Communications to the Editor

A Circular Dichroism Study of the First Excited Electronic State in Propylene Episulfoxide

Sir:

Although the spectra of alkyl and aryl sulfoxides have been subjects of several investigations, the nature of the electronic transitions of the S–O group is still far from being completely understood.[1a,b] In previous papers we have carried out a satisfactory investigation on the excited states of the sulfides using a comparison between experimental and calculated CD spectra of propylene sulfide.[2a,b] We now apply this analysis to the simplest optically active sulfoxide with a fixed geometry: *trans*-propylene episulfoxide.

(+)-(1*S*,2*S*)-Propylene episulfoxide was synthetized starting from (−)-*S*-propylene sulfide, having $[\alpha]_D$ −42.05° (pure liquid, optical purity 82%),[3] using the procedure described for the racemic compound.[4] The episulfoxide obtained had $[\alpha]^{20}_D$ +95.27° (*c* 0.7, cyclohexane). CD spectra were recorded using a Jouan II dichrograph; uv spectra were recorded with a Cary 15 spectrophotometer.

The CD and uv spectra are shown in Figure 2 and the characteristic data are summarized in Table I. The isotropic maxima correspond well to the CD maxima; a typical blue shift is observed for both CD and uv in passing from cyclohexane to ethanol.

SCF and CI computations were performed to obtain approximate wave functions for the ground and the lowest excited states of the molecule. The orbital basis is a minimal basis set but includes 3d and 4s orbitals on sulfur, since the latter orbital was found to be important in interpreting the uv absorption spectra of organic sulfides in the region 2000–2600 Å.[2b] Single, double, and triple excitations from the ground electronic configurations (altogether 700 singlet states) were considered in the interaction expansions of the configurations.

Intensity and rotational strengths were computed next using both the coordinate and the momentum representation of the electric dipole operator.[5] A comparison between the computed and the experimental data indicates that, contrary to what was found in the parent sulfide, the first transition has a prevalent $\sigma \rightarrow \sigma^*$ character. The two molecular orbitals involved are schematically represented in the Figure 3. The occupied molecular orbital is approximately antisymmetric with respect to the plane perpendicular to the C–C bond, and contributes both to the three-center bonding in the ring and to the sulfur-oxygen π bonding, which was found to have essentially a p–d character. The orbital is strongly polarized towards the oxygen atom and keeps in the molecule part of the lone pair character of the p_y orbital of oxygen.

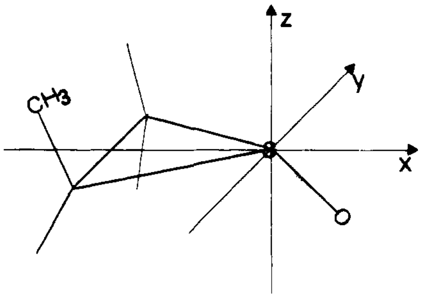

Figure 1. Reference frame for (+)-*S*-propylene episulfoxide.

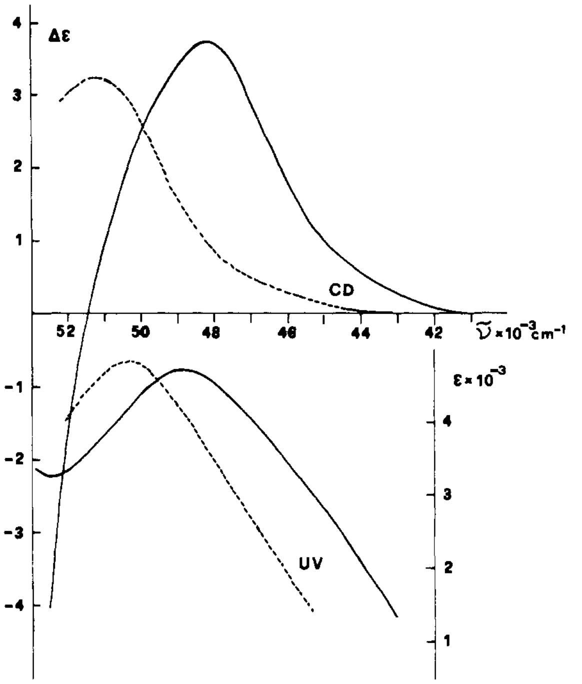

Figure 2. The absorption and the circular dichroism spectra of (+)-*S*-propylene episulfoxide in ethanol (dotted line) and cyclohexane (full line).

