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

<i>T</i> , °C	Slope, M	$ au imes 10^{10}$, sec	$k_3 imes 10^{-9}, \ M^{-1} \ { m sec}^{-1}$
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 ¹S transstilbene 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

<i>T</i> , ℃	Slope, M	$ au imes 10^{10}$, sec	$k_3 imes 10^9, \ M^{-1} \mathrm{sec}^{-1}$
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.⁸ 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 $k_3 =$

$$^{1}t + O \stackrel{k_{e}}{\longleftarrow} exciplex$$
 (9)

exciplex
$$\xrightarrow{h_{a}}$$
 adduct (10)

 $k_{\rm e}[k_{\rm a}/(k_{\rm a} + k_{\rm -e})]$. The expression $k_{\rm e}[k_{\rm a}/(k_{\rm a} + k_{\rm -e})]$ is the product of the rate constant for exciplex formation and the fraction of exciplex which gives adduct.¹

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Supramolecular Bonding Orbitals from Molecular Antibonding Orbitals. Structure of the Radical Anion of Sulfuryl Chloride¹

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 γ irradiation,² and this method has been used to generate SO₂Cl₂.-. 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 SO₂ and Cl₂ molecules.

Figure 1 shows the esr spectrum of γ -irradiated polycrystalline SO₂Cl₂ 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 ³⁵Cl³⁵Cl and ³⁵Cl³⁷Cl species are particularly well resolved. From the positions of these lines we obtain the values $A_{11}^{35} = 64.1$ G, $A_{11}^{37} = 53.3$ G, and $g_{11} = 64.1$ 2.0050. The perpendicular features are not readily distinguished, but they must lie inside the $m_{\rm I} = -1$ 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 $a_{iso} =$

⁽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 (CCl₄) shows a singlet at δ 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).

⁽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 γ -irradiated polycrystalline sulfuryl chloride at 77°K. Irradiation dose, 3 Mrads.

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

It is difficult to reconcile this large chlorine anisotropy with the structures which have been proposed for other 33-valence-electron radicals³ such as PF_4 ,⁴ SF_4 , +, 4^c and PCl_4 , 5^s where the unpaired electron resides almost entirely on the central atom.⁶ An estimate of the chlorine anisotropy to be expected in this latter case is furnished by the results for $PCl_2 \cdot 5$ and α -substituted aliphatic radicals,⁷ 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 2Bvalue of 10 G or less. Clearly, then, the lower limit of 2B = 32 G found for SO₂Cl₂. - 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 2Bvalue of ca. 100 G,³ 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 SO_2Cl_2 - and Cl_2 - ⁸ except for the obvious disparity in the hyperfine couplings. The value of A_{\parallel}^{35} has been measured for Cl_2 . – in a wide variety of matrices and lies in the narrow range 98-102 G,8-10 so the observed radical cannot be Cl2.-. However, the sim-

(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 $SO_2Cl_2 \cdot \overline{}$.

ilarity suggests that $Cl_2 \cdot \overline{}$ is a contributing structure and since SO₂ · - is known to be a π radical, ¹¹ the SO₂Cl₂ · radical can be regarded as a resonance hybrid of SO_2 , $Cl_2 \cdot - and SO_2 \cdot -, Cl_2$. 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 SO_2 and 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 π orbital of SO₂ with the $3p\sigma_{u}$ antibonding orbital of Cl_2 can be considered as a supramolecular pseudo- π bonding orbital. From the value^{9,10} of 61.2 G for $2B(Cl_2, -)$ we can estimate the extent to which the spin density is localized on the chlorines. This is given by the ratio $2B(SO_2Cl_2 \cdot -)/2B(Cl_2 \cdot -)$, 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 ³³S.

The formation of SO_2Cl_2 · – with the proposed structure by the addition of an electron to SO_2Cl_2 implies a drastic rearrangement in the molecular structure. However, the $C_{2\nu}$ symmetry of the parent molecule¹² is retained, and the OSO angle should not be greatly altered because the angles in SO₂Cl₂,¹² SO₂,¹² and $SO_2 - 11$ 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 SO₂ and Cl₂ moieties decreases. Extended Hückel calculations using a modified version of the program developed by Hoffmann¹³ are in general accord with the ideas presented here. Thus, neither the trigonal-bipyramid structure nor structures with geometries closely related to the SO₂Cl₂ molecule (S-Cl = 0.20 nm, 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 $e^{-}(CH_3CN)_2$ is produced in γ -irradiated

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

⁽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 POCl3. - is also quite similar to these other radicals, being most easily described as a distorted trigonal bipyramid with the unpaired electron in an sp² equatorial orbital. From the magnitude of the phosphorus isotropic hfs ($a_{\rm P} = 1370$ G), this orbital is deduced to have ca. 37% s character on the phosphorus atom, which agrees well with the values found for PF4.4 and PCl4.5

^{(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

⁽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).

acetonitrile crystal I.¹⁴ Detailed esr results¹⁵ for this electron-excess center in CD₃CN single crystals are consistent with a structure in which the unpaired electron occupies a supramolecular σ -bonding orbital. This is derived by addition of the separate molecular antibonding π orbitals which overlap with their axes in the plane of the two antiparallel molecules.

Finally, we recall that the symmetry properties of what are essentially supramolecular orbitals have been used extensively in the formulation of the Woodward– Hoffmann rules for concerted chemical reactions.¹⁶ This communication indicates that the esr method can provide definitive structural information about such orbitals in suitable systems.

Acknowledgment. We wish to acknowledge a useful discussion with Dr. Ralph G. Pearson on the structure of the acetonitrile dimer radical anion. We also thank Dr. J. E. Bloor for the use of the computer program and advising us on the calculations.

