C(2)–C(8) and C(4)–C(6) distances are extremely close (1.949 (7) and 2.054 (7) Å, respectively) as are the corresponding C-(2)–C(1)–C(8) and C(4)–C(5)–C(6) bond angles (81.5 (5)° and 88.7 (4)°, respectively). Collectively, the solid-state structure of **1** represents the closest approach to a bishomoaromatic system (**1′** in this case) thus far reported. Scrutiny of the nonbonded distances indicates that there are no unusually short contacts involving, e.g., the $AlCl_4^-$ gegenion. However, the thermal ellipsoids of C(6) and C(8) are significantly larger than those of the other atoms. The delocalized solid-state structure of **1** stands in sharp contrast to its localized solution-phase structure. Since the barrier to the Cope rearrangement for **1** is similar in magnitude to that of other barbaralanes,[7] we are reluctant to invoke any special solvent interactions in the solvation of **1**. The structural differences are, therefore, most probably due to crystal packing forces.

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Supplementary Material Available: Tables of bond lengths, bond angles, torsional angles, atomic coordinates, and thermal parameters for **1** (6 pages). Ordering information is given on any current masthead page.

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(9) Crystal data for **1**: $C_{10}H_{14}AlNPCl_5$, M_r = 383.45, monoclinic, space group $P2_1/c$ (No. 14), a = 6.667 (1) Å, b = 17.149 (3) Å, c = 14.976 (3) Å, β = 93.50 (2)°; V = 1709.0 Å^3, Z = 4; D_c = 1.491 g cm^{-3}; λ (Mo Kα) = 0.7107 Å, μ(Mo Kα) = 9.8 cm^{-1}. An empirical absorption correction was applied. The intensities of 2766 reflections were measured on an Enraf-Nonius CAD-4F diffractometer at room temperature ($3.00 \leq 2\theta \leq 48.00$). The structure was solved by direct methods and refined by full-matrix least squares using 1306 unique observed reflections ($I \gtrsim 3.0\sigma(I)$). The reflection to parameter ratio was 8:1. The final residuals were R = 0.0730 and R_w = 0.0750. All calculations were performed using the SDP-Plus program package.[10]

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Selenoformaldehyde Phosphorescence Observed in the Reaction of Molecular Fluorine with Dimethyl Diselenide

Robert J. Glinski*†

National Center for Atmospheric Research§
Boulder, Colorado 80307

Elizabeth A. Mishalanie‡ and John W. Birks

Department of Chemistry and Cooperative Institute
for Research in Environmental Sciences (CIRES)
University of Colorado, Boulder, Colorado 80309

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The spectroscopy and chemistry of formaldehyde analogues have recently become of wide interest.[1,2] Chemiluminescence (CL) methods have been successful in obtaining useful spectral data on the difficult-to-study formaldehyde analogues thioformaldehyde (CH_2S)[3] and silanone (SiH_2O).[4] The only previous study of the optical spectrum of selenoformaldehyde (CH_2Se) was that of Judge and Moule.[5] These workers obtained absorbance spectra of CH_2Se ($\tilde{a}^3A_2$) over a 68-m path length after pyrolysis of dimethyl selenide. The microwave spectrum[6] and photoelectron spectrum[7] of CH_2Se have also been studied only within the last several years.

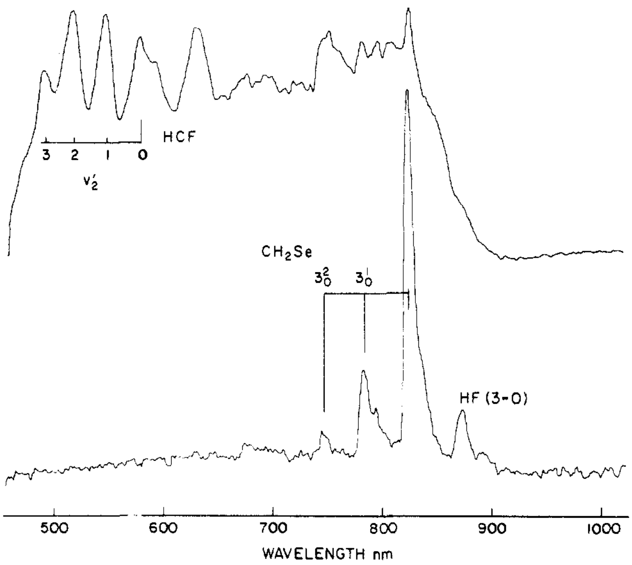

Figure 1. Uncorrected diode array spectra obtained in the reactions of dimethyl diselenide with a 10% F_2/He mixture. Upper trace: 10 mtorr of DMDSe and 330 mtorr of F_2/He. Lower trace: 60 mtorr of DMDSe and 270 mtorr of F_2/He. Although a short progression in ν'_3 is labeled in the lower trace, other transitions may account for some intensity in those bands (see text). The precision of the wavelength measurement is ±1 diode or ±1.2 nm.

