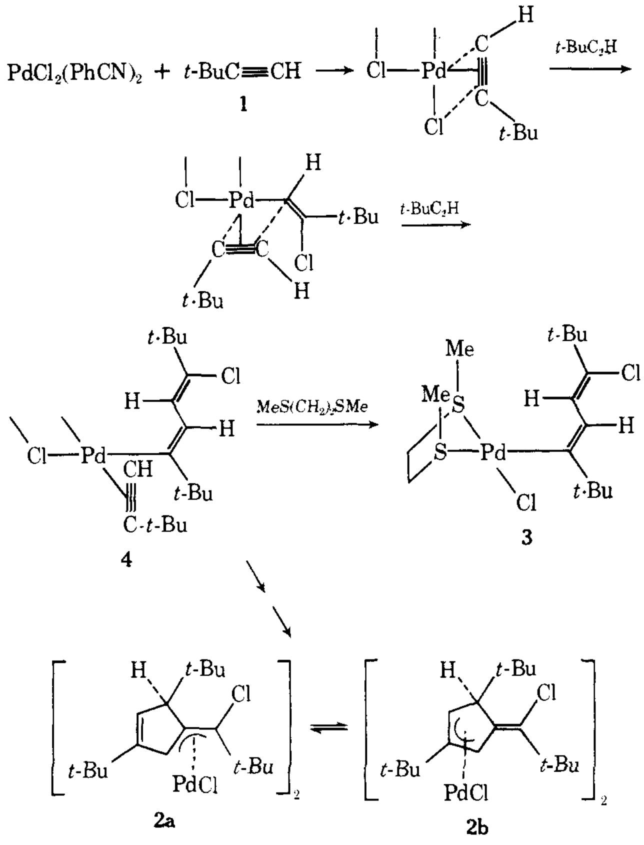
Scheme I



down the reaction of the Pd-butadienyl σ-bond with the coordinated acetylene in **4** thereby making it possible to isolate derivatives such as **3**; however, **4** is clearly an intermediate in the formation of **2**. The probable mechanism of this latter type of transformation has already been described in general terms[5] and will be further discussed in a full paper.

A noteworthy feature of the structure of **3** is an angle of 89.5° between the plane defined by the atoms Pd, S(1), S(2), Cl(1), and C(3) (rms deviation 0.031 Å) and the plane defined by C(3), C(4), C(5), and C(6) (rms deviation 0.026 Å). The distance of the hydrogen on C(5) (calculated assuming a trigonal geometry around C(5)) from the metal is 2.63 Å, and the angle H(5)-Pd-C(3) is 68°; this, together with the observation that the NMR resonance of this hydrogen is at anomalously low field (δ 7.18), indicates the possibility of an interaction between the metal and this hydrogen both in the solid state and in solution.[9,10]

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(10) NOTE ADDED IN PROOF. We have recently shown that a sample of complex **3**, made from $(CH_3)_3CC{\equiv}CD$, reacted with $(CH_3)_3C{\equiv}CH$ in the presence of Ag^+ (to remove Cl^-) to give 1,3,5-tri-*tert*-butylbenzene containing d_2 on the benzene ring. 1,3,5-Tri-*tert*-butylbenzene is the major product from the reaction of $PdCl_2(PhCN)_2$ and **1** in acetone [M. Avram, E. Avram, G. D. Mateescu, I. G. Dinulescu, F. Chiraleu, and C. D. Nenitzescu, *Chem. Ber.*, **102**, 3996 (1969)] and hence **4** is the likely intermediate both in its formation and that of **2**.

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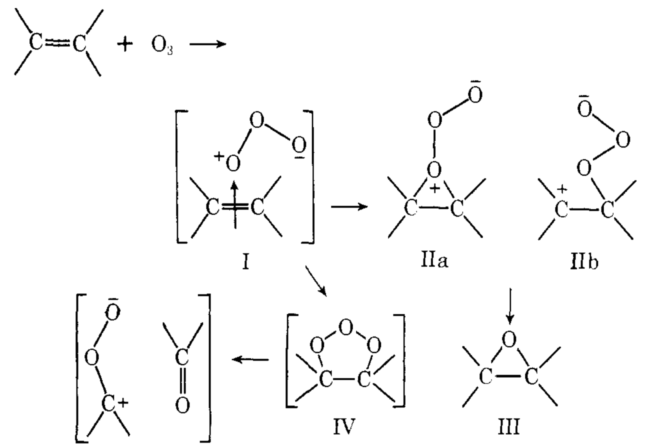
Ozonolysis of *cis*- and *trans*-1,2-Difluoroethylene. Stereoselectivity in Epoxide Formation

Sir:

