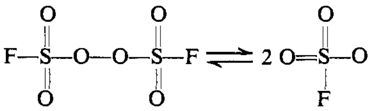
An Electron Spin Resonance Study of the $S_2O_6F_2$–$SO_3F\cdot$ Equilibrium. Enthalpy of Cleavage[1]

Paul M. Nutkowitz and Gershon Vincow[2,3]

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98105. *Received February 21, 1969*

Abstract: The fluorosulfate free radical ($SO_3F\cdot$, II) is produced by the homolytic thermal cleavage of neat liquid peroxydisulfuryl difluoride ($S_2O_6F_2$, I), and its esr spectrum is investigated over the temperature range $4° \leq t \leq 180°$. The spectrum consists of a single structureless component with $g = 2.0108 \pm 0.0001$ and a width which is unusually large and is temperature dependent [$\Delta H_{ms} \approx 25$ G (17°); $\Delta H_{ms} \approx 48$ G (180°)]. An analysis of measurements of the esr intensity as a function of temperature ($125° \leq t \leq 150°$) leads to a determination of the enthalpy of thermal dissociation of I. The value obtained is 22.4 ± 0.9 kcal/mole. This result is in good agreement with values of the enthalpy change for this reaction in the gas phase which have been previously obtained using PVT and spectrophotometric techniques.

Only a few inorganic molecule–radical equilibrium systems have been investigated using esr.[4] Below we report such a study for the equilibrium between neat liquid peroxydisulfuryl difluoride ($S_2O_6F_2$, I) and the fluorosulfate free radical ($SO_3F\cdot$, II).



$$F{-}S(=O)_2{-}O{-}O{-}S(=O)_2{-}F \rightleftharpoons 2\,O{=}S(=O)(F){-}O\cdot$$

I II

The goal of our work is the evaluation of $\Delta H°$ for the homolytic thermal cleavage of I. Our result bears comparison with those of other workers who have measured $\Delta H°$ for this system in the gas phase using PVT and spectrophotometric techniques.[5]

This is the first report of the $SO_3F\cdot$ radical in liquid solution. This species has previously been detected in a solid matrix at low temperature.[6]

Experimental Section

The $S_2O_6F_2$ used in this study was synthesized according to the method of Dudley and Cady.[7] Preliminary purification was achieved by the method of Shreeve and Cady[8] and was checked using ir and molecular weight measurements. Further purification of I was accomplished by bulb-to-bulb distillation using an all-Pyrex system[9] in which the final receiver was fitted with a Teflon stopcock (Fischer-Porter 4-mm threaded glass valve). The material was considered pure if it lacked color and if the esr measurements were reproducible under repeated thermal cycling.

Samples of neat liquid $S_2O_6F_2$ for the esr studies were deoxygenated and sealed under vacuum in quartz tubes.

The line width of the $SO_3F\cdot$ resonance in these $S_2O_6F_2$ samples was measured relative to the total extent of the esr spectrum of di-*t*-butyl nitroxide in *n*-C_7H_{16}, 30.22 ± 0.09 G.[10]

Samples containing the $SO_3F\cdot$ radical in the solid state were prepared as follows. The radical was generated by thermal dissociation of $S_2O_6F_2$ in the gas phase at 150° and was deposited on a cold finger at −196° in a matrix of its dimer. The cold finger was then transferred to the esr cavity.

The esr spectrometer used and the apparatus employed to vary and to measure the sample temperature have been described elsewhere.[11]

Results and Discussion

An esr signal is detected *at room temperature* using samples of neat liquid I. This resonance consists of a single very broad line, approximately Lorentzian in shape, with $g = 2.0108 \pm 0.0001$ and $\Delta H_{ms} \approx 25$ G (17°). Both the line width and peak height increase with increasing temperature, denoting an increase in radical concentration. These changes are reversible in the temperature range studied, $4° \leq t \leq 180°$. The samples also exhibit a reversible thermochromism, turning yellow at about 75°.

