with 2 and 5 of reduced intensity. This observation of incomplete saturation at 35 kG is consistent with magnetic moment data which also shows incomplete magnetic saturation of the powder at this field and temperature. $Fe(4,4'\text{-diMe-}2,2'\text{-bipy})Cl_2$ and the 5,5'-dimethyl analog, both of which show large quadrupole effects (3.5 mm/sec), also exhibit magnetic hyperfine splitting at 4.2 K.

In an effort to determine T_c more precisely for the preceding materials, the temperature dependence of the Mössbauer spectra over the range 2–10 K is presently under investigation. X-Ray, near-infrared, and other spectral data bearing on the structure of and nature of ferromagnetic interaction in the foregoing materials have been completed and will be published elsewhere. The X-ray data and near-infrared–visible spectral absorptions at $\sim$6000 and 10,000 cm^{-1} confirm solid state association through bridging chlorines resulting in a polymer containing iron(II) having either five or six coordination. An extensive new series of mono-polyimine ferrous halides having a variety of electron-releasing and -withdrawing substituents and of structure similar to $Fe(phen)Cl_2$ has been prepared.[5] Investigation of the variation of T_c in this group should provide a novel method of studying substituent electronic and packing effects.

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Chemically Induced Polarization of Fluorine-19 Nuclei. Fluorine-Substituted Phenyl Radicals

Sir:

Chemically induced dynamic nuclear polarization (CIDNP)[1] is a sensitive indicator for radical-pair reactions. The theory underlying this effect has been developed to a stage where the experimentally observed signal directions and intensity patterns can be used to derive the initial spin multiplicity of the radical pair or the esr parameters of the individual radicals.[2] The application of CIDNP to the determination of the *signs* of hyperfine coupling constants (*a* values) can be of particular interest, since the magnitudes of these parameters are available directly from esr spectra, whereas their signs are less readily accessible and subject occasionally to controversy. Examples of the use of the CIDNP technique to establish or confirm the signs of electron–hydrogen hyperfine interactions include the hydroxybenzyl,[3a] phenoxyl,[3b] and cyclopropyl[3c] radicals.

We have observed ^{19}F polarization in coupling and radical-transfer products derived from pentafluorophenyl and monofluorophenyl radicals and, on the basis of the spectral patterns, have determined the signs of the hyperfine coupling constants for fluorine nuclei in the ortho, meta, and para positions of these radicals.

When a solution of di(pentafluorobenzoyl) peroxide (**1**) in tetrachloromethane was photolyzed in the probe of an nmr spectrometer,[4] seven enhanced multiplets were observed (Figure 1). Three multiplets represented the phenoxyl segment of pentafluorophenyl pentafluorobenzoate (**2**): the ortho and meta nuclei appeared in enhanced absorption (A), the *p*-fluorine in emission (E). A fourth, very weak multiplet (E) was assigned to the *o*-fluorines of the benzoyloxy fragment of **2**. The remaining three multiplets had the chemical shifts of the radical-transfer product, chloropentafluorobenzene (**3a**); their polarization was opposite to the corresponding nuclei of **2** (F_o, F_m, E; F_p, A). Decomposition of **1** in protio- or deuteriotrichloromethane produced similar spectra with **2** and **3b** or **3c** as spin-polarized products. All signals appear to show only net polarization (*e.g.*, Figure 2).

