Thus, the dissociation constant of 3,5-dinitrobenzoic acid in acetonitrile is found to be $10^{-15.1}$ as compared to $10^{-2.82}$ in water,[11] a difference of 12.3 pK units. The value of p$(K_dK_f)_{AN}$ − (p$K^f_{BH^+})_W$ is 1.2 units greater for aniline and diethylaniline than for the substituted

pyridines, indicating that $K^f_{BH^+}$ for the former two bases in only $10^{3.8}$ instead of 10^5 times greater in AN than in water. This result is in excellent agreement with that of Coetzee and Padmanabhan,[10] obtained by potentiometric measurements with the glass electrode, who found $K^f_{BH^+}$ for aniline $10^{3.8}$ times greater in AN than in water.

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d-Orbital Participation in Silane Conjugation

Lionel Goodman, Aaron H. Konstam, and Leo H. Sommer

A substituent interference experiment on the intensity of the ^1L_b bands in phenylsilanes demonstrates that the SiH$_3$ group actually does withdraw electrons from the benzene ring into Si 3d-orbitals. Such an experiment has general applicability for ascertaining participation of d-orbitals in a conjugation scheme.

Introduction

Although 3d-orbital participation is frequently advanced as the explanation for some of the differences in the properties of organosilicon as compared to organic compounds, definitive evidence for such participation has been lacking. Reviews of the possible effects of postulated availability of the 3d-orbitals of silicon are available.[1,2]

In this paper a spectroscopic experiment is reported which should show quite definitely whether or not a group utilizes dπ-orbitals in interacting with a benzene ring. The experiment is applied to phenylsilanes; the results clearly require the silicon 3d-orbitals to strongly interact with the π-orbitals of the phenyl ring.

When a silicon atom is attached to a phenyl ring, two effects become apparent. The silicon, being more electropositive than carbon, has an inductive effect of releasing electrons into the ring (+I effect).[3] Resonance interaction between the silicon and the ring, however, either releases or withdraws π-electrons. Some of the principal resonance structures expected for phenyltrimethylsilane based on the postulated availability of the 3d-orbitals are shown below.

Contributions from structure III, which represents a type of hyperconjugation previously postulated for alkylbenzenes,[5] tend to reinforce the inductive effect of

the silicon represented by structure II. Contributions from structures IV and V oppose the inductive and hyperconjugative effects by withdrawing electrons from the ring into the d-orbitals of the silicon (−T effect). Much of the work of previous investigators in this field has been devoted to determining the relative magnitudes of these opposing effects. In this paper some attention is also given to this problem.

Previous investigations have used dipole moment measurements,[6,7a] reaction kinetics,[7] and nuclear magnetic resonance spectroscopy[8] to determine these magnitudes. Taken individually, these results are inconclusive and, in some cases, contradict the results of other investigations. However, when all the results are examined as a whole, a definite trend emerges. The greater portion of the evidence points to the silicon having a small +I effect and a slightly larger −T effect.

d-Orbital Perturbation of the Benzene Analog $^1A \rightarrow {}^1L_b$ Transition

For substituted benzenes of C_{2v} or higher symmetry, the probability of the 2600-Å. benzene analog transition ($^1A \rightarrow {}^1L_b$) is related to the electronic distributions (in both ground and excited states) of the ring alone.[9,10] The unique feature of this transition is that it is forbidden in benzene itself, but, upon either C_{2v} monosubstitution or *para* disubstitution, the transition becomes allowed with the transition moment perpen-

(1) C. Eaborn, "Organosilicon Compounds," Academic Press, Inc., New York, N. Y., 1960, pp. 94–113.

(2) F. G. A. Stone and D. Seyferth, *J. Inorg. Nucl. Chem.*, **1**, 112 (1955).

(3) Clark, Murrell, and Tedder[4] in distinguishing between inductive effects on π- and σ-electrons in halobenzenes have pointed out that if there is sufficient repulsion between a lone pair on the substituent group and the π-distribution, then it is possible to have −$I\Sigma$ and +$I\pi$. In −SiH$_3$, however, the absence of a lone pair makes it highly likely that $I\pi$ is quite small and parallel to $I\Sigma$.