We have found that *cis*-1,2-difluoroethylene oxide and formyl fluoride are the major products from the ozonolysis of both *cis*- and *trans*-1,2-difluoroethylene in methyl chloride. Lesser amounts of *cis*- and *trans*-1,2-difluoroethylene ozonide are formed as well as a trace product from the cis olefin which is identified as *cis*-1,2,3-trifluorocyclopropane. In isobutane solvent, a striking solvent effect was observed. The ozonide isomers and formyl fluoride are the major products, and the cis epoxide is the minor product from both olefin isomers. No trace of *cis*-1,2,3-trifluorocyclopropane could be detected in the products from the cis olefin in isobutane. A cis/trans ozonide ratio of approximately 10/90 was determined by gas chromatography for the ozonolysis of both olefin isomers in either solvent.[1]

Epoxides have been reported as products in the ozonolysis of olefins,[2-7] but the mechanism of their formation is not well-understood. Bailey and Lane[3] proposed that for sterically hindered 1-olefins a competition exists between 1,3-dipolar cycloaddition to give normal ozonolysis products via IV and electrophilic attack of ozone to give epoxide III via a π complex (I)[8] and possibly a σ complex (IIa or IIb).[9-11] Murray and Suzui found that *cis*- and *trans*-1-(1-naphthyl)-1-phenyl-1-propene gave epoxides stereospecifically with retention of configuration.[5] They suggested IIa as the intermediate although IIb is consistent if ring closure is faster than C-C bond rotation.



Different mechanisms were proposed for epoxide formation in the ozonolysis of olefins with halogen substituents at the double bond.[6,7] Gozzo and Camaggi found perfluoroethylene oxide and carbonyl fluoride as the major ozonolysis products of tetrafluoroethylene in perhalogenated solvents.[6] Polytetrafluoroethylene was also observed as well as minor amounts of perfluorocyclopropane and a trace of perfluoroethylene ozonide. An ionic mechanism was considered unlikely, and the results were rationalized in terms of a radical mechanism.[6,12] In this scheme, tetrafluoroethylene reacts with ozone to give difluorocarbonyl oxide[13] and carbonyl fluoride. The epoxide results from the olefin reacting with difluorocarbonyl oxide.[14] Deoxygenation of the difluorocarbonyl oxide leads to difluorocarbene which adds to tetrafluoroethylene to give perfluorocyclopropane. Griesbaum and Bruggemann suggested that in the ozonolysis of *trans*-2,3-dibromo-2-butene, 3,3-dibromobutanone (a rearrangement product of the trans dibromo epoxide) is formed by the reaction of a zwitterionic form of the carbonyl oxide with the olefin.[7]

The appearance of only one epoxide isomer, *cis*-1,2-difluoroethylene oxide, from the ozonolysis of *cis*- and *trans*-1,2-difluoroethylene indicates that, via the mechanism of Bailey and Lane,[3] the form IIb is the likely intermediate. However, it is possible that the epoxide is formed via an intermediate of type IIa in the case of the cis olefin. These results may also be explained by epoxidation of the olefin with fluorocarbonyl oxide if C–C bond rotation or bond breaking occurs in the olefinic C–C bond prior to epoxide formation. Isotopic labeling experiments are underway to test this possibility.

It is likely that *cis*-1,2,3-trifluorocyclopropane is formed by the addition of fluorocarbene to *cis*-1,2-difluoroethylene.[15] The carbene may be generated by loss of oxygen from fluorocarbonyl oxide via the mechanisms of Bailey and Lane[3] or Gozzo and Camaggi.[6] The possibility that *trans*-1,2,3-trifluorocyclopropane is formed from either the cis or trans olefin is under investigation.

The observed cis/trans ozonide ratio of 10/90 obtained from both *cis*- and *trans*-1,2-difluoroethylene can be rationalized by orbital symmetry arguments.[16] However, it does not correlate well with the general tendency of trans olefins to yield more trans ozonide as the olefin substituents become bulkier. This seems to indicate that the diaxial conformer of the trans initial ozonide is the most stable form in spite of the absence of bulky substituents. Perhaps this is a result of the anomeric effect in which halogen substituents of carbons bonded to oxygen prefer the axial site.[17] Microwave studies of the ozonide isomers should confirm the stereochemical assignment and determine whether the fluorine substituent prefers the axial or equatorial position in the final ozonides.[18]

