NO^-) and 555 G (F_3SO).

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A Novel Photorearrangement of Cephalosporins

Sir:

An extreme lability of cephalosporin C to uv light was observed in early investigations on this important class of antibiotics.[1] Because photolysis resulted in destruction of cephalosporin C antibiotic activity,[1] the β-lactam dihydrothiazine nucleus was suggested as the site of photoreactivity.

In view of previous observations, we attempted to clarify the mode of the photodegradation of 3-cephem derivatives. The present communication describes that irradiation of 3-cephem derivatives *in alcohols* (methanol or ethanol) causes a novel photorearrangement leading to thiazole derivatives, which involve incorporation of alcohols into an intermediate photoproduct. This type of photochemistry is general for 7-acylamido-3-cephem derivatives.

Methyl 7-phenylacetamido-3-methyl-3-cephem-4-carboxylate (**1a**) (0.01 *M*) in methanol[2] was irradiated by a 400-W high-pressure mercury arc lamp through Pyrex filter under nitrogen until disappearance of **1a** (monitored by TLC) was complete (about 8 hr). The solution was concentrated under reduced pressure to leave an oily residue which was subjected to chromatography on silica gel. Elution with $CHCl_3$-$(CH_3)_2CO$, evaporation of the initial elute, and recrystallization of the residue from ether-*n*-hexane gave 2-benzylthiazole-4-carboxamide derivative **2a** in 50% yield (mp 123-125°; ir (KBr) 3390 (NH), 1730 (*C*OOCH₃), 1680 cm^{-1} (*C*ONH); NMR ($CDCl_3$) δ 1.89 (3 H, broad s, CH_3—C=CH_2), 3.34 (3 H, s, -OCH_3), 3.87 (3 H, s, -$COOCH_3$), 4.37 (2 H, s, $C_6H_5CH_2$-), 5.27 and 5.53 (each 1 H, m, and broad s, isopropenyl vinyl protons), 7.40 (5 H, broad s, phenyl protons), 8.05 (1 H, s, thiazole-ring proton), 8.65 (1 H, broad N*H*, deuterium exchangeable)). Further elution afforded a small amount of an isomeric compound **3a** (vide infra) (mp 111-113°; ir (KBr) 3350 (N*H*), 1700 (*C*OOCH₃), 1660 cm^{-1} (*C*ONH); uvλ_{max}^{MeOH} nm (ϵ): 240 (8000); NMR ($CDCl_3$) δ 1.96 (3 H, broad s, =C—CH_3), 3.35 (3 H, s, -OCH_3), 3.80 (3 H, s, -$COOCH_3$), 4.34 (2 H, s, $C_6H_5CH_2$-), 4.40 (2 H, broad s, -CH_2OCH_3), 7.37 (5 H, broad s, phenyl protons), 8.06 (1 H, s, thiazole-ring proton), 8.67 (1 H, broad, N*H*)). Attempts to isolate other minor products from further eluates failed.

The isolated products, **2a** and **3a**, were insensitive to the irradiation under the analogous conditions. Microanalytical and mass spectral data of both the products established a molecular formula, $C_{18}H_{20}O_4N_2S$, respectively. These products were optically inactive.

Cooper et al.[3] have reported the transformation of penicillin V sulfoxide into the 2-phenoxymethylthiazole-4-carboxamide derivative. Analogously, penicillin G sulfoxide methyl ester was converted to optically active 2-benzylthiazole-4-carboxamide derivative **5**, mp 62-63°, ($[\alpha]^{15}$D −51(*c* 1.0, $CHCl_3$)) in 80% yield.

The NMR spectrum of **5** is similar to that of **2a**, except for the presence of a methine proton signal at 5.26 (1 H, d, *J* = 8 Hz, coalesced to a singlet by deuterium exchange) instead of a methoxy signal in **2a**. The uv spectrum of **2a** (λ_{max}^{MeOH} (ϵ) nm; 228 (sh 8000)) is superimposable on that of **5**.