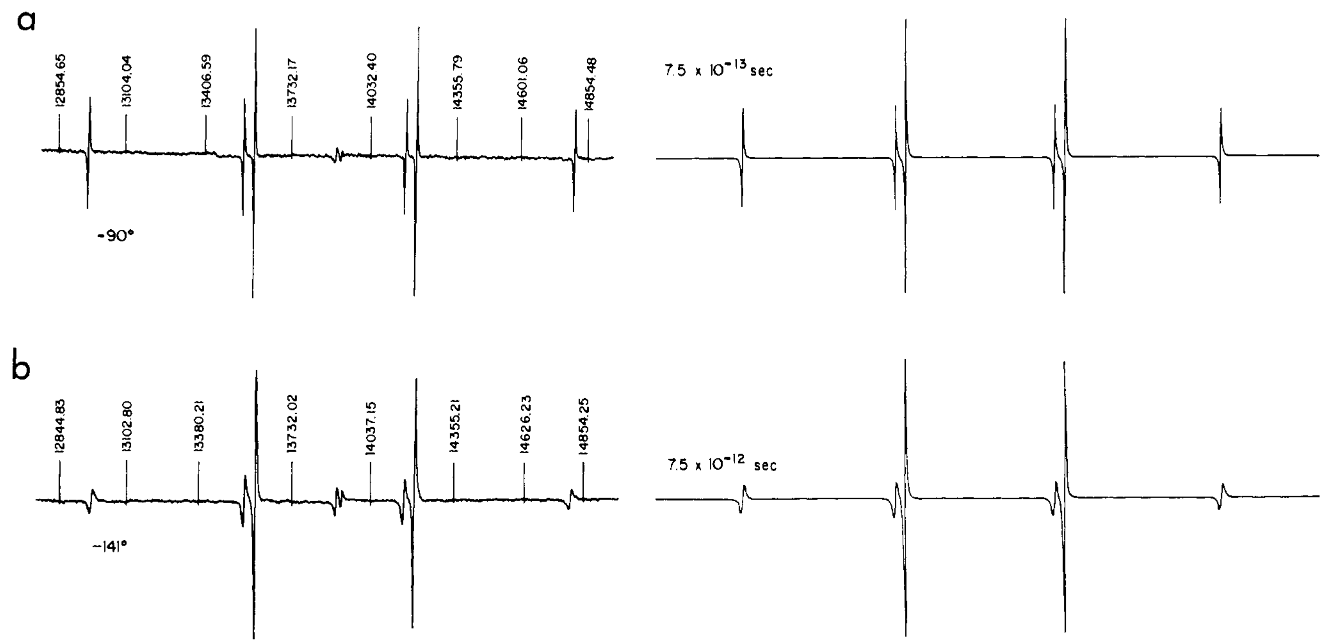


Figure 3. Esr spectra of the trifluoromethyl radical at two temperatures with the calculated spectra (Redfield relaxation matrix theory) for two rotational correlation times. The radical was generated by photolysis of a solution containing di-*tert*-butyl peroxide, dimethyl phosphite, and bromotrifluoromethane (1:1:5, v/v/v).

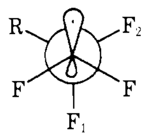
$J_0 = 2\tau_c$, $J_w = 2\tau_c(1 + \omega^2\tau_c^2)^{-1}$, and τ_c is the correlation time for the rotational tumbling. The details of the line-shape calculations will be reported elsewhere.[18]

The experimental spectra for the $\cdot CF_3$ radical were fit by this theory using Lorentzians with line-width parameters $T_2(M_I,I)$ given by

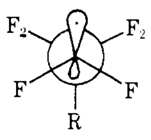
$$[T_2(M_I,I)]^{-1} = [T_{2d}(M_I,I)]^{-1} + T_{2_0}^{-1}$$

where T_{2_0} accounts for other relaxation processes. In these calculations $A_{\parallel}$ was taken to be 108 G[14] and T_{2_0} was chosen to give best agreement with the experimental spectra ($T_{2_0} = 75 \times 10^{-9}$ sec). It is seen in Figure 3 that the agreement is quite good. The resulting rotational correlation times (Figure 3) compare well with values for small molecules obtained by other means.[19]

