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Received February 10, 1975

The Chlorine Hexafluoride Radical. Preparation, Electron Spin Resonance Spectrum, and Structure[1]

Sir:

Chlorine hexafluoride is the only unreported molecule of the series ClF_n (n = 1-6) to date. This hypervalent radical possesses one electron more than SF_6 and one valence electron less than XeF_6 so that the unpaired electron is expected to occupy the a^*_{1g} orbital in O_h symmetry. Since the a^*_{1g} orbital is thought to play a pivotal role in the unusual structural dynamics of XeF_6,[2-4] it is of interest to ascertain the composition of this antibonding orbital in related radicals by ESR studies. We now wish to report the preparation and ESR identification of the ClF_6 radical.

The title radical was generated by γ radiolysis of SF_6 containing 5 mol % of ClF_5 at −196°. Fessenden and Schuler[5] have described the use of solid SF_6 as a suitable matrix for the observation of isotropic ESR spectra during in situ irradiation.[6] Similarly, we find that isotropic spectra are observed for radicals which are sufficiently long-lived to be detected in a γ-irradiated SF_6 matrix at −165°.

In the spectrum shown in Figure 1, the outer lines consist predominantly of two separate 1:6:15:20:15:6:1 septets at low field together with a corresponding septet at high field. Allowing for the effect of radical decay during the sweep from low to high field, these three septets are of comparable intensity. Accordingly, the pattern is interpreted as a 1:1:1:1 quartet of binomial septets, the missing septet being masked by the more intense lines from SF_5[7] and ClF_4[8] in the center of the spectrum. The septet substructure is attributed to hyperfine interaction with six equivalent fluorine ($I = \frac{1}{2}$) nuclei while the quartet splitting originates from coupling to one ^{35}Cl ($I = \frac{3}{2}$) nucleus.[9] This interpretation is verified by the observation of the outer components from the weaker spectrum of the ^{37}Cl ($I = \frac{3}{2}$) radical, as indicated in Figure 1.

Because of the large hyperfine interactions, the ESR parameters were calculated by including terms up to fourth order in the solution of the isotropic ESR spin Hamiltonian.[10] These values were then refined until forward calculations by means of an accurate expression[11] derived from the Breit-Rabi equation reproduced the experimental field positions of the outer ($M_I(Cl) = \pm\frac{3}{2}$) components, the following results being obtained: $a(^{35}Cl)$ = 771 G, $a(^{37}Cl)$ = 642 G, $a(^{19}F)$ = 89 G, and $g = 2.015 \pm 0.001$. It is estimated that the hyperfine coupling constants are accurate to ±1 G. The ratio of $a(^{35}Cl)/a(^{37}Cl)$ is 1.201 ± 0.002, in satisfactory agreement with the value of 1.2015 for the $^{35}Cl/^{37}Cl$ ratio of nuclear g factors. An additional check on the parameters was made by calculating the field positions for the $M_I(^{35}Cl) = +\frac{1}{2}$ set of components, these values agreeing with the observed positions to better than 1 G.

The spectrum of interest is assigned to the ClF_6 radical formed by fluorine atom addition or transfer to ClF_5. The most remarkable feature is the large ^{35}Cl coupling of 771 G which is more than twice the value (288 G) for ClF_4.[8] Since an isotropic coupling of only 82 G has been calculated for complete occupancy of the chlorine 4s orbital,[8a] it is evident that the unpaired electron in ClF_6 must populate the chlorine 3s orbital. In this case the coupling corresponds to a spin density of 0.46. This finding is consistent with the occupation of the totally symmetric a^*_{1g} orbital for a regular octahedral geometry. Also, the interaction with six equivalent fluorines accords with this description.

Although the results conform to O_h symmetry, they do not eliminate the possibility that ClF_6 undergoes deformations similar to those deduced for XeF_6.[2a] First, such motions would lead to such a rapid modulation of the spin distribution that the fluorines would be equivalent on the ESR time scale. Secondly, the results of Hückel MO calculations indicate that the HOMO of XeF_6 is stabilized by deformations from O_h to C_{3v} symmetry when there is a large contribution from the xenon 5s orbital to this antibonding orbital.[2b] Therefore the large spin density in the chlorine 3s orbital of ClF_6 is quite compatible with a fluctuating structure involving deformations to nonoctahedral configurations.