Reactions of molecular fluorine with organosulfur compounds generate rich, gas-phase CL spectra. Vibrationally excited HF and electronically excited HCF and CH_2S have been identified in emission spectra from the reactions of F_2 with a number of organosulfur compounds under various conditions.[3,8-10] In addition, the novel species FCS has also been tentatively identified.[10]

In a CL study similar to that which has yielded a CH_2S phosphorescence spectrum,[3] we have obtained emission spectra from the reaction of $(CH_3Se)_2$ with F_2 corresponding to the $\tilde{a}^3A_2 \rightarrow \tilde{X}^1A_1$ transition in CH_2Se. We have also obtained spectral evidence for the production of HF†, HCF*, and a fourth unidentified intense emitter from the $F_2/(CH_3Se)_2$ reaction.

The CL was observed as it occurred in our chromatography detector cell that has been described in detail elsewhere.[8,9] The entrance slit to the 512 channel intensified diode array spectrophotometer (focal length 0.25 m) was set close to a quartz window at one end of the cell.

Emission spectra recorded during the reaction of a 10% F_2/helium mixture (Matheson) with dimethyl diselenide (DMDSe, Alfa Products) under two different conditions of reactant pressure are presented in Figure 1. The lower trace was obtained with 60 mtorr of DMDSe and 270 mtorr of F_2/He. The location of three prominent bands, not assignable to HF†, is consistent with expected selenoformaldehyde phosphorescence features on the basis

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† CIRES visiting fellow (1983–1984).

‡ Present address: National Center for Atmospheric Research, Boulder, CO 80307.

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of comparison with the optical absorption spectrum of Judge and Moule.[5] The most intense band corresponds to the electronic origin of the $\tilde{a}^3A_2 \rightarrow \tilde{X}^1A_1$ transition and is located at 823.3 ± 1.2 nm (12, 146 ± 18 cm^{-1}), measured at the band maximum. The bands located at 693 ± 25 cm^{-1} and 1357 ± 25 cm^{-1} to the blue of the origin are consistent with emission from excited vibrational levels in the $\tilde{a}$ state. The band at 693 cm^{-1} is consistent with the overlapping 3^1_0 (C═S stretch) and 4^2_0 (out-of-plane bend) bands that were observed in absorption[5] at 707 and 687 cm^{-1}, respectively. These bands appear to be merged into one because of the resolution of this study (~60 cm^{-1}). The feature at 1357 cm^{-1} is also consistent with the merged 3^2_0 and $3^1_0 4^2_0$ bands of Moule and Walsh.[5] A weak feature, 517 ± 25 cm^{-1} to the blue of the origin, is not assigned and may be a combination band. The overlap of the two transitions in the minor bands at 693 and 1357 cm^{-1} above the origin interferes with what might be observed as red shading in the bands.

It is notable that no bands to the red of the origin corresponding to transitions of the kind $v' = 0 \rightarrow v'' = n$ $(n \neq 0)$ are identifiable in the spectrum. The 2^0_1 and 3^0_1 bands might especially be expected to appear because of their presence in the CH_2S phosphorescence spectrum. Two factors may affect the observability of any CH_2Se bands to the red of the origin: the potential presence of the HF (3-0) band at 879 nm and the greatly reduced response of the diode array spectrophotometer beyond 880 nm. We have assigned the band at 870 nm to HF (3-0), but have not ruled out the possibility that CH_2Se transitions may account for some of the intensity under the band.

The upper trace of Figure 1 is a spectrum obtained from the reaction of 10 mtorr of DMDSe with 370 mtorr of the 10% F_2/He mixture. The two traces are markedly different, although the major features of the lower trace can be discerned in the upper trace. The CH_2Se bands and HF (3-0) band are visible in the red shoulder of the extensive band of the upper trace. The HCF ($\tilde{A}^1A'' \rightarrow \tilde{X}^1A'$) spectrum is also observed and is clearly identifiable by its 0*n*0 → 000 (bending mode) progresssion between 475 and 600 nm and the 000 → 010 band at 630 nm.[11]