We explain the observed polarization as being induced in the radical pair, pentafluorobenzoyloxy–pentafluorophenyl[5] (Scheme I). Generated in the singlet state[5b,c] this pair can couple to yield **2**. Pentafluorophenyl radicals escaping from their partners can form the radical-transfer products, **3a**–**c**. The pentafluorobenzoyloxy radical should have a considerably larger *g* factor than the pentafluorophenyl radical. If these apparently reasonable assumptions are correct, the signal directions observed for coupling product **2** and radical-transfer product **3** indicate that the fluorine hyperfine coupling constants of the pentafluorophenyl radical are positive in the ortho and meta positions (a_F^o, $a_F^m > 0$), but negative for the para position ($a_F^p < 0$). From the intensity of the CIDNP spectra it appears that $a_F^o > a_F^m > |a_F^p|$. Because of possible relaxation effects we did not attempt to determine the exact ratios of these coupling constants.[6]

We also studied the photodecomposition of the symmetrical di(fluorobenzoyl) peroxides in tetrachloromethane. The polarized products observed in these reactions indicated that the fluorine hyperfine interactions of both *o*- and *p*-fluorophenyl radicals are

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(1) (a) J. Bargon, H. Fischer, and U. Johnson, *Z. Naturforsch.*, *A*, **22**, 1551 (1967); (b) H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5518 (1967).

(2) (a) G. L. Closs, *ibid.*, **91**, 4552 (1969); (b) G. L. Closs and A. D. Trifunac, *ibid.*, **91**, 4554 (1969); (c) R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, 4, 195, 214 (1969); (d) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 2183, 2186, 7227 (1970); (e) G. L. Closs, C. E. Doubleday, and D. R. Paulson, *ibid.*, **92**, 2185 (1970).

(3) (a) G. L. Closs and D. R. Paulson, *ibid.*, **92**, 7229 (1970); (b) M. L. Kaplan and H. D. Roth, *Chem. Commun.*, 970 (1972); (c) R. Kaptein, Ph.D. Thesis, Leiden, The Netherlands, 1971.

(4) The nmr spectra were recorded on a Jeolco C-60 HL spectrometer at 56 MHz. This instrument contained a quartz probe and was fitted with two mirrors to permit uv irradiation (200-W high-pressure mercury lamp) of the samples in the area of the receiver coil. All samples were deaerated with argon. Products 2 and 3 were identified by comparison of their chemical shifts with those of authentic materials.

(5) *Cf.* (a) E. Lippmaa, T. Pehk, A. L. Buchachenko, and S. V. Rykov, *Dokl. Akad. Nauk SSSR*, **195**, 632 (1970); *Chem. Phys. Lett.*, **5**, 521 (1970); (b) R. Kaptein, J. A. Den Hollander, D. Antheunis, and L. J. Oosterhoff, *Chem. Commun.*, 1687 (1970); (c) S. R. Fahrenholtz and A. M. Trozzolo, *J. Amer. Chem. Soc.*, **93**, 251 (1971).

(6) To our knowledge, no esr study of the pentafluorophenyl radical has as yet been published. Upon photolysis of **1** at −196° in a benzene matrix, an esr spectrum was observed with $g = 2.0015$ and an apparent 1:2:1 triplet splitting of $\sim$20 G. We are indebted to Mr. J. H. Marshall for informing us of these results.