(4) D. T. Clark, J. N. Murrell, and J. M. Tedder, *J. Chem. Soc.*, 1250 (1963).

(5) (a) R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941); (b) E. B. Berliner and F. J. Bonhus, *ibid.*, **68**, 2355 (1946); **70**, 854 (1948).

(6) (a) C. Curran, R. Witucki, and P. McCusker, *ibid.*, **72**, 4471 (1950); (b) H. Soffer and T. DeVries, *ibid.*, **73**, 5817 (1951); (c) A. Freiser, M. V. Eagle, and J. Speier, *ibid.*, **75**, 2821 (1953).

(7) (a) J. D. Roberts, E. A. McElhill, and R. Armstrong, *ibid.*, **71**, 2923 (1949); (b) J. D. Roberts and C. M. Regan, *ibid.*, **75**, 4101 (1953); (c) J. Speier, *ibid.*, **75**, 2930 (1953); (d) R. A. Benkeser and P. E. Brumfield, *ibid.*, **73**, 4770 (1951); (e) C. Eaborn, *J. Chem. Soc.*, 4858 (1956); C. Eaborn and D. E. Webster, *ibid.*, 4449 (1957).

(8) R. W. Taft, *et al., J. Am. Chem. Soc.*, **81**, 5352 (1959); R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960).

(9) A. L. Sklar, *J. Chem. Phys.*, **10**, 135 (1942); *Rev. Mod. Phys.*, **14**, 232 (1942).

(10) L. Goodman, I. G. Ross, and H. Shull, *J. Chem. Phys.*, **26**, 474 (1957).

dicularly polarized to the substituent-ring axis.[9,11] This feature is important in what follows; because of it, one need only deal with electronic distortions in the ring and not those on the substituent. Hence, structures of types II and IV cannot contribute to the intensity but those of types III and V may do so.
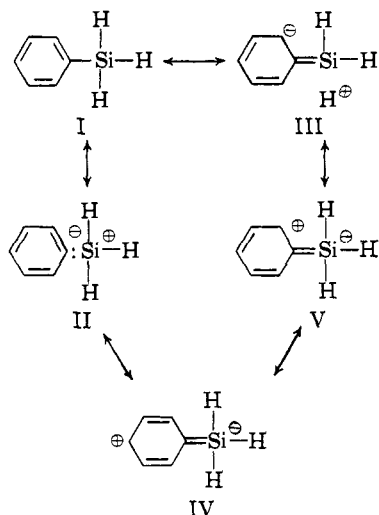
The intensification of this band has been shown to arise principally from two sources[10,12]: (1) borrowing from the well-known N → V band at 1850 Å., and (2) contributions of structures like III and V to a migration moment. The first effect is the more important, provided the perturbation is not too strong. A third source, vibronic intensification, will not play a significant role in the experiment which will be described here (vide infra).

The transition moment for A → L_b, M_{L_b}, is readily expressed in terms of the transition moment for A → B_b, M_{B_b}, the component of appropriate symmetry of the N → V transition at 1850 Å. in benzene, and in terms of the migration moment for the B_{2u} state, $M_{B_{2u}}$

$$M_{L_b} = \cos \Lambda \, M_{B_{2u}} + \sin \Lambda \, M_{B_b} \qquad (1)$$

The second term on the right in eq. 1 represents source 1; the first term, the less important source 2. The ratio of the magnitudes of the two component moments $M_{B_b}/M_{B_{2u}}$ is greater than 10^2 for not too strongly conjugating substituents (i.e., NH_2 would not fulfill this condition, but CH_3 or Cl would). The quantity Λ is determined by the degree of mixing of the benzene B_{2u} and E_{1u} analog wave functions caused by the substituent perturbation.[8] The larger the value of sin Λ, the greater the degree of N → V character in A → L_b, and hence the greater the intensity and conversely. To a first-order approximation[13]

$$\sin \Lambda = \langle \psi_{B_{2u}} |H| \psi_{E_{1u}} \rangle/(E_{B_{2u}} - E_{E_{1u}}) \qquad (2)$$

