

**Table I.** Kinetic Parameters for the Photochemical Addition of *trans*-Stilbene to Tetramethylethylene

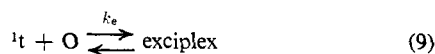
$T, ^\circ\text{C}$	Slope, $M$	$\tau \times 10^{10}$ , sec	$k_3 \times 10^{-9}$ , $M^{-1} \text{sec}^{-1}$
54	8.06	1.33	0.93
44	7.00	1.52	0.94
34	5.88	1.74	0.98
25	4.20	1.98	1.20
5	2.94	2.70	1.33
-5	1.34	3.23	2.52
-10	0.94	3.50	4.47
-22	0.28	4.42	8.10

for a greater range of temperatures than that previously available. The values of  $k_3$  given in Table I ignore any temperature effects on diffusion which would operate in the opposite direction. Inclusion of these effects would enhance the negative temperature dependence of  $k_3$ . If the temperature effect on the lifetime of  $^1\text{S}$  *trans*-stilbene were the only temperature effect on the addition,  $k_3$  should be constant and all olefins should show the same temperature dependence. This is not the case. It is clear that  $k_3$  has a negative temperature dependence. Table II shows  $k_3$  values for the addition

**Table II.** Kinetic Parameters for the Photochemical Addition of *trans*-Stilbene to 1-Methylcyclohexene

$T, ^\circ\text{C}$	Slope, $M$	$\tau \times 10^{10}$ , sec	$k_3 \times 10^9$ , $M^{-1} \text{sec}^{-1}$
56	156	1.29	4.74
43	134	1.54	4.86
34	108	1.74	5.37
25	89.4	1.98	5.67
-21	29.4	4.33	8.14

of *trans*-stilbene to 1-methylcyclohexene.<sup>8</sup> The negative temperature dependence is observed in this case as well. Furthermore, comparison of the ratios of the slopes at the extreme temperatures for tetramethylethylene (28.5) and 1-methylcyclohexene (5.3) shows that the temperature dependence for addition to these two olefins is not the same. Although a quantitative treatment of this temperature dependence indicates that the above mechanism is incomplete (*i.e.*, at least one more activated process must be available to the exciplex), the observed negative temperature dependence of  $k_3$  is consistent with reversible exciplex formation as suggested in ref 1. Expansion of eq 3 to include reversible exciplex formation (eq 9 and 10) gives  $k_3 =$



$k_e[k_a/(k_a + k_{-e})]$ . The expression  $k_e[k_a/(k_a + k_{-e})]$  is the product of the rate constant for exciplex formation and the fraction of exciplex which gives adduct.<sup>1</sup>

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(8) The product of the addition of *trans*-stilbene to 1-methylcyclohexene is 1-methyl-7,8-diphenylbicyclo[4.2.0]octane. The mass spectrum shows the parent ion at  $m/e$  276 and the base peak at  $m/e$  180 (stilbene). The nmr spectrum ( $\text{CCl}_4$ ) shows a singlet at  $\delta$  7.11 (10 H, aromatic protons), a multiplet at 3.2–4.2 (2 H, benzylic protons), a multiplet at 0.80–2.50 (9 H, methylene and methine protons), and a singlet at 0.88 (3 H, methyl protons).

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## Supramolecular Bonding Orbitals from Molecular Antibonding Orbitals. Structure of the Radical Anion of Sulfuryl Chloride<sup>1</sup>

Sir:

Just as atomic orbitals are used to obtain molecular orbitals, so molecular orbitals can be combined to form supramolecular orbitals. Of particular interest here is the combination of two *antibonding* orbitals from separate molecules, which gives rise to a supramolecular *bonding* orbital between the molecules. Application of this proposition suggests that a radical anion may enter into chemical combination with a neutral molecule in a geometrical configuration which permits the antibonding orbitals to have positive overlap.

Molecules with low-lying vacant orbitals frequently undergo electron capture during  $\gamma$  irradiation,<sup>2</sup> and this method has been used to generate  $\text{SO}_2\text{Cl}_2^{\cdot-}$ . We find that the esr spectrum of this species can be most satisfactorily interpreted according to a novel structure in which the unpaired electron resides in a supramolecular bonding orbital derived from a combination of the lowest unoccupied antibonding orbitals of individual  $\text{SO}_2$  and  $\text{Cl}_2$  molecules.