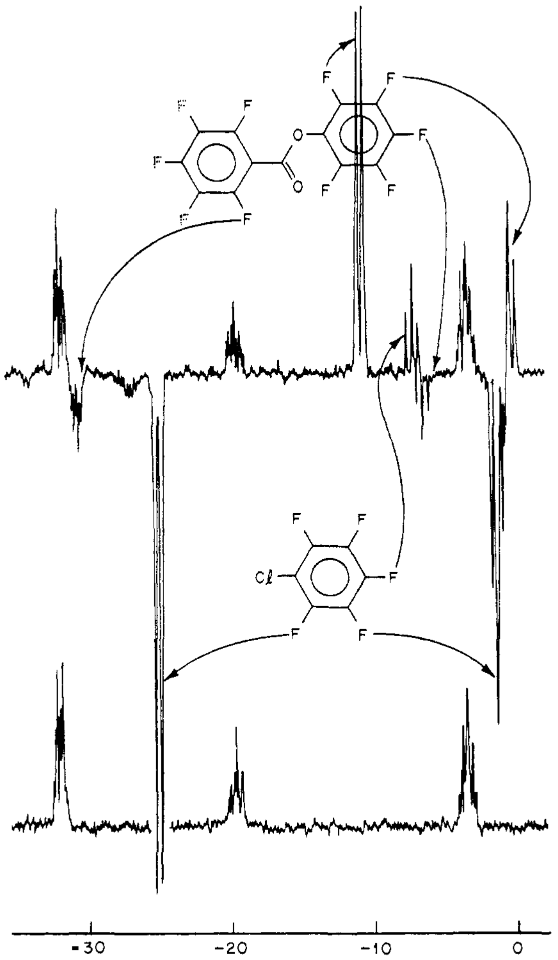


Figure 1. The ^{19}F nmr spectrum (56 MHz) of a 0.1 M solution of di(pentafluorobenzoyl) peroxide in tetrachloromethane in the dark (lower trace) and of the same sample during ultraviolet irradiation (upper trace). Sweep rate, 20 Hz/sec. The frequency scale is given relative to hexafluorobenzene.

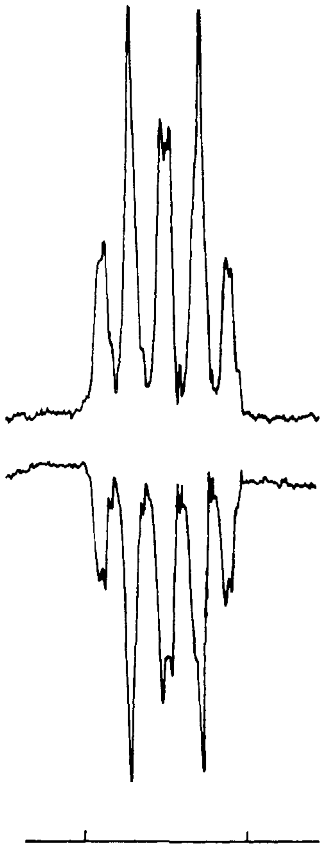


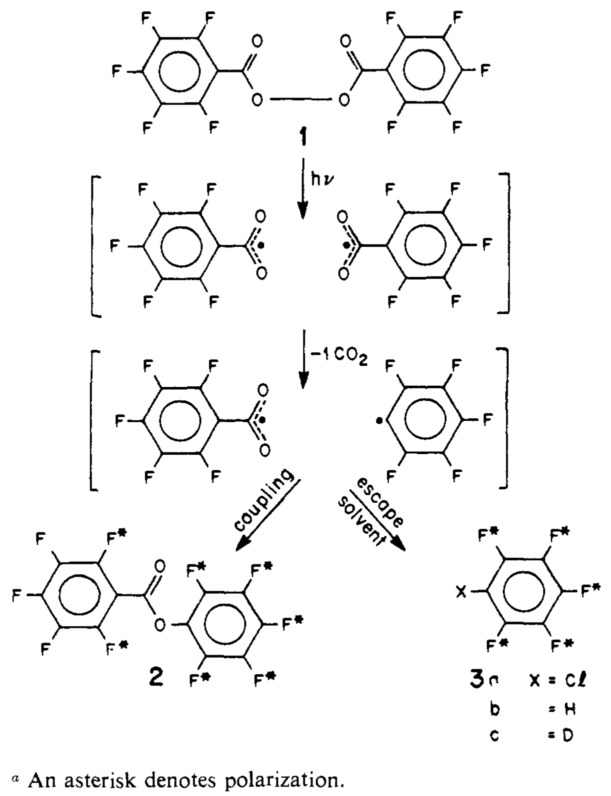
Figure 2. The ^{19}F nmr spectrum (56 MHz) of the ortho nuclei of pentafluorobenzene (upper trace) and of the same spectral region during the decomposition of a 0.1 M solution of **1** in trichloromethane (lower trace). Sweep rate, 5 Hz/sec. The spectrum covers 1 ppm.

positive and that $a_{\mathrm{F}}^{\mathrm{o}}$ is larger than $a_{\mathrm{F}}^{\mathrm{p}}$. We were unable to determine the sign of $a_{\mathrm{F}}^{\mathrm{m}}$, because the coupling and radical-transfer products derived from di(*m*-fluorobenzoyl) peroxide have nearly identical chemical shifts and overlap with the starting material.