Finally, it is noteworthy that the lines of the ClF_6 spec-

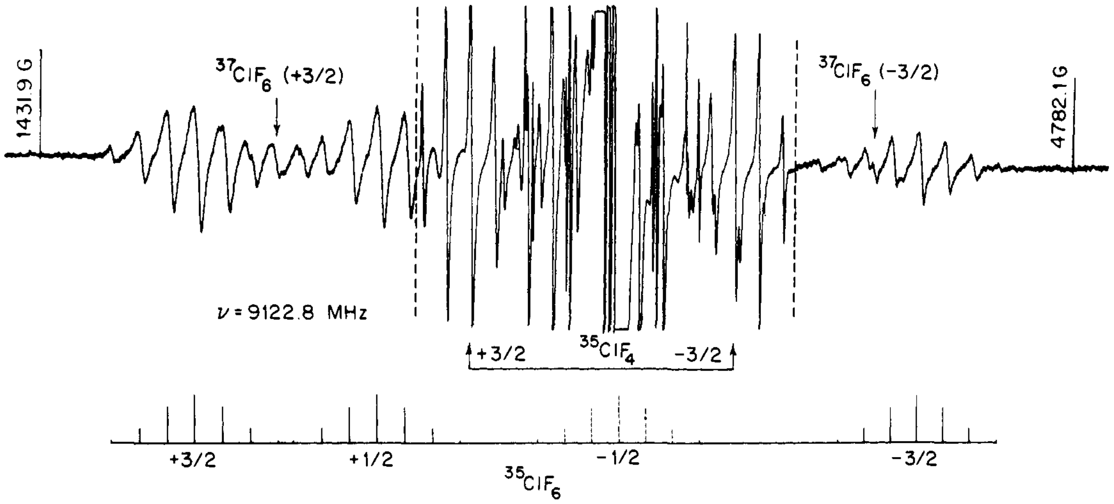

Figure 1. First-derivative ESR spectrum of γ-irradiated SF_6 containing ClF_5 at −165°. The center portion of the spectrum was recorded at approximately half the gain in order to show the outer quintets of the ClF_4 spectrum; strong lines from SF_5 are also present in the center region. The line positions for the $^{35}ClF_6$ spectrum are indicated by the stick diagram and the arrows above the spectrum mark the center lines of the outer septets of $^{37}ClF_6$.

trum are much broader than those of the ClF_4 spectrum in Figure 1. The broadening appears to be uniform for the different components and therefore is not attributable to a modulation of the spin distribution (on the ESR time scale) nor to anisotropic broadening resulting from incomplete tumbling of the ClF_6 radical. It is conceivable that the broadening is caused by enhanced spin-lattice relaxation through a mechanism of spin-orbit coupling.[12] Such a mechanism might well be operative if there is a mixing of the $(a^*_{1g})^1$ ground state configuration with the orbitally degenerate $(a^*_{1g})^0\ (t^*_{1u})^1$ excited state during the course of deformations about a mean of octahedral geometry. A pseudo-Jahn-Teller effect of this type has been discussed[2a] in the analogous case of XeF_6.

Acknowledgment. We wish to thank Dr. F. Q. Roberto of the Air Force Rocket Propulsion Laboratory, Edwards AFB, Calif., for a sample of chlorine pentafluoride.

References and Notes

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(8) (a) J. R. Morton and K. F. Preston, *J. Chem. Phys.*, **58**, 3112 (1973). (b) Also, an intense ESR spectrum of ClF_4 was observed after γ irradiation of SF_6 containing chlorine trifluoride. This method of generation differs from that used by Morton and Preston[8a] and thereby confirms their identification of the ClF_4 radical.
(9) The absence of a central septet spectrum with 500-fold greater intensity rules out the possibility that the quartet of septets is due to ^{33}S ($I = \frac{3}{2}$) satellites in natural abundance. Also, the spectrum reported in this paper is clearly different from a weak spectrum noted previously[5] for a radical with six equivalent fluorines and thought to be SF_6^-. The latter spectrum ($a(^{19}F) = 195$ G; $g = 2.006$) possessing well-resolved second-order fluorine splittings has been also observed in our studies of γ-irradiated SF_6 without additives.
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Received February 18, 1975