(14) (a) M. A. Bonin, K. Tsuji, and F. Williams, *Nature (London)*,
218, 946 (1968); (b) K. Takeda and F. Williams, *Mol. Phys.*, 17, 677 (1969); (c) R. J. Egland and M. C. R. Symons, *J. Chem. Soc. A*, 1326 (1970).

(15) K. Takeda and F. Williams, Abstracts, Second Symposium on Electron Spin Resonance (Division of Physical Chemistry of the American Chemical Society), Athens, Ga., Dec 1970, No. F4.

(16) R. B. Woodward and R. Hoffmann, Angew. Chem., Int. Ed. Engl., 8, 781 (1969).

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The Nature of the Intermediate Procreated in Substitution Reactions of Group VI Metal Carbonyls

Sir:

The possibility that a five-coordinated intermediate, [Mo(CO)₅], is generated by the decomposition of Mo-(CO)₅-amine complexes in the presence of Lewis bases (L) to form substituted Mo(CO)₅L species (L = phosphines and arsines) has been discussed elsewhere.¹ A similar process is reported for the tungsten analogs.²



This reaction can also occur via an SN2 process; however, the second-order process is easily suppressed by employing low concentrations of the Lewis base.

The nature of the intermediate in these reactions is of particular interest, since it is this same intermediate which is believed to be present in both the photochemical³ and thermal⁴ substitution reactions of the group VI hexacarbonyls. This communication describes some experiments which lead to a differentiation between two of the commonly considered possible forms suggested for $[Mo(CO)_5]$ in solution, namely, the trigonal bipyramid and the square pyramid.



Figure 1. Infrared spectra of 13 CO-enriched Mo(CO)₅NHC₅H₁₀ in hexane solution. Peaks a, e, and f are for the all- 12 CO species; peaks b, d, and g are for the 13 CO_{eq} species; peak i is for the 13 CO_{ax} species; and peaks c and h are for the di- 13 CO_{eq} species.⁶

A method for discriminating between these two possibilities arises from the ability to preferentially substitute ¹³CO for equatorial carbonyl groups over axial carbonyl groups in $Mo(CO)_5NHC_5H_{10}$. This is accomplished using ultraviolet irradiation in tetrahydrofuran solution. Mo(CO)₅NHC₅H₁₀ was irradiated in solution in a quartz vessel at 25° for 1.7 hr using a Hanovia 550-W lamp in the presence of excess ¹³CO. The THF was removed under vacuum conditions at room temperature and the ¹³CO-enriched product was extracted in hexane solution. The infrared spectrum in the CO stretching region showed an abundance of ¹³CO in the equatorial position (Figure 1). There was $40.5 \pm 0.5\%$ enrichment of the equatorial position with a single ¹³CO group (peak b) and 3.7 ± 0.2% enrichment of the axial position (peak i).⁵ Since statistically the equatorial position should be populated more than the axial position by a factor of 4, the enhancement in equatorial enrichment is approximately 2.8 times as great as the axial enrichment.

If the labeled $Mo(CO)_4({}^{13}CO)NHC_5H_{10}$ species reacts to produce a five-coordinate intermediate, then the nature of the intermediate can be deduced from the distribution of the ${}^{13}CO$ in the product $Mo(CO)_5L$. Clearly, if *in the transition state and in the intermediate* the axial and equatorial CO groups maintain their integrity, the distribution of ${}^{13}CO$ in the product Mo- $(CO)_5L$ will be the same as that in the starting material $Mo(CO)_5NHC_5H_{10}$.

⁽¹⁾ D. J. Darensbourg and T. L. Brown, Inorg. Chem., 7, 1679 (1968).

⁽²⁾ C. M. Ingemanson and R. J. Angelici, *ibid.*, 7, 2646 (1968).

^{(3) (}a) W. Strohmeier, Angew. Chem., 76, 873 (1964); (b) W. Strohmeier and K. Gerlach, Chem. Ber., 94, 398 (1961).

^{(4) (}a) H. Werner, J. Organometal. Chem., 5, 100 (1966); (b) R. J. Angelici and J. R. Graham, J. Amer. Chem. Soc., 88, 3658 (1966).

⁽⁵⁾ The percentages of ${}^{13}\text{CO}_{eq}$ and ${}^{13}\text{CO}_{ax}$ were determined from the relative band areas in the corresponding ${}^{13}\text{CO}$ and ${}^{12}\text{CO}$ species, *e.g.*, bands a and b (Figure 1) for the equatorial abundance and bands f and i for the axial abundance. This procedure is approximately correct, since the ratios of these bands in the parent natural-abundance ${}^{13}\text{CO}$ species for both the amine and arsine complexes are very close to the ratio expected for the presence of 1% ${}^{13}\text{CO}$. In addition, the coupling of axial and equatorial modes, as indicated by the L_{ij} matrix elements, in both the amine-and arsine-carbonyl complexes is roughly the same. Imbedded in this method also is the assumption that the intensities for a ${}^{12}\text{CO}$ or ${}^{16}\text{CO}$ group are the same. This is in agreement with experimental results [see, *e.g.*, G. Bor and G. Jung, *Inorg. Chim. Acta*, 3, 69 (1969)]. Spectra were recorded employing a linear absorbance

⁽⁶⁾ Frequencies were calculated with an iterative computer program using an energy-factored block matrix for the carbonyl stretching vibrations as described elsewhere [see, *e.g.*, D. J. Darensbourg, *ibid.*, 4, 597 (1970)]. Agreements between calculated and observed frequencies were generally within ± 0.5 cm⁻¹.