Figure 1 shows the esr spectrum of  $\gamma$ -irradiated polycrystalline  $\text{SO}_2\text{Cl}_2$  at 77°K. Much of the hyperfine structure inside the hydrogen-atom lines is typical of a radical with an axially symmetric hyperfine tensor. The parallel features of this anisotropic (powder) spectrum are clearly attributable to interaction with two equivalent chlorine nuclei and the outermost lines due to the  $^{35}\text{Cl}^{35}\text{Cl}$  and  $^{35}\text{Cl}^{37}\text{Cl}$  species are particularly well resolved. From the positions of these lines we obtain the values  $A_{\parallel}^{35} = 64.1$  G,  $A_{\parallel}^{37} = 53.3$  G, and  $g_{\parallel} = 2.0050$ . The perpendicular features are not readily distinguished, but they must lie inside the  $m_I = -1$  and  $m_I = +1$  parallel components and limits of 0 and 16 G can be set for  $A_{\perp}^{35}$ . This large degree of anisotropy was verified qualitatively by experiments on samples exhibiting preferential orientation. In none of these experiments with aligned samples did the total width of the spectrum exceed that of the polycrystalline spectrum, and at orientations close to the parallel direction, there was a marked collapse in the spectral width on rotation of the sample through an angle of 90°. If  $A_{\parallel}$  and  $A_{\perp}$  are both assumed to be positive, the above values lead to the limits  $a_{\text{iso}} =$

(1) This research was supported by the U. S. Atomic Energy Commission under Contract No. AT-(40-1)-2968; this is AEC Document No. ORO-2968-60.

(2) D. J. Whelan, *Chem. Rev.*, **69**, 179 (1969).

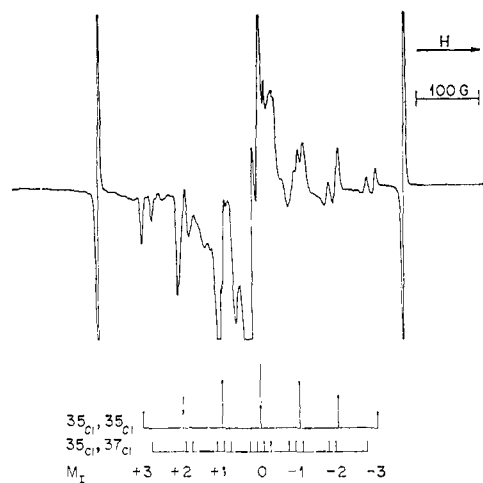


Figure 1. ESR spectrum of  $\gamma$ -irradiated polycrystalline sulfuryl chloride at 77°K. Irradiation dose, 3 Mrads.

21.3 G,  $2B = 42.6$  G and  $a_{\text{iso}} = 32$  G,  $2B = 32$  G for the hfs parameters of the  $^{35}\text{Cl}^{35}\text{Cl}$  species.

It is difficult to reconcile this large chlorine anisotropy with the structures which have been proposed for other 33-valence-electron radicals<sup>3</sup> such as  $\text{PF}_4^+$ ,<sup>4</sup>  $\text{SF}_4^+$ ,<sup>4c</sup> and  $\text{PCl}_4^+$ ,<sup>5</sup> where the unpaired electron resides almost entirely on the central atom.<sup>6</sup> An estimate of the chlorine anisotropy to be expected in this latter case is furnished by the results for  $\text{PCl}_2^+$ <sup>5</sup> and  $\alpha$ -substituted aliphatic radicals,<sup>7</sup> where the principal values and direction cosines of the chlorine hyperfine tensor indicate that the anisotropy arises mainly from positive spin density in a chlorine p orbital with a  $2B$  value of 10 G or less. Clearly, then, the lower limit of  $2B = 32$  G found for  $\text{SO}_2\text{Cl}_2^{\cdot-}$  is incompatible with any model in which the bulk of the spin density remains on the central atom. Further, since unit spin density in the p orbital on chlorine corresponds to a  $2B$  value of ca. 100 G,<sup>8</sup> we can immediately state that more than half the spin density is associated with the chlorines.

There is a striking resemblance between the spectra of  $\text{SO}_2\text{Cl}_2^{\cdot-}$  and  $\text{Cl}_2^{\cdot-}$ <sup>8</sup> except for the obvious disparity in the hyperfine couplings. The value of  $A_{\parallel}$ <sup>8b</sup> has been measured for  $\text{Cl}_2^{\cdot-}$  in a wide variety of matrices and lies in the narrow range 98–102 G,<sup>8–10</sup> so the observed radical cannot be  $\text{Cl}_2^{\cdot-}$ . However, the sim-

(3) P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier, Amsterdam, 1967.

(4) (a) J. R. Morton, *Can. J. Phys.*, **41**, 706 (1963); (b) P. W. Atkins and M. C. R. Symons, *J. Chem. Soc.*, 4363 (1964); (c) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **45**, 1845 (1966); (d) J. Higuchi, *ibid.*, **50**, 1001 (1969); (e) W. Nelson, G. Jackel, and W. Gordy, *ibid.*, **52**, 4572 (1970).

(5) G. F. Kokoszka and F. E. Brinckman, *J. Amer. Chem. Soc.*, **92**, 1199 (1970).