The observed line width is two orders of magnitude larger than is usually found for organic free radicals and is quite temperature dependent ($\Delta H_{ms} \approx 48$ G at 180°).[12]

We ascribe the observed esr signal to the fluorosulfate radical on the strength of (1) the similarity of its isotropic *g* value with an apparent *g* value reported for $SO_3F\cdot$ in the solid state (2.013),[6] (2) the parallel temperature variation of the esr intensity and the intensity of the yellow color (this band has been ascribed to II in the gas phase[5,13]), (3) the reversibility of the variation of esr intensity with temperature indicating that the radical is

---

[1] Supported by the U. S. Army Research Office—Durham.

[2] Alfred P. Sloan Foundation Fellow.

[3] To whom inquiries should be addressed.

[4] (a) C. H. Holm, W. H. Thurston, H. M. McConnell, and N. Davidson, *Bull. Am. Phys. Soc.*, [2] 397 (1956); (b) P. W. Atkins, N. Keen, and M. C. R. Symons, *J. Chem. Soc.*, 2873 (1962); (c) L. H. Piette, F. A. Johnson, K. A. Booman, and C. B. Colburn, *J. Chem. Phys.*, **35**, 1481 (1961); (d) H. E. Doorenbos and B. R. Loy, *ibid.*, **39**, 2393 (1963); (e) R. Ettinger and C. B. Colburn, *Inorg. Chem.*, **2**, 1311 (1963); (f) D. M. Gardner and G. K. Fraenkel, *J. Am. Chem. Soc.*, **78**, 3279 (1956).

[5] (a) F. B. Dudley and G. H. Cady, *ibid.*, **85**, 3375 (1963); (b) E. Castellano, R. Gatti, J. E. Sicre, and H. J. Schumacher, *Z. Physik. Chem.* (Frankfurt), **42**, 174 (1964). (c) The symbol PVT designates the measurement of the variation of total pressure with temperature at constant volume.

[6] F. Neumayer and N. Vanderkooi, Jr., *Inorg. Chem.*, **4**, 1234 (1965).

[7] F. B. Dudley and G. H. Cady, *J. Am. Chem. Soc.*, **79**, 513 (1957).

[8] (a) J. M. Shreeve and G. H. Cady, *ibid.*, **83**, 4521 (1961); J. M. Shreeve and G. H. Cady, *Inorg. Syn.*, **7**, 124 (1963). (b) It should be noted that there is a by-product of this reaction, FSO_3F, which is explosive.

[9] We are indebted to Professor J. M. Shreeve for informing us of this technique.

[10] The sample of di-*t*-butyl nitroxide was kindly supplied by Dr. A. K. Hoffman.

[11] G. Vincow, M. L. Morrell, F. R. Hunter, and H. J. Dauben, Jr., *J. Chem. Phys.*, **48**, 2876 (1968).

[12] (a) For further details see P. M. Nutkowitz, Ph.D. Thesis, University of Washington, Seattle, Wash., 1967; copies of this thesis are available from University Microfilms, Inc., Ann Arbor, Mich., Order No. 68-9316. (b) This aspect of our results will be presented in detail in a forthcoming publication.

[13] A determination of $\Delta H°$(g) based on the spectrophotometric intensity of this band leads to good agreement with a determination based on PVT measurements (ref 5).

present at equilibrium, (4) the failure to observe a second resonance which would be a concomitant of unsymmetrical homolytic cleavage, and (5) the known chemistry of I which strongly indicates the involvement of II.[5a]

One possible discrepancy in our assignment is the failure to observe a doublet spectrum due to fluorine hyperfine interaction. We propose that this is due to the large magnitude of the line width; *i.e.*, $|a^F|$ is considerably smaller than ΔH_{ms} for an individual component of the doublet.

Confirming evidence for this suggestion has been obtained from the esr of $SO_3F\cdot$ in an $S_2O_6F_2$ matrix at −170° (see Figure 1). The spectrum is a nearly symmetric *doublet* with spacing 9.45 ± 0.1 G, component width *ca.* 3 G, and apparent $g = 2.0117$ (position of the center of the doublet). These results are in good agreement with those obtained previously from the uv photolysis of 15% FSO_3F in CCl_3F at $-132° \geqslant t \geqslant -175°$, namely $|a^F| = 9.5$ G and $g = 2.0132$.[6] Over the temperature range $-130° \geqslant t \geqslant -170°$, we find that $|a^F|$ is independent of temperature, within our experimental uncertainty. It can be safely assumed that at the temperatures of interest in the liquid–solution work the splitting is only about 10 G; therefore no hyperfine structure is resolved.