We also examined the spectra of the *n*-perfluoropropyl[1,4] and *n*-perfluoroheptyl radicals from the corresponding bromides. At $-60°$ the spectrum of the former consists of a triplet of triplets caused by the two α-fluorines (86.2 G) and the two β-fluorines (15.1 G) split into quartets by the γ-fluorines (3.61 G). At room temperature the spectrum of the latter is likewise a triplet of triplets (86.0 and 16.4 G) split into an apparent quintet of 1.5 G. The α-fluorine couplings indicate radical sites of comparable geometry to that in perfluoroethyl. In both radicals the magnitudes of the β-fluorine couplings *increase* notably as the temperature is raised. Save for the dipolar broadening of the wing lines, particularly severe for the *larger* heptyl radical, no additional line-shape effect was apparent down to $-100°$. This behavior is consistent with the presence of a barrier to rotation about the C_α–C_β bonds with minima corresponding to conformations IV and V. Conformation V should lead to the smallest value



IV



V

for the β-fluorine coupling (*cf.* I). The observation of a positive temperature coefficient for $a_{\beta\text{-F}}$ must then mean that this rotamer is the more populated at low temperatures and hence the more stable. A fuller analysis of the internal dynamics in these and other perfluoroalkyl radicals is in progress.

Acknowledgments. We are grateful to Professor J. K. Kochi (Indiana) for a sample of perfluoropropionic acid *tert*-butyl perester, to Dr. D. P. Carlson (Du Pont) for samples of perfluoropropionyl peroxide, and to Mr. B. F. Gordon for technical assistance.

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(18) P. Meakin and J. P. Jesson, *J. Magn. Resonance*, **11**, 182 (1973). The line widths were calculated using a modified version of a computer program written for the simulation of multipulse and Fourier transform nmr experiments. This program calculates all of the elements of the relaxation matrix in Liouville space in the basis in which the Liouville operator is diagonal. The spectrum is then calculated by diagonalizing ($R - iL$). In this particular case the computer program gives results in agreement with those from eq 4.

(19) W. G. Rothschild, *J. Chem. Phys.*, **59**, 3265 (1970).

(20) Contribution No. 2051.

A Photochemical Reaction with a Preequilibrium Step. Acid-Catalyzed Photochemical Wallach Rearrangement

Sir:

Under excitation by 320-nm monochromatic light, azoxybenzene undergoes an isomerization to *o*-hydroxyazobenzene, the well-known photo-Wallach rearrangement.[1]

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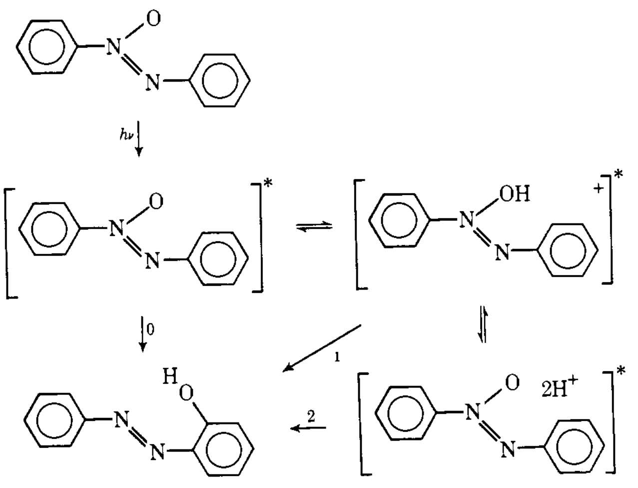
(1) E. Buncel in "Mechanisms of Molecular Migrations," Vol. 1, B. S. Thyagarajan, Ed., Wiley, New York, N. Y., 1968.

We have recently measured the quantum yields for this isomerization as a function of acidity in the aqueous, ethanolic, sulfuric acid system used in our previous studies of azoxybenzene.[2] The solid curve in Figure 1 represents the assumption that the quantum yield observed is the sum of quantum yields of two species related by an acid–base equilibrium. The pK of azoxybenzene in the ground state is -6.45 ± 0.05;[2b] consequently, the curve observed cannot relate to the ground-state acid–base reaction. This is further confirmed by the complete absence of any detectable absorption due to the conjugate acid of azoxybenzene (λ_{max} 480 nm (ϵ 17,000)) in our substrate. These findings lead us to the conclusion that *azoxybenzene undergoes a rapid protonation in its first excited state prior to the rearrangement occurring with high Φ in strongly acidic solution.*