In principle, the pattern of hyperfine interactions derived here for the pentafluorophenyl radical is very similar to the one found for the phenyl radical,[7] *i.e.*, $a_{\mathrm{H}}^{\mathrm{o}} > a_{\mathrm{H}}^{\mathrm{m}} > a_{\mathrm{H}}^{\mathrm{p}}$. Both experiment[7b] and calculation[7c] indicated that all three couplings are positive. CIDNP studies on di(*p*-chlorobenzoyl) peroxide[8a] and di(*p*-anisoyl) peroxide[8b] confirmed that the *a* values for the ortho and the meta hydrogens are positive, while polarization has yet to be observed for the para hydrogen.

A comparison of the pentafluorophenyl radical with fluorine-substituted π radicals is illuminating. In π radicals, fluorine substituents at the centers of high-spin density can form π bonds to the aromatic system. As a result the electron–fluorine interactions in both ortho and para positions are large and positive, whereas

Scheme I[a]



[a] An asterisk denotes polarization.

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(7) (a) J. E. Bennett, B. Mile, and A. Thomas, *Proc. Roy. Soc., Ser. A*, **293**, 246 (1966); (b) P. H. Kasai, E. Hedaya, and E. B. Whipple, *J. Amer. Chem. Soc.*, **91**, 4364 (1969); (c) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **90**, 4201 (1968).

(8) (a) M. Lehnig and H. Fischer, *Z. Naturforsch., A*, **24**, 1771 (1969); (b) H. D. Roth, unpublished results.

the a values for m-fluorines are weaker and negative.[9] Such a pattern is quite different from the one we derive for the pentafluorophenyl radical, implying that this radical does not have appreciable π character.

The theoretical understanding of fluorine hyperfine interactions appears to be less than adequate.[10] Nevertheless, we explain the large positive coupling of ortho substituents by a direct interaction with the half-filled σ orbital at C-1. For the meta and para positions the contributions of direct coupling will be smaller and the a values of these nuclei will depend on a variety of factors including the polarization of the C–F bond and the s electrons of the fluorine atoms due to the unpaired spin on carbon and on fluorine. Since it is conceivable that these contributions are sensitive to the nature of substituents, the observed difference in the sign of $a_{\mathrm{F}}{}^{\mathrm{p}}$ for the p-fluorophenyl and the pentafluorophenyl radical does not appear internally inconsistent.

We conclude with a comment on the benzoyloxy radicals which we and others have assumed as intermediates. We have observed weak CIDNP signals for the o-fluorine nuclei of the benzoyloxy segments of **2** and of o-fluorophenyl o-fluorobenzoate. These signals indicate that the hyperfine coupling constants ($a_{\mathrm{F}}{}^{\mathrm{o}}$) of o-fluoro- and pentafluorobenzoyloxy radicals are positive. This limited information falls far short of elucidating the nature of fluorine-substituted benzoyloxy radicals.[11]

(9) (a) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Mol. Phys.*, **5**, 407 (1962); (b) A. Carrington, A. Hudson, and H. C. Longuet-Higgins, *ibid.*, **9**, 377 (1965); (c) A. Hinchcliffe and J. N. Murrell, *ibid.*, **14**, 147 (1968); (d) W. G. Esperen and R. W. Kreilick, *ibid.*, **16**, 577 (1969); (e) J. W. Rakshys, *Chem. Commun.*, 579 (1970).

(10) A. Hudson and K. D. J. Root, *Advan. Magn. Resonance*, **5**, 1 (1971).