In order to determine $\Delta H°$, the enthalpy of the homolytic thermal dissociation of the neat liquid dimer, from the esr intensity data for $SO_3F\cdot$ we use the following equation

$$2 \ln h(T)[w(T)]^2T - 2 \ln d_{R_2}(T) = -\frac{\Delta H°}{RT} + \text{constant} \quad (1)$$

where h and w are the peak-to-peak amplitude and width, respectively, of a *single component* of the first-derivative esr spectrum at temperature T°K, and d_{R_2} is the density of the dimer.[14] This relationship has been derived elsewhere[15] and holds provided (1) the dimer is only slightly dissociated, (2) Curie's law applies to the radical, (3) $\Delta H°$ may be assumed constant, and (4) the esr line shape is independent of temperature over the experimental range of interest. Equation 1 is applicable to the $S_2O_6F_2$–$SO_3F\cdot$ system since (1) $[SO_3F\cdot]$ is only *ca.* 1×10^{-3} M at 100°,[12a,16] (2) the esr peak-height data have been collected within a 25° interval ($125° \leq t \leq 150°$) over which $\Delta H°$ may be assumed constant, and (3) an experiment has been performed which indicates that the line shape at 125° is the same as that at 150°.[12a]

We have employed a spectrum-reconstruction scheme to determine the width and height of a single component of the $SO_3F\cdot$ spectrum, w and h, respectively, from measurements on the observed broad line (width and height, W and H). The spectrum is simulated assuming that it consists of two equally intense Lorentzian lines separated by $|a^F| = 9.45$ G. This calculation has been coded for the IBM 7094 computer.[12a] The computed spectral shape is in good agreement with the experimental shape. A table has been constructed[12a] in which are listed values of w (varied from 15 to 55 G in 0.1-G steps) and corresponding values of W, W' (see below), and h/H which are obtained from the simulations. Two examples will illustrate the type of results obtained. If the observed width between points of maximum slope $W = 35$ G then $w = 32.1$ G and $h/H = 0.531$ ($t \approx 125°$); if $W = 40$ G then $w = 37.6$ G and $h/H = 0.523$ ($t \approx 150°$).

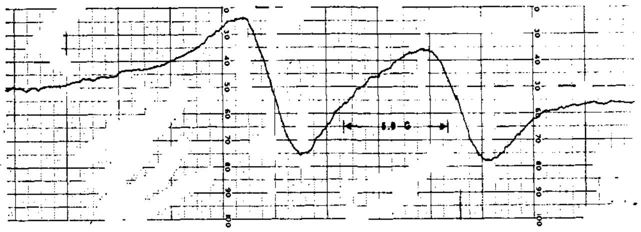


Figure 1. Spectrum of $SO_3F\cdot$ in polycrystalline $S_2O_6F_2$ at −170°.

Since the esr spectrum of $SO_3F\cdot$ is very flat at the field values where W is measured, the estimated uncertainty in this quantity is large, ±2 G. As a check, an alternative reconstruction scheme has also been employed to determine w. A width parameter W' has been measured between the center of the spectrum and a point on the base line which lies outside the derivative extrema and has ordinate $\pm 0.4H$. Corresponding values of w are obtained from W' using the spectrum-simulation program. For example, if $W' = 28.5$ or 32.8 G, then $w = 32.1$ or 37.6 G, respectively.

We have made five sets of measurements of the temperature dependence of the esr intensity between 398 and 423°K. For each set of measurements the component widths and amplitudes have been analyzed in two ways, according to the two procedures described above. The five sets of spectra therefore yielded ten sets of data. For each set of data an unweighted linear least-squares analysis of $\{2 \ln hw^2T - 2 \ln [2.3959 - 2.434 \times 10^{-3}T]\}$ *vs.* T^{-1} has been performed. The values of $\Delta H°$ obtained from each set of data are listed in Table I along with error estimates and the number of measurements of the widths and amplitudes. The average value obtained from the ten sets of data is $\Delta H° = 22.4 \pm 0.9$ kcal/mole.