The matrix element in eq. 2 reduces to the difference in energy between the configurations entering into the

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(12) J. N. Murrell, "The Theory Of The Electronic Spectra of Organic Molecules," Methuen, London, 1963, Chapters 9 and 10.
(13) L. Goodman and H. Shull, J. Chem. Phys., 27, 1388 (1957).

symmetry-determined benzene B_{2u} and $(B_b)E_{1u}$ wave functions

$$\langle \psi_{B_{2u}} |H| \psi_{E_{1u}} \rangle = (E_{\bar{1}2} - E_{1\bar{2}})/2 \qquad (3)$$

Here E_{ij} refers to the energy of the configuration generated by the promotion $i \to j$. The numbering is energy ordered, and j refers to an orbital nodal through the substituent ring axis, and hence unperturbed by C_{2v} substitution.

Now consider the effect of a single substituent containing a d-orbital sufficiently low lying to interact with the benzene π_1- and π_2-orbitals. This situation is illustrated in the orbital perturbation diagram given in Figure 1b, and it requires sin $\Lambda < 0$. The important point is that π_2 is depressed more than π_1. In Figure 1a the effect of a low-lying valence orbital or hyperconjugative group orbital is illustrated. This case requires sin $\Lambda > 0$. Figure 1b must apply directly to the Si 3d-orbital. If, for example, it were lower than the π_2-orbital, a new band should appear in the spectrum of phenylsilane; this is not observed (vide infra). Figure 1a applies to H_3 hyperconjugative orbitals and to the valence pπ-orbitals in O, N, Cl, etc.
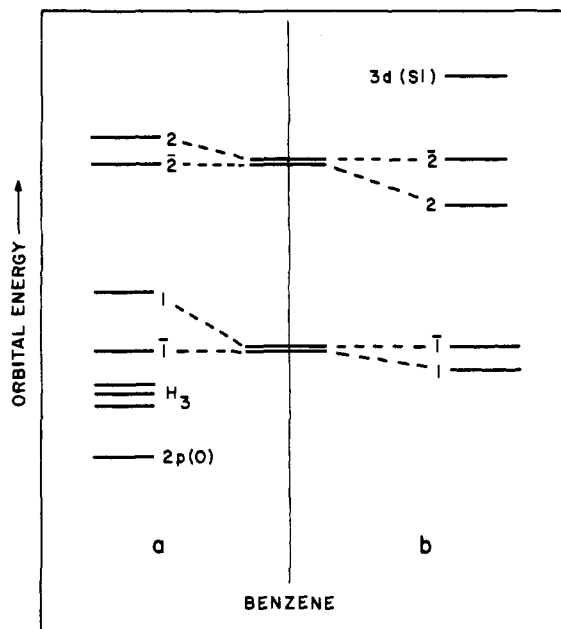

Figure 1. Substituent perturbations on the π-orbitals entering the ^1L_b state of benzene: (a) showing the effect of H_3 hyperconjugation or O 2p-conjugation; (b) showing the effect of Si 3d-conjugation. Orbitals $\bar{1}$ and $\bar{2}$ are nodal, hence are unaffected by a conjugating substituent.

The important conclusion obtained from the analysis of Figure 1 is that a difference in phase is predicted for the benzene A → L_b transition moment induced by substitution, depending on whether the primary cause of conjugation is through d-orbitals satisfying the requirements in Figure 1b, or through either H_3 hyperconjugation or typical low-lying pπ-conjugation. If both effects are present, the *stronger interaction* will determine the over-all phase of **M**. Since the dipole strength D is determined by the square of the

transition moment, no fundamental information can be obtained from the intensity of the transition in phenylsilane itself, $D_{L_b} \approx \frac{1}{2} \sin^2 \Lambda\, D_{E_{1u}}$. Extension of eq. 2 to disubstituted benzenes in terms of the $E_{1u} - B_{2u}$ matrix elements for each group alone (R and S) yields $\sin \Lambda = \sin (\Lambda_R + \Lambda_S)$. For *para* disubstitution the resulting intensification in terms of the dipole strength resulting from each group alone (D_R and D_S) is then