We believe the mechanism to be either of the following two shown below. It is likely that path 1 is the



path in ethanol and path 2 the path in acidic solution; however, it is conceivable that the ethanol path is path zero, and path 1 is the acid-catalyzed one. Actually, we are not certain of the details of the mechanism. Calculations by the Förster cycle indicate that the pK of azoxybenzene in its first $\pi \rightarrow \pi^*$ state is about 11.[3] Consequently, we can assume this state of azoxybenzene to be fully, nor nearly fully, protonated in hydroxylic solvents without addition of acid, and must assume that the protonation reaction shown by Figure 1 is actually a second protonation. This suggestion is consistent with our knowledge of the thermochemical acid-catalyzed Wallach rearrangement, which has been shown to proceed through a doubly protonated intermediate (or transition state)[2] shown.

Unfortunately, there is no way at this time to eliminate a possible alternative explanation of our observations. CNDO/S-CI calculations[4] indicate that two $n \rightarrow \pi^*$ transitions, to the ^1W and ^1U states (Platt notation), are submerged in the long-wavelength "tail" of the much more intense $\pi \rightarrow \pi^*$ (^1B) state. In heptane one expects the $n \rightarrow \pi^*$ states to be approximately at the energy calculated. However, as the proton-donating ability of the solvent increases, the $\pi \rightarrow \pi^*$ state is expected to undergo a slight red shift, but the $n \rightarrow \pi^*$ states should shift considerably to the blue. The increase in quantum yield could conceivably be interpreted as the crossing of the second of the $n \rightarrow \pi^*$ states through the origin of the $\pi \rightarrow \pi^*$ state. However, it seems extremely unlikely that the behavior with H_0 of such a crossing would appear so much like an acid–base reaction.

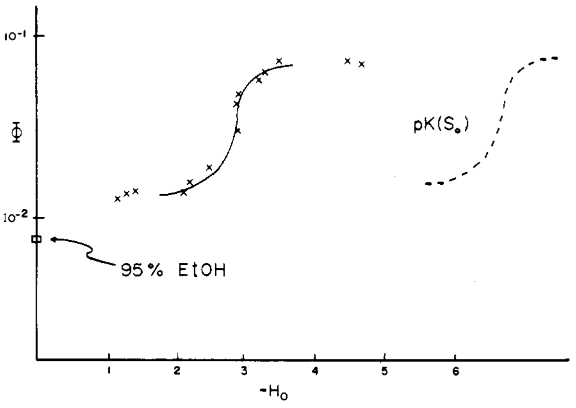


Figure 1. The H_0 dependence of the quantum yield of the photochemical Wallach rearrangement.

Finally, it must be noted that the photo-Wallach reaction observed in low acidity and in ethanol must be based on a different mechanism. In this relation it is interesting to note that Buncel[5] has recently observed a much slower thermochemical Wallach not involving a second protonation step.

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[2] (a) C. S. Hahn and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 946, 949 (1962); (b) C. S. Hahn, K. W. Lee, and H. H. Jaffé, *J. Amer. Chem. Soc.*, **89**, 4975 (1967).

[3] (a) H. H. Jaffé, D. L. Beveridge, and H. L. Jones, *J. Amer. Chem. Soc.*, **86**, 2932 (1964); (b) H. H. Jaffé and H. L. Jones, *J. Org. Chem.*, **30**, 964 (1965).

[4] G. W. Kuehnlenz, C. A. Masmanidis, and H. H. Jaffé, *J. Mol. Struct.*, **15**, 445 (1973), and references cited therein.

(5) E. Buncel, private communication.

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On the Polarity of 1,3-Butadiene, 2,3-Dichloro-1,3-butadiene, and Their van der Waals Adducts with Ethylene[1]

Sir:

The formation of molecular complexes appears to be the prerequisite of numerous chemical and biochemical reactions. Thus the understanding and prediction of intermolecular forms represents a major task of theoretical chemistry. It is of prime interest to know the geometric and energetic properties of molecular complexes in the gas phase, since such data may shed light on the nature of both molecular interactions and reactivities.

The molecular beam electric deflection technique has been used to investigate the possible existence of polar conformers of 1,3-butadiene and 2,3-dichloro-1,3-butadiene. In addition, these compounds were mixed with ethylene and expanded through a supersonic nozzle producing molecular complexes among which one might find a "pre-Diels–Alder" complex (1,4 complex) or a 1,2 complex as might occur in a photochemical 2 + 2 cycloaddition process.

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