In a typical reaction, 6 mmol of the olefin[19] were ozonized in 7 ml of solvent at −78° to 60% completion using ozone flow rates of 0.25–0.40 mmol of O_3/min.[20] The volatile products were separated from the solvent by low-temperature fractional distillation and further purified by GLPC using a 12 ft Teflon column packed with 10% Halocarbon oil on 40–60 mesh Chromosorb T at 25°. Formyl fluoride was identified by its known microwave and infrared spectra.[21,22] *cis*-1,2-Difluoroethylene oxide was characterized by spectral means. A number of b and c type transitions were observed in the microwave region and identified by their Stark effects. The rotational constants (MHz) which fit the observed transitions are $A = 9063.16 \pm 0.02$, $B = 5184.49 \pm 0.01$, and $C = 3857.93 \pm 0.01$. These values can be compared with those calculated from a reasonable molecular structure: $A = 8599$, $B = 4847$, and $C = 3584$.[23] The ^{19}F and ^{1}H NMR spectra are identical as expected for a $AA'XX'$ spin system and consist of six transitions located centrosymmetrically at 29.0, 41.1, and 69.3 Hz from the center. The ^{19}F and ^{1}H chemical shifts in acetone-d_6 are 165 ($CFCl_3$ external standard) and 5.81 ppm (TMS internal standard), respectively. The mass spectrum is in agreement with the molecular formula and with the published mass spectra of other fluorinated epoxides.[24] A strong band in the gas phase infrared spectrum at 1460 cm^{-1} is consistent with the group frequency (ascribed to a ring-breathing mode) found in the 1450–1600-cm^{-1} region for fluorinated cyclopropanes and fluorinated ethylene oxides.[24,25] *cis*- and *trans*-1,2-Difluoroethylene ozonide were characterized by infrared spectroscopy and mass spectrometry. In agreement with published gas phase infrared spectra of ozonides,[26] two strong bands between 1050 and 1150 cm^{-1} were observed for both isomers and the spectra lacked any significant carbonyl stretching absorption. Mass spectral fragmentation patterns were consistent with those observed for other ozonides.[27] *cis*-1,2,3-Trifluorocyclopropane has been identified by its strong symmetric top microwave spectrum. The J = 0–1, 1–2, 2–3, and 3–4 transitions were identified by their first- and second-order Stark effects. The rotational constant which fits the spectrum is 4064.86 ± 0.05 MHz. This value may be compared with a calculated rotational constant of 4006 MHz.[28] A dipole moment of 3.89 ± 0.08 D was determined from second-order Stark shifts of the J = 2–3 transition.[29]

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(29) Using the structure in ref 28, bond dipole calculations give a dipole moment of 4.70 D (C–F bond dipole = 1.41 D and C–H bond dipole = 0.4 D).

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Diffusion in Mixed Solvents. On the Viscosity Question[1]

Sir:

Linear plots of reaction rate constant vs. reciprocal of solvent viscosity have long been used as the classifying criteria for diffusion controlled reactions in fluid solution. These criteria in mixed hydroxylic solvents like glycerol and water have also been used to determine reaction mechanisms. Presented here are data which show that the above mentioned criteria are insufficient in many cases, where nonideal mixed solvent systems are used to increase solvent viscosity. Data correlations given below, suggest that the excess functions predominately determine the variation in reaction rate constants.

A mixed solvent study for the following irreversible reaction is reported

$$\mathrm{T} + \mathrm{Fe(CN)_6}^{3-} \xrightarrow{k_Q} \mathrm{P}^{+\cdot} + \mathrm{Fe(CN)_6}^{4-}$$

where T and $P^{+\cdot}$ are respectively the triplet state and radical monocation of zinc uroporphyrin. The reaction is charge controlled[2,3] and encounter limited in aqueous solution;[3] the distance of nonadiabatic electron transfer is 22 ± 4 Å, some 11 Å greater than the molecular radii.[3] Consequently, it is an ideal reaction with which to study nonequilibrium thermodynamics in fluid solution. The systems methanol-water and sucrose-water were chosen for reagent purity, compatibility with reactants, and the differences in the behavior of their excess functions.[4,5] For aqueous methanol,[4,6] ethanol,[4,6] and glycerol[6] systems, ΔG^E is positive, while $\Delta H^M > T\Delta S^E$ are negative; for the aqueous sucrose system,[5,7] the partial molal excess functions per mole of water are all negative, $\partial T\Delta S^E/\partial n_2 > \partial\Delta G^E/\partial n_2 > \partial\Delta H^M/\partial n_2$. Since small amounts of methanol or sucrose *increase* the observed rate constant, even though the viscosity is greater (Table I), the complete dependence on ΔG^E is negated (or k_Q would increase in one case and decrease in the other). The similar shapes[4,6] of the ΔH^M and $T\Delta S^E$ functions vs. methanol mole fraction (X_1) render determination of specific dependence on these functions impossible in this case, since there is no directly applicable theory of solutions. For sucrose, however, the partial molal excess enthalpy and entropy vs. sucrose mole fraction (X_1) functions are different in shape.[5] Figure 1 shows the dependence of the rate constants, k_Q, on the enthalpy and entropy excess functions, and viscosity for aqueous sucrose solutions. Similarly plotted data in methanol-water do not show such differences due to the similarity in the shapes of the excess functions; however, the nonagreement with the usual thoughts on reciprocal viscosity dependence is obvious (Table I).