$$D = D_R + D_S + \sin \Lambda_R \sin \Lambda_S\, D_{E_{1u}} \qquad (4)$$

We focus attention on the interference term $\sin \Lambda_R \sin \Lambda_S\, D_{E_{1u}}$ in eq. 4. If both $\sin \Lambda$'s are in phase, the interference is constructive and the resulting intensification will be greater than for either group alone. For the out-of-phase case the resulting destructive interference requires a decrease in intensity from that of the single group causing the most intensification. Hence, the intensity of a *para*-substituted phenylsilane, with a substituent of known phase, clearly uniquely determines the sense of the SiH_3 $E_{1u} - B_{2u}$ mixing term and thus the mode of SiH_3 conjugation with the ring.
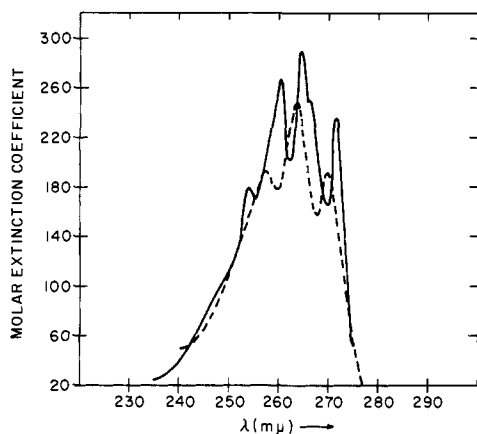

Figure 2. Spectra of phenylsilane, ——, and *p*-methylphenylsilane, -------- (solvent, cyclohexane).

It is convenient to consider this argument in another way. Sklar,[9] Forster,[14] and Platt[15] have shown that in disubstituted benzenes the transition moment arising from the two different groups can be expressed in terms of the transition moments ("spectroscopic moments") arising from each of the groups. Platt[15] has discussed the validity of this relationship for a large number of substituents. In effect, the above analysis shows that the phase of the spectroscopic moment of a group conjugating through its d-orbitals with the conditions imposed by Figure 1b will be that of a normal electron-withdrawing group (such as CN) and opposite to that of an electron-donating group. However, the sign of the postulated interference effect is not dependent upon assumptions inherent in spectroscopic moment theory and hence remains a valid criterion of d-orbital interaction even when spectroscopic moment additivity rules fail.

Spectra of Phenylsilanes

The silane group (SiH_3) was chosen as the silicon-containing substituent necessary to perform a substituent interference experiment involving the intensity of the L_b band. In silane the silicon 3p-orbitals are effectively removed from the conjugation scheme, and complicating inductive effects are also minimized. Near-ultraviolet spectra of phenylsilane, *p*-methoxyphenylsilane, and *p*-methylphenylsilane were determined. Both methoxy and methyl provide examples of substituent groups fulfilling the condition that sin $\Lambda > 0$,[16] and hence, if the silicon actually does interact strongly with the ring π-system through its 3d-orbitals, a phase difference will exist in the spectroscopic moments in the *para*-substituted compounds, so that the interference term in eq. 4 will destructively depress the intensity. The methoxy group was chosen because its large spectroscopic moment provides a sizeable interference term, and because the perturbed 2600-Å. band still retains the required benzene-like character,[14] so that the analysis in terms of eq. 1 and 2 remains valid. Vibronic effects are expected to play an unimportant role in anisole spectra because of the considerable allowedness of the L_b transition as evidenced by the prominant 0–0 band.[17] Methyl was included though it does not have the above advantages attributed to methoxy, because it provides an example of a small perturbation and thus acts as a "probe." The spectra obtained are shown in Figures 2 and 3.
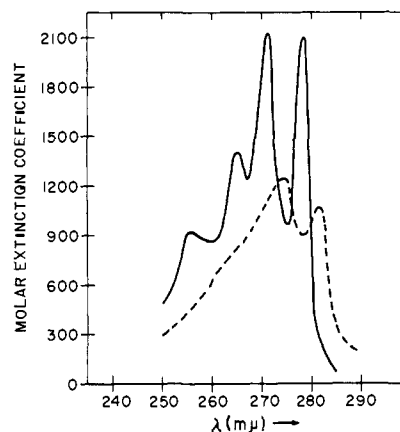