Table I. Results for the Enthalpy of Cleavage, $\Delta H°$, of Neat Liquid $S_2O_6F_2$

No. of measurements	$\Delta H°$, kcal/mole: w from W	$\Delta H°$, kcal/mole: w from W'
9	22.6 ± 1.5[a]	23.1 ± 1.1
8	21.7 ± 1.9	23.4 ± 2.1
8	21.4 ± 3.3	22.9 ± 3.8
8	20.6 ± 2.2	20.8 ± 2.0
15	23.4 ± 1.3	24.4 ± 0.9

[a] This precision measure is twice the square root of the variance of the linear least-squares slope, multiplied by R.

This result is in approximate agreement with values obtained for the $S_2O_6F_2$–$SO_3F\cdot$ system using other techniques, namely, $\Delta H°(g) = 22.0$ kcal/mole (PVT),[5a] 21.8 kcal/mole (PVT),[5b] and 23.5 kcal/mole (spectrophotometric).[5a] A precise comparison cannot be

---

[14] The density of liquid $S_2O_6F_2$ over the temperature range 308.7–319.0°K is given by $d_{R_2}(T) = 2.3959 - 2.434 \times 10^{-3}T$ (ref 7). The density in the range $125° \leq t \leq 150°$ was estimated by linear extrapolation of this result.

[15] G. Vincow, H. J. Dauben, Jr., F. R. Hunter, and W. V. Volland, *J. Am. Chem. Soc.*, **91**, 2823 (1969).

[16] The concentration of $SO_3F\cdot$ was determined relative to the "strong pitch" esr intensity standard of Varian Associates.

made since the previous work was carried out in the gas phase.[17]

The good concordance (1) verifies the validity of the esr method for determining the enthalpy of homolytic thermal cleavage of neat liquids[15] and (2) confirms that the O–O peroxy bond in $S_2O_6F_2$ is quite weak, having a bond dissociation energy of 22–24 kcal/mole.[18]

Acknowledgments. We wish to thank Professor George H. Cady for suggesting an investigation of this system and for helpful discussions. We also wish to thank Professor D. D. DesMarteau and Professor F. B. Dudley for supplying the $S_2O_6F_2$ used.

---

(17) From (1) our value of ΔH° in the liquid phase, (2)$\Delta H_{\mathrm{vap}}(S_2O_6F_2)$ = 7.6 kcal/mole (67°, ref 7), and (3) a *crude* estimate of $\Delta H_{\mathrm{vap}}(SO_3F\cdot) \approx$ 5 kcal/mole, we compute an approximate value $\Delta H^\circ(g) \approx 25$ kcal/mole, which is in fairly good agreement with the enthalpy changes previously measured.

(18) NOTE ADDED IN PROOF. An esr study of the $S_2O_6F_2$–$SO_3F\cdot$ equilibrium in the gas phase has been reported [R. A. Stewart, S. Fujiwara, and F. Aubke, *J. Chem. Phys.*, **48**, 5524 (1968)]. It is not possible to compare our ΔH° with the results obtained by these workers because they employed an incorrect statement of the van't Hoff equation in their analysis.

Chemistry of Metal Complexes with Polydentate Ligands. Complexes of N-Hydroxyethylethylenediamine

B. Das Sarma and John C. Bailar, Jr.

Contribution from West Virginia State College, Institute, West Virginia, and the W. A. Noyes Laboratory of the University of Illinois, Urbana, Illinois.