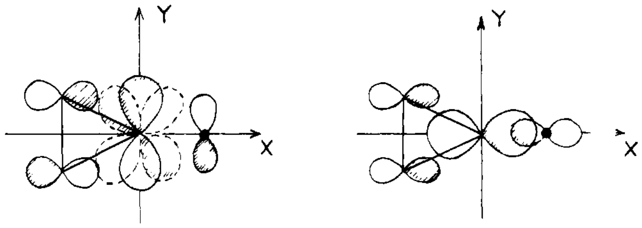

Figure 3. Sketch of the (a) and (b) MO's involved in the first transition of episulfoxide. The oxygen nucleus is marked by a black disk and lies below the plane of the ring.

Table I. Uv and CD Spectral Characteristics of (+)-(1*S*,2*S*)-Propylene Episulfoxide

	Uv			CD		
Solvent	λ_{max}, nm	ϵ_{max}	*f*	λ_{max}	$\Delta\epsilon_{max}$	*R*, cgs
Cylohexane	205	4779	0.08	206	+3.7	$+10 \times 10^{-40}$
Ethanol	198	4842		197	+3.9	$+9.2 \times 10^{-40}$

The σ virtual MO is an antibonding MO of the three-membered ring with symmetry opposite to that of the previous molecular orbital and with a large contribution from the p_x AO on oxygen.

The computed value of the rotational strength in the dipole length representation is 7.4×10^{-40} cgs units, in agreement with the experimental value, and is relatively insensitive to the choice of the origin. In the dipole velocity representation the computed rotational strength agrees in sign but is considerably larger (42×10^{-40}). The magnetic dipole of the transitions has a prevalent one-center component arising from the $p_y p_x$ transition density of the oxygen atom. In this respect, the transition is similar to the n → π^* transition in ketones. The high charge density around the oxygen in the σ molecular orbital also provides an explanation to the solvent shift of the transition (Table I) and to the fact that the protonation site of sulfoxides is at the oxygen atom.[6]

References and Notes

(1) (a) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy", Wiley, New York, N.Y., 1962, p 491; (b) J. N. Murrel "The Theory of the Electronic Spectra of Organic Molecules", Methuen, 1963, p 176.

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(3) T. Taunetsugu, J. Furukawa, and T. Fueno, *J. Polym. Sci.*, **3**, 3529 (1971).

(4) K. Kondo and A. Negishi, *Tetrahedron*, **27**, 4821 (1971).

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(6) G. Gatti, A. Levi, V. Lucchini, G. Modena, and G. Scorrano, *J. Chem. Soc., Chem. Commun.*, 251 (1973).

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Received December 9, 1975

Assignment of a Methylated Sulfur Dioxide Structure, $[CH_3O{=}S{=}O]^+$, to the Species Present in $CH_3F\text{-}SbF_5\text{-}SO_2$ Solutions and Precipitation of a Salt of $[CH_3O{=}S{=}O]^+$ upon Addition of SO_2 to $CH_3F\text{-}SbF_5\text{-}SO_2ClF$

Sir:

The question of the structure of methyl fluoride-antimony fluoride mixtures in SO_2 and other solvents has received detailed study in Olah's group[1] and Gillespie's.[2] We now report that reaction of SO_2 with $CH_3F\text{-}SbF_5$ in SO_2ClF at −78° gives a white, filterable precipitate which is inferred, from experiments to be described, to contain the cation **1**, the product of methylation of sulfur dioxide. The accompanying anion may be SbF_6^- (eq 1) or $Sb_2F_{11}^-$.

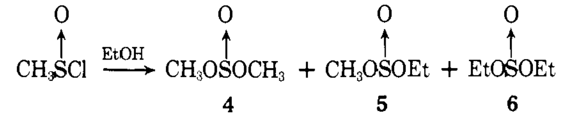
$$\mathrm{CH_3F\text{-}SbF_5 + SO_2 \xrightarrow{SO_2ClF} \underset{\mathbf{1}}{[CH_3O{=}S{=}O]^+} + SbF_6^-} \qquad (1)$$

We further propose that **1** is the principal[2] carbon-containing species present in SO_2 solutions of $CH_3F\text{-}SbF_5$. Presently, various Lewis complex structures, e.g., **2a** or **2b**, have been proposed to accomodate the rather extensive body of data pertaining to this system.[1,2] In **2a** or **2b**, but not in **1**, rapid exchange of carbon–fluorine bonds must be postulated to account for the absence of coupling to ^{19}F in the ^1H and ^{13}C NMR spectrum.

$$\underset{\mathbf{2a}}{\mathrm{CH_3F \longrightarrow SbF_5}} \qquad \underset{\mathbf{2b}}{\mathrm{CH_3F \longrightarrow Sb_2F_{10}}}$$

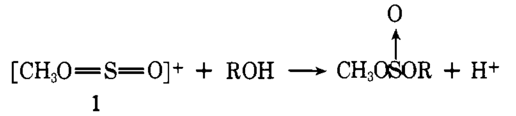
We have found that the solid formed from SbF_5 and CH_3F in SO_2ClF reacts with methanol or ethanol at −65° to give substantial amounts of dimethyl sulfite (**4**) or methyl ethyl sulfite (**5**).[3] Similarly, solutions of $CH_3F\text{-}SbF_5$ in SO_2 (1 M) appear to give sulfite esters in good yields upon reaction with methanol or ethanol. These products suggest that **1** is the reactant present in $CH_3F\text{-}SbF_5\text{-}SO_2$ and in the solid precipitated from SO_2ClF (eq. 1).

