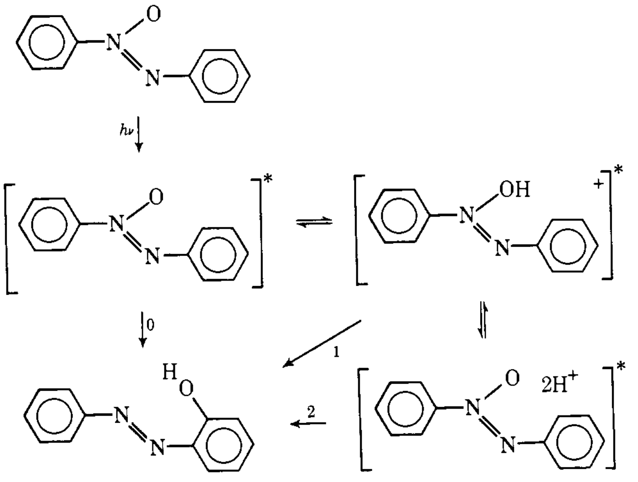
We have recently measured the quantum yields for this isomerization as a function of acidity in the aqueous, ethanolic, sulfuric acid system used in our previous studies of azoxybenzene.[2] The solid curve in Figure 1 represents the assumption that the quantum yield observed is the sum of quantum yields 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.

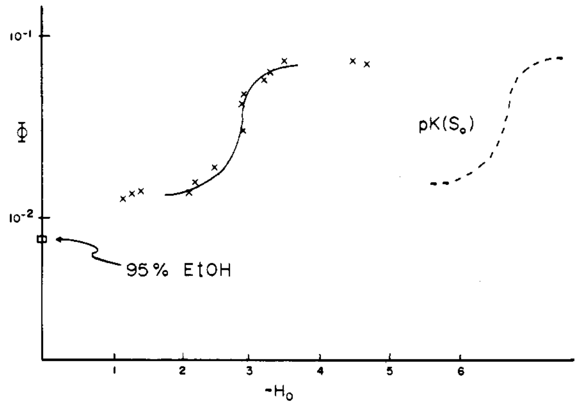


Figure 1. The H_0 dependence of the quantum yield of the photochemical Wallach rearrangement.

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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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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(1) Supported by the National Science Foundation.

Molecular beams of the species of interest are produced either by effusion from a source into the high vacuum of the apparatus (mean free path > size of opening) or the molecules are expanded through a supersonic nozzle into the apparatus (mean free path ≪ size of opening). In the effusive case the molecules present in the beam are merely a sample of the equilibrium species in the source. Supersonic expansion produces two dramatic effects. First, substantial cooling occurs as the internal energy of the gas is converted into kinetic energy of forward motion; for example, rotational temperatures of 10°K are not uncommon. Second, weakly bound van der Waals molecular complexes are formed (by three body collisions) and are stable in the molecular beam since these complexes do not possess enough internal energy to dissociate.

The apparatus is an electric resonance spectrometer. In this work we utilize only the electrostatic quadrupole focusing fields (A and B fields). The presence of an electric dipole moment is determined by observing an increase in beam intensity when voltage is applied to the A and B fields. In general the sensitivity of the experiment is such that a permanent electric dipole moment of the order of 0.2 D is readily observable.[2]

Detection of the various neutral molecular species present in the beam is accomplished by electron bombardment ionization followed by mass analysis of the resulting ions. The apparatus and the electric deflection scheme have been described elsewhere.[3]

The beam source for both 1,3-butadiene and 2,3-dichloro-1,3-butadiene is effusive with temperature control. We have examined 1,3-butadiene at 195°K and at room temperature; in both instances the molecule was observed to defocus (nonpolar behavior). In contrast, 2,3-dichloro-1,3-butadiene was observed to increase in polarity with temperature over the temperature range 273–318°K as shown in Table I.

Table I. Polarity of 2,3-Dichloro-1,3-butadiene

Temp (approx.), °C	% refocusing (A, B = 20, 20 kV)[a]
45	1.3
25	1.2–1
0	0.75
Cooling by supersonic expansion with ethylene	0.0
Cooling by supersonic expansion with argon	0.2

[a] The per cent refocusing is the observed change in beam intensity when the straight through beam is blocked by the stop wire obstacle and 20 kV is applied to both the A and B fields. A negative number indicates that when the fields were applied, a decrease in intensity of the small residual scattered beam was observed. All intensities are normalized with respect to the intensity of the beam of the molecular species of interest with the stop wire obstacle removed.

When 1,3-butadiene is mixed with ethylene and expanded through a supersonic nozzle at an ambient temperature of 195°K, a weakly bound complex is formed consisting of one butadiene and one ethylene molecule. This complex is seen to be slightly polar. Ethylene dimer is also formed and is observed to be nonpolar.