A Photochemical Rearrangement without Light. Dioxetane Effected Photochemistry by Direct Intramolecular Excitation[1]

Sir:

The term "photochemistry without light" was coined[2] in regard to experiments designed to place a molecule midway on the hypersurface leading from excited state reactant to ground state product by indirect generation of photochemical species[2] (e.g., zwitterionic). A second type of photochemistry without light begins with the excited state itself, this generated by intermolecular energy transfer from dioxetane derived sensitizer.[3]

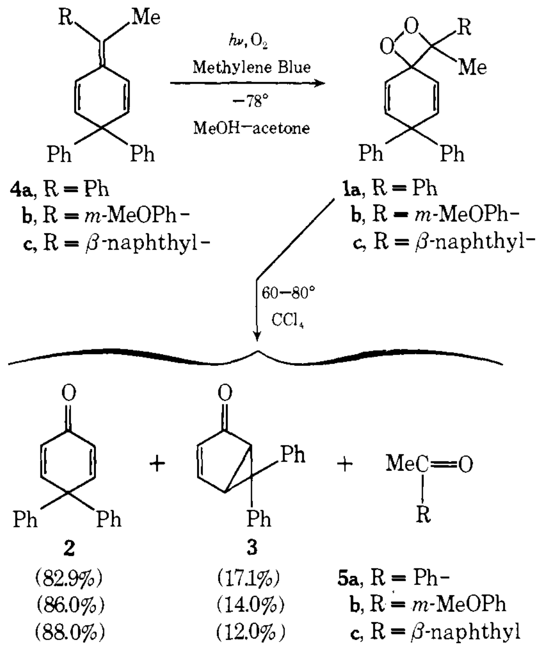
Thus there are two versions of photochemistry without light. That starting with excited state might be termed "vertical" and that placing a molecule on the photochemical reaction coordinate at a later stage could be termed "nonvertical".

Recently, an example of a very novel type of vertical photochemistry without light was reported by Foote.[4] Here the reacting ketonic moiety was incorporated in the initial dioxetane and no energy transfer step was involved. Foote noted referee criticism that an alternative, nonexcited state, free-radical mechanism could account for his reaction products, but he provided evidence against this alternative.

The present communication reports the following. (a) The synthesis of a series of dioxetanes (**1a–c**) which are formal adducts of 4,4-diphenylcyclohexadienone (**2**) and a series of ketones. (b) The thermal decomposition of these to give 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**3**) in the Type A rearrangement characteristic of the photochemistry of this dienone.[5] This provides the first example of a skeletal rearrangement of an excited state generated directly, without intermolecular energy transfer. Here free-radical alternatives do not apply. (c) Direct determination of the efficiency of excited state formation. (d) Efficiencies remarkably independent of the energy and configuration of excited states available to the second ketonic fragment. (e) Direct generation of n-π^* triplet 4,4-diphenylcyclohexadienone and observation of its behavior.

The desired dioxetanes (**1a–c**) were obtained from the reaction of singlet oxygen with the exocyclic double bond of the corresponding 1-methylene-4,4-diphenyl-2,5-cyclohexadienes[6] (**4a–c**) (note Chart I). The dioxetanes were isolated by chromatography at −20°. Crystallization proved effective in two cases to give mp 88–92° dec for methyl phenyl dioxetane **1a** and mp 89–94° dec for methyl β-naphthyl dioxetane **1c**.

Chart I. Preparation and Reaction of Dioxetanes



These dioxetanes were decomposed thermally between 60 and 80°.[7] The products obtained in each of the three cases proved to be 4,4-diphenylcyclohexadienone (**2**), 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**3**), and the corresponding methyl ketone (i.e., acetophenone, *m*-methoxyacetophenone, or β-acetonaphthone). Note Chart I.

Since the efficiency of formation of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**3**) starting with either singlet or triplet 4,4-diphenylcyclohexadienone (**2**) is known[5b] to be 0.86 (i.e., $\phi_{isc} = 1$), we calculate the efficiency of generation of excited dienone to be (1/0.86) times the 17.1, 14.0, and 12.0% yields of bicyclic ketone **3** derived from the three