Figure 3. Spectra of anisole, ——, and *p*-methoxyphenylsilane, -------- (solvent, cyclohexane).

The intensity of the band (as measured by ϵ_s and f) shows a sizable decrease in going from anisole to *p*-methoxyphenylsilane (compare the *increase* in going to *p*-methoxytoluene). Hence, the interference term in eq. 4 is clearly destructive, and, consequently, of the various ways in which the SiH_3 group can affect the ring, d-orbital conjugation predominates. The smaller decrease in intensity in going from phenylsilane to *p*-methylphenylsilane is consistent with the above. It has already been observed that silicon is inductively

(14) T. Forster, Z. *Naturforsch.*, **2a**, 149 (1949).
(15) J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951).

(16) (a) J. R. Hoyland and L. Goodman, *J. Phys. Chem.*, **64**, 1816 (1960); (b) L. Goodman and L. J. Frolen, *J. Chem. Phys.*, **30**, 1361 (1959).
(17) J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, **37**, 1305 (1959).

electron donating because it is more electropositive than carbon, and hence any inductive affect on the intensity will oppose the d-orbital effect. These observations then strongly support the idea that the SiH_3 group is withdrawing electrons from the benzene ring into its 3d-orbitals, and hence the SiH_3 spectroscopic moment is negative (whereas that for CH_3 is positive).

The red shift of the A → L_b transition in substituted benzenes can be related to its intensification.[12,13,18,19] This relationship was derived by Forster[14] and Herzfeld[18] and shown to hold for a number of substituents. There have been further elaborations on this point.[19] For the purposes here a first-order expression for the major term contributing to the energy shift suffices. This is

$$\Delta^2 E_{L_b} = \sum (\sin^2 \Lambda_i)(E_{B_{2u}} - E_{E_{1u}}) \qquad (5)$$

where $\Delta^2 E$ is the energy shift relative to benzene, and i is summed over the substituents in the case of polysubstitution. In the case of disubstitution (where the substituents provide weak perturbations, i.e., $|\Lambda| \ll \pi/2$), eq. 1 and 5 lead to the following expression for the dipole strength in terms of the energy shift and the interference term.

$$2D_{L_b} = D_{E_{1u}}[\Delta^2 E_{L_b}/(E_{B_{2u}} - E_{E_{1u}}) + 2 \sin \Lambda_R \sin \Lambda_S] \qquad (6)$$

It is clear that in the case of constructive interference a red shift requires intensification. An example of this is given in Table I by the 0–0 band energies and extinc-

Table I. Data Obtained from the Ultraviolet Spectra

Compound	$\epsilon_s{}^a$	$f \times 10^3$	$\lambda_{0-0}{}^b$ mμ
p-Methoxyphenylsilane	1075	17.75	280.6
Phenylsilane	242.5	3.56	271.1
p-Methylphenylsilane	216	3.35	269.8
Anisole	1560^c	20.0	275.1
Toluene	205^d	3.1^e	268.3^f
p-Methoxytoluene	1820^c		283.3
Benzene	150^d	1.60^e	(264.0)^{f,g}

^{a} The smoothed molar extinction coefficient ϵ_s was calculated by averaging the molar peak and trough extinction coefficients. ^{b} In cyclohexane or isooctane solution. ^{c} L. Goodman and L. J. Frolen, J. Chem. Phys., 30, 1361 (1958). ^{d} J. R. Platt, ibid., 19, 263 (1951). ^{e} H. Sponer and D. S. Lowe, J. Opt. Soc. Am., 39, 840 (1949). ^{f} F. A. Matsen, W. W. Robertson, and R. L. Chuoke, Chem. Rev., 41, 273 (1947). ^{g} H. Sponer, G. Nordheim, A. L. Sklar, and E. Teller, J. Chem. Phys., 7, 207 (1939).