When 2,3-dichloro-1,3-butadiene is expanded with ethylene or argon through the supersonic nozzle, the usual effective cooling takes place and the compound appears nonpolar. Under these conditions a dimer and possibly higher van der Waals clusters of the dichlorobutadiene are formed. The "dimer" is seen to be nonpolar. The cracking pattern of the dimer is complicated and masks the mass spectrum of the adduct of ethylene and dichlorobutadiene. Thus we can make no statement about the existence or polarity of that species. Table II lists the molecules discussed and their polarity.

Table II

Molecule	Temp	Polarity	% refocusing (A, B, = 20, 20 kV)
1,3-Butadiene	25°	Nonpolar	−0.2
2,3-Dichloro-1,3-butadiene	25°	Polar	+1
	Supersonic	Nonpolar	0
1,3-Butadiene–ethylene	Supersonic	Polar	+1
(2,3-Dichloro-1,3-butadiene)$_n$, n = 2?	Supersonic	Nonpolar	−0.6
(Ethylene)$_2$	Supersonic	Nonpolar	0

Our interpretation of these various results is as follows. The lowest energy conformation of both 1,3-butadiene and 2,3-dichloro-1,3-butadiene are nonpolar species. The absolute intensity and the variation with temperature of the refocused beam of 2,3-dichloro-1,3-butadiene indicates the existence of a polar isomer 3 kcal/mol above the nonpolar form. The absence of refocusing for 1,3-butadiene places the polar form greater than 2 kcal/mol above the corresponding nonpolar isomer.

Nonempirical computations indicate that among the various rotameric conformations of butadiene, the most stable polar form (a *ca.* 20° out of plane distorted *s-cis*-butadiene) is about 2.0–2.5 kcal/mol higher in energy than the nonpolar *s-trans*-butadiene.[4,5]

The experimental energy difference between *s-cis*- and *s-trans*-butadiene amounts to 2.3[6] or 1.7 ± 0.5[7] kcal/mol. Ir studies have shown that 2,3-dichlorobutadiene is in the *s-trans* form,[8] in agreement with our deflection results. The present results are the first, to our knowledge, which establish the presence of a higher energy polar conformer. It would be tempting to postulate that the polarity of this complex comes from the ethylene rotating the butadiene into its *s*-cis conformer and associating with it in a "pre-Diels–Alder" geometry. However, in such a complex one would have to overcome the energy difference between *s*-cis and *s*-trans conformers of butadiene; in addition, almost any complex between butadiene and ethylene would be asymmetric and therefore slightly polar.

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To conclude, it is worth noting that although the results presented here are mainly qualitative, the technique employed allows (1) the detection of the presence of different conformers of a molecule in the gas phase and the estimation of their energy differences and (2) the detection of molecular complexes and the study of their polarity, which gives insight into their structure and symmetry.

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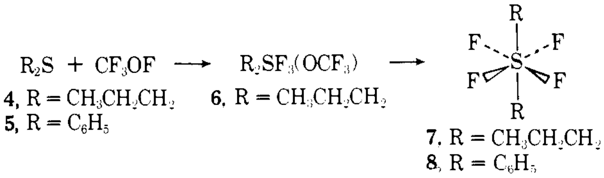
Dialkyl- and Diaryltetrafluoropersulfuranes[1]

Sir:

Recently it was reported that dialkyl and diaryl sulfides react with trifluoromethyl hypofluorite (1) to yield dialkyl- and diaryldifluorosulfuranes (2).[2] At

$$\underset{\mathbf{1}}{CF_3OF} + R_2S \longrightarrow \underset{\mathbf{2}}{R_2SF_2} \xrightarrow{CF_3OF} \underset{\mathbf{3}}{R_2SF_4}$$

that time it was noted that di-*n*-propyl sulfide appeared to react further with 1 to give di-*n*-propyltetrafluoropersulfurane. This observation prompted an investigation of the reactions of compounds 2 with excess 1. Treatment of di-*n*-propyl sulfide (4) with excess 1 at