Received October 14, 1968

Abstract: It has been found that N-hydroxyethylethylenediamine can act either as a bidentate or a tridentate ligand, coordinating, in the first case, through the amino nitrogens, and in the second case, by the hydroxyl oxygen also. When the hydroxyl group coordinates, the hydrogen atom becomes more acidic, so that, in the presence of a proton acceptor, the ligand becomes a tridentate oxyethylethylenediamine ion. This behavior has been shown to explain the formation of different types of complexes with Co(III), Pt(II), Pd(II), and Ni(II). The nature of these complexes has been studied through their electrical conductivities and their electronic, ir, and nmr spectra. Tentative arguments for the absence of any tris complex and the reason for the apparent inactivity of the noncoordinated hydroxyethyl group have been presented. It has been shown that the uncoordinated hydroxyl group is not inactive and it can be acetylated even under mild conditions.

The formation of a coordinatively saturated complex, Ml_n, where l is a unidentate ligand, statistically involves *n* steps. If the ligand (L) is a polydentate one, with *m* coordination sites sterically available to one metal ion M, the complex formed in presence of excess of ligand is $ML_{n/m}$. Since complex formation or ligand substitution is stepwise even with polydentate ligands, we may expect that polydentate ligands, particularly those with nonequivalent coordinating atoms, will exhibit varying dentate natures. Thus, the normally bidentate ethylenediamine can be monodentate[1] as $NH_2CH_2CH_2NH_3^+$ in the Cr(III) complex $[Cr(NH_2CH_2CH_2NH_3^+)(H_2O)_5]_4^+$, and ethylenediaminetetraacetic acid may coordinate as a bi- to hexadentate ligand.

It may be expected that this variation in the polydonation of a ligand will be especially marked for those ligands that contain donor atoms with quite varying affinities toward the metal ion. Such groups, with N and O as the coordinating elements, may be

$$-\underset{\cdot\cdot}{N}\Big\langle,\ -\underset{\cdot\cdot}{N}{=},\ -\underset{\cdot\cdot}{\ddot{N}}-^{-},\ \equiv N,\ -\underset{\cdot\cdot}{\ddot{O}}-,\ =\ddot{O}{:},\ -\underset{\cdot\cdot}{\ddot{O}}{:},\ \text{etc.}$$

It may further be expected that the most important factors affecting the dentate nature of a polydentate ligand will be pH, solvent, the coordinated groups, the relative metal to ligand concentration, and any factors that may affect the mechanism of ligand substitution.

There has been a number of investigations[2] on the nature of the complexes formed with multidentate ligands containing the N-hydroxyethyl group, particularly on the activity of the noncoordinated hydroxyl group. This paper is concerned with complexes formed with N-hydroxyethylethylenediamine, $NH_2CH_2CH_2NHCH_2CH_2OH$.[3]

It has been found that, depending on the conditions of synthesis and the nature of the coordinated metal, this unsymmetrical and potentially tridentate ligand yields a number of different types of complexes according to the following scheme

$$Ml_n + (x + y + z)\text{etolenH} \longrightarrow \left[\begin{array}{c}(\text{etolenH})_x\\ \text{M}(\text{etolen}H)_y(\text{l})_{n-2x-3y-3z}\\ (\text{etolen})_z\end{array}\right] + z\text{H}^+$$

$$\text{M} = \text{Co(III), Pt(II), Pd(II), Ni(II)}$$

$$\text{l} = H_2O,\ NH_3,\ NO_2^-,\ Cl^-$$

$$x = 0, 1, 2;\ y = 0, 1;\ z = 0, 1, 2$$

---

(1) R. F. Childers, Jr., K. G. Vander Zyl, Jr., D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, 7, 749 (1968).

(2) (a) R. A. Krause and S. D. Goldby, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 143; (b) R. N. Keller and L. J. Edwards, *J. Am. Chem. Soc.*, 74, 215 (1952); (c) W. C. Drinkard, H. F. Bauer, and J. C. Bailar, Jr., *ibid.*, **82**, 2992 (1960); (d) B. Das Sarma, G. J. Tennenhouse, and J. C. Bailar, Jr., *ibid.*, **90**, 1362 (1968).

(3) Henceforth the expression "etolenH" will be used to indicate the ligand coordinated through only the two nitrogen atoms; "etolen*H*" will indicate the ligand coordinated through the oxygen of the OH in addition to the two N's; "etolen" will represent the tridentate deprotonated ligand, attached through the two N's and oxygen of O^-.