tion coefficients of methoxytoluene, toluene, and anisole. When there is destructive interference, however, no general statement can be made. If the interference term is sufficiently large, then the red-shift-intensification rule will be violated. This is just found to be the case in comparing (in Figure 3 and Table I) the 0–0 band energies with the oscillator strengths or extinction coefficients of p-methoxyphenylsilane and anisole. Even though the intensity of the methoxysilane is low-

(18) K. Herzfeld, Chem. Rev., 41, 233 (1957).
(19) J. Petruska, J. Chem. Phys., 34, 11, 1120 (1961).

ered from anisole there is a substantial red shift. While not as definitive as the intensity experiments,[20] the energy shifts are consistent with strong d-orbital participation.

Experimental

I. Instruments Used. The spectra were measured in quartz cells using a Spectracord made by Warren Electronics Inc., Bound Brook, N. J.

II. Preparation of Samples. The compounds were first distilled on a Nester and Faust 20-in. × 0.25-in. semimicro spinning-band fractionating column. To further purify the samples, they were degassed and subjected to a molecular distillation into glass vials which were then sealed. When needed, solutions of the samples to be used in obtaining spectra were prepared by withdrawing small portions of the sample from these sealed vials and diluting them to the proper concentration (from 10^{-3} to 10^{-4} M) in Spectrograde cyclohexane, obtained from Phillips Petroleum Co.

III. Preparation of Compounds. A. (p-Methoxyphenyl)trichlorosilane. p-Methoxyphenylmagnesium bromide was formed by reaction of 31.7 g. (0.17 mole) of p-bromoanisole with 20 g. (1.6 g.-atoms) of magnesium in 300 ml. of anhydrous diethyl ether. The Grignard solution formed was then added to 200 ml. (296 g., 1.74 moles) of silicon tetrachloride in 200 ml. of anhydrous diethyl ether. The magnesium salts that formed were filtered and the solution was distilled, yielding 32.65 g. (0.41 mole, 42%) of (p-methoxyphenyl)trichlorosilane, b.p. 128° (0.5–1.0 mm.).
Anal. Calcd. for $C_7H_7OSiCl_3$: Cl, 44.3. Found: Cl, 44.7.

B. p-Methoxyphenylsilane. (p-Methoxyphenyl)trichlorosilane (25 g., 0.10 mole) was reduced by slow addition to a solution of 25 g. (0.66 mole) of lithium aluminum hydride in 30 ml. of anhydrous diethyl ether. Upon the completion of the reaction, the excess hydride was destroyed by adding acetone, and the reaction mixture was extracted with a dilute aqueous solution of hydrochloric acid. The organic phase was dried and distilled. A yield of 7.32 g. (0.053 mole, 53%) of p-methoxyphenylsilane was obtained, b.p. 73° (15 mm.).
Anal. Calcd. for $C_7H_7OSiH_3$. Si, 20.3. Found: Si, 20.5.

C. (p-Methylphenyl)trichlorosilane. This preparation was effected from 30 ml. (42 g., 0.24 mole) of p-bromotoluene, 6 g. (0.5 g.-atom) of magnesium, and 65.8 g. (0.386 mole) of silicon tetrachloride in the same way as (p-methoxyphenyl)trichlorosilane was prepared above. The yield was 21.6 g. (0.096 mole, 40%) of (p-methylphenyl)trichlorosilane, b.p. 65° (1.0–1.2 mm.).
Anal. Calcd. for $C_7H_7SiCl_3$: Cl$_3$, 42.4. Found: Cl$_3$, 42.1.