(11) Apparently, the thermal decomposition of **1** in cyclohexanone[12a] or hexachlorobutadiene[12b] gives more information about these species.

(12) (a) L. S. Kobrina, L. V. Vlasova, and V. I. Mamatjuk, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 2, 92 (1971); (b) J. Bargon, *J. Amer. Chem. Soc.*, **93**, 4630 (1971).

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Thermal Generation of Organic Molecules in Electronically Excited States. Evidence for a Spin Forbidden, Diabatic Pericyclic Reaction[1]

Sir:

The understanding of the mechanisms by which molecules undergo reactions involving a change in electronic state is among the more intriguing problems occupying the attention of photochemists,[2] spectroscopists,[3] and kineticists.[4] Many types of interesting questions can be asked concerning interconversion of electronic states (*i.e.*, electronic relaxation[3]) during a reaction such as the following. (a) Can a singlet–triplet conversion occur during a concerted reaction (*i.e.*, violation of Wigner's[5] "spin conservation rule")? (b) Are specific vibronic interactions required to promote interconversion of electronic states, and, if so, which nuclear motions are most effective? (c) What are the relationships, if any, between unimolecular adiabatic ground-state reactions and radiationless transitions such as internal conversion, intersystem crossing, and primary photochemical reactions? (d) What are the electronic requirements for thermal generation of an electronically excited organic molecule? We report here a study of the effect of solvent on the activation parameters for thermolysis of tetramethyl-1,2-dioxetane (**1**), and we show how our new data, when coupled to information available in the literature and to the concepts of molecular spectroscopy, can lead to the inference of a rather detailed picture of the mechanism of decomposition of **1** and some fresh insights relevant to questions a–d, and demonstration of a close connection between some radiationless electronic relaxation processes and certain photochemical primary processes.

Solutions of **1** (approximately 0.05 M) in various aerated solvents were heated in a thermostated sample holder of a Hitachi–Perkin-Elmer spectrophotofluorimeter and the decay of intensity of acetone fluorescence was measured and taken to be the rate of fragmentation of **1**. The measured rates were strictly first order in all cases and have been shown[6] to equal the rates of decomposition of **1**. The activation parameters for thermolysis of **1** in several solvents were then determined in a standard manner[7] and are reported in Table I.

We now consider two distinct types of mechanisms to explain our new data and other previously reported data on the thermolysis of 1,2-dioxetanes, *i.e.*, the high yield of acetone triplets formed when **1** is thermolyzed.[8] The first mechanism involves a transition state which very closely resembles a biradical (**2**), which can then be stabilized to the point of achieving the status of a real intermediate (eq 1); the second mechanism involves a structurally unspecified transition state ($\mathbf{1}^{\neq}$) which proceeds directly to the observed products without the occurrence of any intermediates, *i.e.*, products are formed from **1** in an elementary chemical step.

Mechanism 1 might be expected (a) to proceed in nonpolar solvents with the occurrence of a substantially positive value of $\Delta S^{\neq}$, based on analogy to the decomposition of di-*tert*-butyl peroxide[9] ($\Delta S^{\neq} \sim +10$ eu) and the biradical-like fragmentation of cyclobutanes[9] ($\Delta S^{\neq} \sim +10$ eu); (b) to show little variation in rate with structural substitution since the O–O bond breaking is dominant in achieving the transition state; (c) to exhibit a substantial rate increase in polar solvents

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(5) The quantitative nature of the effect of spin conservation on the rate of a chemical reaction has not, except for statistical factors, been considered, to the best of our knowledge.

(6) The rate of disappearance of **1** was found to be identical when measured by nmr spectroscopy or fluorimetry.

(7) We feel that a very conservative error limit of our values of $\Delta H^{\neq}$ is ± 2 kcal/mol. Thus, perhaps the value of $\Delta H^{\neq}$ for acetonitrile as solvent is not much different than that for cyclohexane as solvent. Refinement of the data is in progress.

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