Table I. Kinetic Parameters for Sucrose–Water and Methanol–Water Solvent Systems for the Reaction

$$\mathrm{T} + \mathrm{Fe(CN)_6}^{3-} \xrightarrow{k_Q} \mathrm{P}^{\cdot+} + \mathrm{Fe(CN)_6}^{4-}$$

X_1	$10^{-6}k_Q^{\mathrm{obsd}}$ $(M^{-1}\ \mathrm{sec}^{-1})^a$	$(k_Q^{\mathrm{obsd}}/k_Q^{\mathrm{H_2O}})_\mu{}^b$	η(cp)	ϵ^e
		Sucrose–Water[c]		
0	2.40	1	0.9[d]	79
0.0080	7.38	3.05	1.3[d]	75.6
0.0196	6.23	2.62	2.4[d]	74.0
0.0412	9.65	2.32	8.0[d]	65.5
0.0592	6.43	1.87	24.6[d]	61.8
		Methanol–Water[c]		
0.194	4.98	1.52	1.56[f]	64.5
0.360	3.28	1.14	1.52[f]	54.9
0.511	5.42	1.87	1.30[f]	47.5

[a] The ionic strength, μ, varied slightly, for different k_Q values: for the methanol–water data, $1.35 \times 10^{-3}\ m < \mu < 1.91 \times 10^{-3}\ m$; for the sucrose–water data, $1.07 \times 10^{-3}\ m < \mu < 1.9 \times 10^{-3}\ m$: there was no trend with X_1. For all determinations pH ⩾7. Errors in $k_Q^{\mathrm{obsd}} \leqslant \pm 10\%$. [b] Corrections for small differences in μ were made by dividing each k_Q by that for the same reaction in water, $k_Q^{\mathrm{H_2O}}$, as reported in ref. 3. For sucrose mole fraction 0.059, an ionic strength variation showed that the ionic charge product of T(–8) and $\mathrm{Fe(CN)_6}^{3-}$ is the same as in water solvent[1–3] (24 within experimental error). [c] All measurements 25°, k_Q values, 25 ± 1°. [d] H. A. Sober, Ed., "Handbook of Biochemistry", Chemical Rubber Co., Cleveland, Ohio, 1968, p j-248. [e] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 2nd ed, Reinhold, New York, N.Y., 1950 p 118. [f] International Critical Tables, 5:22, McGraw-Hill, New York, N.Y., 1929.

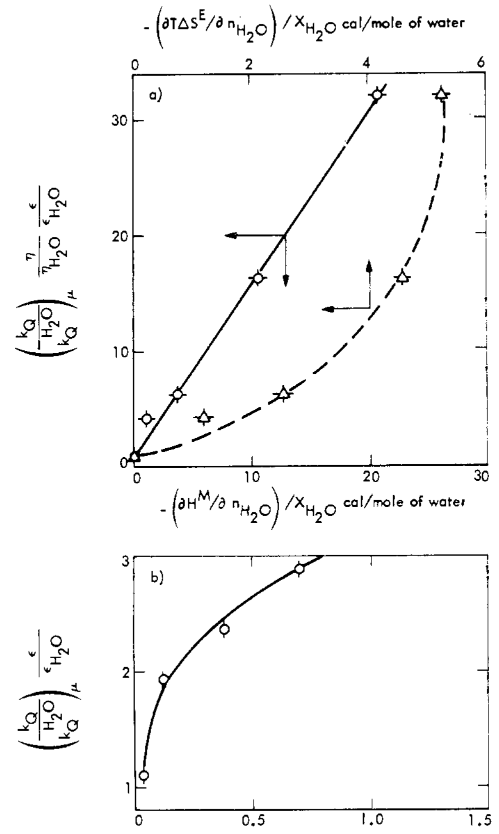

Figure 1. (a) Variation of the rate constant (k_Q) for the reaction $\mathrm{T} + \mathrm{Fe(CN)_6}^{3-} \rightarrow \mathrm{P}^{+\cdot} + \mathrm{Fe(CN)_6}^{4-}$ with the partial enthalpy of mixing and the partial excess entropy for the sucrose-water solvent system. (b) Variation of the rate constant (k_Q) with the reciprocal of the solvent viscosity for the sucrose-water solvent system. $(k_Q/k_Q^{\mathrm{H_2O}})_\mu$ is the rate constant in a given concentration of sucrose, divided by that in water for a given ionic strength (see footnotes *a* and *b* in Table I); η and ϵ are solvent viscosity and dielectric constant, respectively.