(6) Recent work by the present authors has shown that the structure of  $\text{POCl}_2^{\cdot-}$  is also quite similar to these other radicals, being most easily described as a distorted trigonal bipyramid with the unpaired electron in an  $sp^2$  equatorial orbital. From the magnitude of the phosphorus isotropic hfs ( $a_P = 1370$  G), this orbital is deduced to have ca. 37% s character on the phosphorus atom, which agrees well with the values found for  $\text{PF}_4^+$  and  $\text{PCl}_4^+$ .<sup>5</sup>

(7) (a) D. Pooley and D. H. Whiffen, *Spectrochim. Acta*, **18**, 291 (1962); (b) M. Kashiwagi, *Bull. Chem. Soc. Jap.*, **39**, 2051 (1966).

(8) J. E. Bennett, B. Mile, and B. Ward, *J. Chem. Phys.*, **49**, 5556 (1968).

(9) T. G. Castner and W. Känzig, *J. Phys. Chem. Solids*, **3**, 178 (1957).

(10) (a) D. Schoemaker, *Phys. Rev.*, **149**, 693 (1966); (b) M. C. R. Symons, *Advan. Chem. Ser.*, No. **88**, 1 (1968).

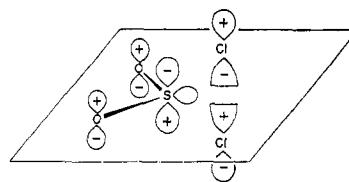


Figure 2. Supramolecular bonding orbital representation of  $\text{SO}_2\text{Cl}_2^{\cdot-}$ .

ilarity suggests that  $\text{Cl}_2^{\cdot-}$  is a contributing structure and since  $\text{SO}_2^{\cdot-}$  is known to be a  $\pi$  radical,<sup>11</sup> the  $\text{SO}_2\text{Cl}_2^{\cdot-}$  radical can be regarded as a resonance hybrid of  $\text{SO}_2$ ,  $\text{Cl}_2^{\cdot-}$  and  $\text{SO}_2^{\cdot-}, \text{Cl}_2$ . The equivalent molecular orbital description is illustrated in Figure 2, and the essential feature here is that the overlap between the lowest unoccupied orbitals which are antibonding in the individual  $\text{SO}_2$  and  $\text{Cl}_2$  molecules can provide bonding between the sulfur and the two chlorine atoms. In other words, the in-phase combination of the  $2b_1$  antibonding  $\pi$  orbital of  $\text{SO}_2$  with the  $3p\sigma_u$  antibonding orbital of  $\text{Cl}_2$  can be considered as a supramolecular pseudo- $\pi$  bonding orbital. From the value<sup>9,10</sup> of 61.2 G for  $2B(\text{Cl}_2^{\cdot-})$  we can estimate the extent to which the spin density is localized on the chlorines. This is given by the ratio  $2B(\text{SO}_2\text{Cl}_2^{\cdot-})/2B(\text{Cl}_2^{\cdot-})$ , which lies between 0.52 and 0.70. Unfortunately, the experimental sensitivity was much too low for us to determine the spin density on sulfur from the natural abundance of  $^{33}\text{S}$ .

The formation of  $\text{SO}_2\text{Cl}_2^{\cdot-}$  with the proposed structure by the addition of an electron to  $\text{SO}_2\text{Cl}_2$  implies a drastic rearrangement in the molecular structure. However, the  $C_{2v}$  symmetry of the parent molecule<sup>12</sup> is retained, and the OSO angle should not be greatly altered because the angles in  $\text{SO}_2\text{Cl}_2$ ,<sup>12</sup>  $\text{SO}_2$ ,<sup>12</sup> and  $\text{SO}_2^{\cdot-}$ <sup>11</sup> are all close to 120°. The parameters which will differ from those of the parent molecule are the Cl-Cl distance, which might be expected to decrease with increased bonding between the chlorines, and the S-Cl distance, which should increase as the interaction between the  $\text{SO}_2$  and  $\text{Cl}_2$  moieties decreases. Extended Hückel calculations using a modified version of the program developed by Hoffmann<sup>13</sup> are in general accord with the ideas presented here. Thus, neither the trigonal-bipyramid structure nor structures with geometries closely related to the  $\text{SO}_2\text{Cl}_2$  molecule ( $\text{S-Cl} = 0.20$  nm,  $\text{Cl-Cl} = 0.33$  nm) are predicted to have unpaired electron distributions corresponding to that observed by esr. On the other hand, calculations for S-Cl and Cl-Cl distances of 0.27–0.31 nm and 0.22–0.24 nm, respectively, give a spin density on chlorine approximating the experimental value and verify that the atomic orbitals which make the main contribution to the orbital containing the unpaired electron are indeed those shown in Figure 2.

Although the proposed structure may appear unusual at first glance, recent work in this laboratory has established that a dimer radical anion conveniently formulated as  $e^-(\text{CH}_3\text{CN})_2$  is produced in  $\gamma$ -irradiated

(11) A. Reuveni, Z. Luz, and B. L. Silver, *J. Chem. Phys.*, **53**, 4619 (1970).

(12) D. E. Martz and R. T. Lagemann, *ibid.*, **22**, 1193 (1954).

(13) (a) R. Hoffmann, *ibid.*, **39**, 1397 (1963); (b) P. C. Van Der Voorn and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 3255 (1966).