D. p-Methylphenylsilane. The preparation of p-methylphenylsilane was carried out in the same manner as that of p-methoxyphenylsilane, using 21.56 g. (0.096 mole) of (p-methylphenyl)trichlorosilane and 3 g. (0.079 mole) of lithium aluminum hydride. The

(20) Because of the lack of an interference term in the energy shift.

yield was 6.48 g. (0.052 mole, 55%) of p-methylphenyl-silane, b.p. 22° (54 mm.).

Anal. Calcd. for $C_7H_7SiH_3$: Si, 23.0. Found: Si, 22.6.

Matrix Infrared Studies of OF Compounds.
I. The OF Radical[1]

**Alfred Arkell, Russell R. Reinhard, and Lewis P. Larson**

*Contribution from the Texaco Research Center, Beacon, New York.
Received October 31, 1964*

The photolysis of OF_2 in a N_2 or Ar matrix at 4°K. has produced the OF radical. The radical has fundamental infrared absorption frequencies of 1028.5 cm.$^{-1}$ in Ar and 1025.5 and 1030.5 cm.$^{-1}$ in N_2. These frequency assignments have been confirmed in parallel runs using isotopic substitution. Some evidence is presented which explains the double absorption for OF in N_2 in terms of two types of matrix sites.

Introduction

The existence of the oxyhalide diatomic radicals, OF, OCl, OBr, and OI has been a matter of interest for over 30 years. During that time direct evidence for OCl, OBr, and OI was obtained from flame emission spectra[2] and flash photolysis coupled with ultraviolet absorption spectra.[3] The early claim for the synthesis of the OF radical by Ruff and Menzel[4] was later refuted by other workers.[5] Schumacher and co-workers[6] have investigated the photolysis and thermolysis of OF_2 and concluded that the mechanism for decomposition of OF_2 under these conditions proceeds by way of a short-lived OF radical intermediate. They were unable to detect the OF radical directly but deduced its presence from the kinetic data, quantum yield, and most convincingly from the light-induced reaction

$$OF_2 + SO_3 \xrightarrow[365\ m\mu]{h\nu} F\!\!-\!\!\overset{\displaystyle O}{\underset{\displaystyle O}{S}}\!\!-\!\!OOF$$
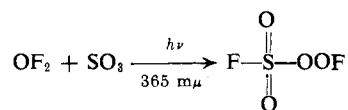
which they argued[7] must proceed by way of the OF

radical. Other indirect evidence for the OF radical was obtained from electron impact studies[8] of OF_2 which indicated a low dissociation energy of about 24 kcal./mole for OF. However, values for OF dissociation derived from thermolysis studies[6c] and theoretical correlations[9,10] range much higher, 45–56 kcal./mole, indicating considerable stability for this species. Green and Linnett[11] meanwhile have argued that molecular orbital theory indicates stability for the OF$^+$ cation but instability for the OF radical. Previous attempts to detect the OF radical spectroscopically in order to resolve these points have failed.[3b]

The first direct and conclusive evidence for the existence of the OF radical has now been obtained using matrix isolation and infrared spectroscopy.

Experimental

All gas blends were prepared by standard manometric procedure using a matrix to reactant ratio (M/R) of 40. The OF_2 (Allied Chemical Co.), N_2 (Airco, prepurified), and argon (Airco) were used without further purification. The $O^{18}F_2$ used in some runs was prepared by the electrolysis of electrolytically dried HF containing about 0.2% of D_2O^{18}. The purified material contained approximately 91% $O^{18}F_2$ and 9% $O^{16}F_2$ according to mass spectrometric and infrared analyses.

The low temperature infrared cell is an all-metal unit similar in general design to the one described by Geiger.[12] It is a double dewar in which the central helium container is shielded from heating due to room temperature radiation by a copper radiation shield maintained at liquid nitrogen temperature (77°K.). The CsBr window on which the matrix is deposited is cooled to 4°K. by being pressed against the copper window holder which forms the bottom of the liquid helium container. Indium metal gaskets are used between the CsBr and copper for good thermal contact.

(1) This research was supported by the Research and Technology Division, AFSC, Edwards, Calif., under Contracts AF 04(611)-6083 and AF 04(611)-9577.

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