Two complicating circumstances must be mentioned. First, sulfite esters proved to undergo facile transesterification in acidic alcohol solutions. Our preparation of the reference sulfite **5** resulted in formation of **4** and **6** also (eq 2).[4,5] Accordingly, it is not surprising that the above mentioned reaction of 1 M $CH_3F\text{-}SbF_5\text{-}SO_2$ with EtOH (3 mol, −65°) gave a mixture of **4** (14%), **5** (41%), and **6** (36%), based on GC analysis of the ethanol solution. Second, SO_2 itself was shown to form some dimethyl sulfite (**4**) upon addition of 1 M SbF_5 in SO_2 to methanol, followed by workup with $H_2O\text{-}CH_2Cl_2$. However, the amount was only 18% of the amount of **4** (101% yield, GC; 82% distilled) formed by addition of 1 M $CH_3F\text{-}SbF_5$ to CH_3OH (3 mol, −65°).



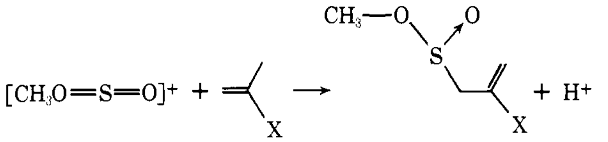
$$\mathrm{CH_3\overset{\overset{O}{\uparrow}}{S}Cl \xrightarrow{EtOH} \underset{\mathbf{4}}{CH_3O\overset{\overset{O}{\uparrow}}{S}OCH_3} + \underset{\mathbf{5}}{CH_3O\overset{\overset{O}{\uparrow}}{S}OEt} + \underset{\mathbf{6}}{EtO\overset{\overset{O}{\uparrow}}{S}OEt}} \qquad (2)$$

Despite the complicating circumstances, the overall results appear to provide strong support for the hypothesis that most of the sulfite esters obtained from $CH_3F\text{-}SbF_5\text{-}SO_2$ arose from the initial reaction of cation **1** according to eq 3. The demonstration[3] that the solid material (eq 1) gives mainly methyl ethyl sulfite upon reaction with ethanol constitutes strong evidence that SO_2 is capable of forming a monomethylated derivative, strengthening the hypothesis that **1** may exist in SO_2 solutions. As expected, the ^1H NMR spectrum of the solid dissolved in SO_2 was identical with that of $CH_3F\text{-}SbF_5$ in SO_2.



$$\mathrm{\underset{\mathbf{1}}{[CH_3O{=}S{=}O]^+} + ROH \longrightarrow CH_3O\overset{\overset{O}{\uparrow}}{S}OR + H^+} \qquad (3)$$

That **1** (instead of **2a** or **2b**) is the *predominant* species present in $CH_3F\text{-}SbF_5\text{-}SO_2$ is indicated by the following argument. If **1** is present only in trace amounts in rapid equilibrium with **2a** or **2b**, the weak nucleophile SO_2 must be alkylated faster by **2a** or **2b** than the much more nucleophilic alcohols, in order to account for the formation of alkyl sulfites upon reaction of $CH_3F\text{-}SbF_5\text{-}SO_2$ with alcohols. A similar situation occurs in the case of the recently reported,[6] high yield "ene" reaction of $CH_3F\text{-}SbF_5\text{-}SO_2$ (eq 4), although in this instance the relative nucleophilicity of SO_2 and alkenes is not obvious.


(4)

Why has structure **2a** or **2b** been accepted while **1** was given only passing consideration? Below we reexamine five principal lines of evidence which provide insight into the situation. The evidence is shown to be compatible with structure **1**.

(1) **Reactions with Alcohols.** Alcohols previously were reported[1b] to give methyl ethers upon reaction with $CH_3F\text{-}SbF_5\text{-}SO_2$. The ethers (which may have been formed under different conditions, e.g., by reaction of moist SO_2 with $CH_3F\text{-}SbF_5$) provided no evidence for the incorporation of SO_2 in the reactant.

(2) **Raman Spectra.** Considerable reliance has been placed