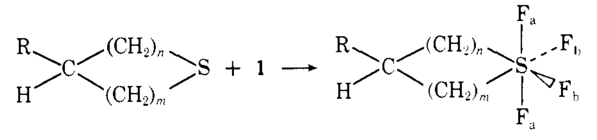


4, R = $CH_3CH_2CH_2$
5, R = C_6H_5
6, R = $CH_3CH_2CH_2$
7, R = $CH_3CH_2CH_2$
8, R = C_6H_5

−80° gave a solution whose ^{19}F nmr spectrum showed three absorptions at δ −47.1, −40.9, and +50.3 in the ratio 1:1:3. These are assigned to the compound **6**.[3] On warming gas was evolved and the ^{19}F nmr spectrum changed to a quintet at δ −60.6, J_{FSCH} = 8.4 Hz. The ^{1}H nmr spectrum at −70° showed a triplet at δ 0.88, J_{HCCH} = 7.5 Hz, which is assigned to the absorption of the hydrogens of the methyl group. There was a multiplet at δ 1.67–2.15 and an apparent quintet of triplets at δ 3.69. The latter absorption is assigned to the hydrogens of the methylene group which is bonded to sulfur. A solution prepared as outlined above was treated with aqueous sodium bicarbonate at −78°. The mixture was allowed to warm to room temperature, and di-*n*-propyl sulfone was found, 61%, by infrared, nmr, and glpc. The above data strongly support the contention that **7** has been formed and that it has the structure shown with the propyl groups trans to each other.

Treatment of diphenyl sulfide with **1** at −78° gave a material whose ^{19}F nmr spectrum had a single absorption at δ −64.5. It is believed that this is due to the presence of **8**. It was noted that conversion of the difluorodiphenylsulfurane was quite slow and a large excess of **1** was required.

The cyclic sulfides, **9–12**, have been allowed to react



9, 13, $n = m = 1$; R = H
10, 14, $n = m = 1$; R = CH_3
11, 15, $n = 1$; $m = 2$; R = H
12, 16, $n = 2$; $m = 2$; R = H

with excess **1** at −78° and in all cases persulfuranes, **13–16**, were formed. The persulfurane from **9** showed two kinds of fluorines in the ^{19}F nmr spectrum. There was a well-defined triplet at δ −84, $J_{\mathrm{F_aSF_b}}$ = 96.5 Hz, and a less well-defined triplet with considerable fine structure at δ −63, $J_{\mathrm{F_aSF_b}}$ = 97 Hz. The ^{1}H nmr spectrum showed two groups of multiplets at δ 2.0–2.35 and 4.4–5.0 in the ratio 2:3.9. Clearly two different fluorine environments are present in **13**, and thus the spectral data are in accord with the assigned structure.

Preparation of **14** allows assignment of the F_a and F_b resonances of **13**. The ^{19}F nmr spectrum of **14** had a three-line pattern at δ −85, a triplet of broad peaks at δ −72.8, and another triplet of multiplets at δ −60.6. These absorptions were in the ratio 1.95:1.0:1.0. The absorption at −85 is due therefore to the F_b fluorines, and, thus, in **13** the F_b fluorines are found at δ −84 and the F_a fluorines at δ −63. The ^{1}H nmr spectrum of **14** had a doublet at δ 1.3, J_{HCCH} = 7.0 Hz, which is assigned to the absorptions of the hydrogens of the methyl group. Three other complex absorptions were found at δ 2.4–3.0, 3.9–4.5, and 4.5–4.9.

Preparation of **15** proceeded smoothly to give a material whose ^{19}F nmr spectrum showed a sharp triplet at δ −98.2, $J_{\mathrm{F_aSF_b}}$ = 92.4 Hz, a triplet which was further split at δ −57.7, $J_{\mathrm{F_aSF_b}}$ = 92.4 Hz. By analogy to **13** and **14** the F_b fluorines can be tentatively assigned to those absorbing at δ −98.2. The ^{1}H nmr spectrum showed two complicated absorptions at δ 1.72–2.12 and 2.73–3.30. Similarly, **16** showed one sharp triplet at δ −118, $J_{\mathrm{F_aSF_b}}$ = 101 Hz; another triplet with slightly broader peaks was found at δ −49.1, $J_{\mathrm{F_aSF_b}}$ = 101 Hz. The ^{1}H nmr spectrum had three complex multiplets at δ 1.56–1.79, 2.03–2.23, and 3.50–3.69.

The above data all support the contention that **1** has reacted to give persulfuranes. In general warming solutions of these materials to room temperature leads to extensive decomposition to unidentified products. If trimethyl-*N*,*N*-diethylaminosilane[4] is added, decomposition is inhibited and solutions of the persulfuranes are stable for several weeks.

Previous preparations of persulfuranes have been limited to monoalkyl- and -arylpentafluoropersulfuranes and perfluorodialkylpersulfuranes,[5] and, thus, this report represents the first indication that the molecules of this report can be prepared and studied.

In most cases evidence was obtained for the formation of an intermediate, $R_2SF_3OCF_3$, which subse-

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[1] This research has been supported by the National Science Foundation and by Public Health Service Research Grant No. CA-10737 from the National Cancer Institute.

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