The features located between 650 and 800 nm in the upper trace of Figure 1 are difficult to identify at this low resolution. Certain identities of this feature can be ruled out. The CF_2,[12] CF_2Se,[13] and SeF_2[14] molecules have electronic spectra that are known or can be estimated to lie to much higher energies. We have obtained evidence for the formation of FCS radical in the reactions of F_2 with organosulfur compounds[10] and speculate that FCSe* may contribute to some of the intensity in this region. It is also possible that CH_2Se in the $\tilde{A}^1A_2$ state may be formed in this reaction; however, the oscillator strength for fluorescence from CH_2Se is expected to be less than that for phosphorescence according to arguments given previously.[5] But fluorescence from CH_2S ($\tilde{A}^1A_2$) is not observed in the CH_3SH/F_2 system,[3] and the fluorescence and phosphorescence are expected to be of similar intensity for CH_2S^* in contrast to CH_2Se^*.

Using the formation of CH_2S^* in the $(CH_3S)_2$ system as a guide,[3] we suggest that CH_3Se radicals react with F_2 molecules to produce CH_2Se^*, HF, and F atoms. The chain is initiated by F_2 attack on $(CH_3Se)_2$ and carried by F atoms and CH_3Se radicals. This scheme proved to be thermochemically acceptable for forming CH_2S in its $\tilde{a}^3A_2$ state in the organosulfur systems.[3,10]

In summary, we have recorded a spectrum of the $\tilde{a}^3A_2 \rightarrow \tilde{X}^1A_1$ transition in selenoformaldehyde. The HF (3-0) band and, under slightly more fuel lean conditions, HCF ($\tilde{A}^1A'' \rightarrow \tilde{X}^1A'$) features were also observed. The acquisition of these spectra by sampling an approximately 1-cm^3 reaction volume for a 12-min intergration time demonstrates the utility of the chemiluminescent technique in observing spectra of hard-to-study species. It is hoped that improved mechanistic and dynamical predictability of chemiluminescent reactions will also be useful to the spectroscopist.

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Diminished Solution Electron Affinities of ^{13}C- and Deuterium-Substituted Anion Radical Precursors Allow Isotopic Enrichment

Gerald R. Stevenson,* Matthew P. Espe, and
Richard C. Reiter

Department of Chemistry, Illinois State University
Normal, Illinois 61761

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Since the dawn of the nuclear age, the problem of isotopic separation has been of considerable interest.

An ESR study carried out in tetrahydrofuran (THF) and dimethoxyethane (DME) has shown that even the substitution of a hydrogen by a deuterium on the benzene anion radical ($BZ^{-}\cdot$) removes the degeneracy of the symmetry (S) and antisymmetric (A) wavefunctions.[1] This apparent electron-releasing nature of the deuterium creates a splitting of about 0.05 kcal/mol in the two wavefunctions.[1] Alkyl groups produce a much larger splitting in the degeneracy of the S and A wavefunctions of benzene$^{-}\cdot$.[2–6] However, this effect is not purely an electronic one as was shown by the vibronic coupling calculations of Alper and Silbey.[7] Further, alkyl groups appear to destabilize both the S and A wavefunctions, as evidenced by the fact that toluene has a smaller solution electron affinity than does benzene.[8] It must be kept in mind that the relative electron affinities in solution are due to counterion and/or solvent interactions, as toluene has a larger EA than benzene in the gas phase.[9] We were motivated to see if deuteration analogously diminishes the solution electron affinity and if this decreased solution EA could be utilized for isotopic enhancement. Both of these situations were realized. In fact, not only are the relative solution EA's of benzene and naphthalene diminised upon substitution of the protons by deuteriums, but also replacement of the ^{12}C atoms with ^{13}C has a similar effect. Further, this diminished solution EA caused by the addition of neutrons to the carbon or hydrogen nuclei can be utilized to enhance isotopic abundance.

When mixtures of carefully measured quantities of naphthalene (NP) and perdeuterated naphthalene (NP-d_8) were reduced with very deficient amounts of potassium metal in THF, the relative intensities of the two simultaneously observed ESR spectra (Figure 1) show that the equilibrium constant at −120 °C for reaction 1 is 0.26 ± 0.04 and $\Delta G°$, which is identical with the enthalpy change,[10] is 0.41 ± 0.15 kcal/mol.

$$NP^{-}\cdot,K^{+} + NP\text{-}d_8 \rightarrow NP + NP\text{-}d_8^{-}\cdot,K^{+} \qquad (1)$$

We have used this threefold diminished capacity for the capture of electrons to enhance the concentration of NP-d_8 from mixtures of NP and the deuterated species. The reduction of a 1:1 mixture of the deuterated and undeuterated naphthalenes with 0.5 mol

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