the existence of a *trans*-molozonide was established by its reduction to the corresponding glycol.[6] No such conclusive evidence has been found for the existence of a *cis*-molozonide, although Greenwood[12] has found some indication of their formation from simple *cis*-olefins.

It is our contention that the ozone–olefin π complex involving hindered *cis*-olefins, instead of always forming a molozonide which would force the bulky substituent groups even closer, has an additional, more attractive path open to it, that is, it may collapse to a σ complex (14), as illustrated for *cis*-diisopropylethylene (13), which we find gives a *cis*:*trans* ozonide ratio of 66:34.[13] We propose that this σ complex, or some variation of it, rearranges in a concerted stereospecific manner to *cis*-ozonide 8b, thus accounting for the high *cis*:*trans* ozonide ratio[1] and for the high yields of total ozonide from *cis*-olefins.[11,13] The observations that highly
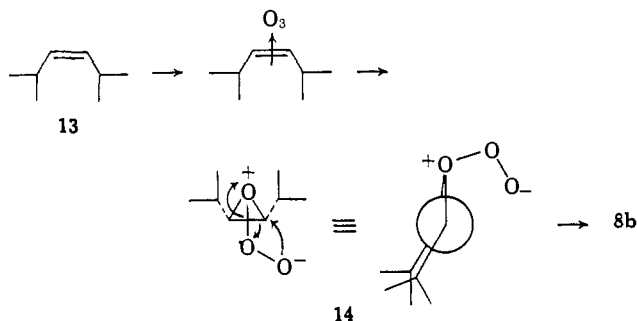
hindered olefins yield epoxides[4] and that ozonolysis of araucarolone diacetate[14] and Feist's acid[15] results in cleavage of the bond adjacent to the olefinic bond also support the σ-complex interpretation.

(11) G. Schröder, *Chem. Ber.*, **95**, 733 (1962).
(12) F. L. Greenwood and B. J. Haske, *Tetrahedron Letters*, 631 (1965).
(13) O. Lorenz and C. R. Parks, *J. Org. Chem.*, **30**, 1976 (1965), report a *cis*/*trans* ratio of 1.
(14) C. R. Enzell and B. R. Thomas, *Tetrahedron Letters*, 225 (1965).
(15) A. T. Bottini and J. D. Roberts, *J. Org. Chem.*, **21**, 1169 (1956).

Paul R. Story

Department of Chemistry, The University of Georgia
Athens, Georgia 30601

R. W. Murray, R. D. Youssefyeh

Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey 07971

Ozonolysis. VIII. Alkene and Ozonide Geometry in the Alkene–Ozone Reaction

Sir:

It has become clear that alkene geometry plays an important role in determining the course of the alkene–ozone reaction. Alkene geometry is important in determining the stability of the molozonide,[1] and with symmetrically disubstituted alkenes it appears to control the amount of reactants that are converted to ozonide. Schröder[2] first noted this with *cis*- and *trans*-di-*t*-butylethylene. In the current studies with the *cis* and *trans* isomers of 2-butene, 2-pentene, and 3-hexene it was uniformly true that, under the same experimental conditions, the *cis* isomer gave superior yields of ozonide.

(1) R. Criegee and G. Schröder, *Chem. Ber.*, **93**, 689 (1960); F. L. Greenwood, *J. Org. Chem.*, **29**, 1321 (1964); F. L. Greenwood, *ibid.*, **30**, 3108 (1965).
(2) G. Schröder, *Chem. Ber.*, **95**, 733 (1962).

Specifically, *cis*-3-hexene was converted to ozonide in 85% yield, whereas from the *trans* isomer 45% was the best yield obtainable. Comparable conversions to ozonide were realized with the other alkenes, with the best yields of ozonide from *cis* alkenes being obtained from a hydrocarbon solvent and from an ether solvent in the case of the *trans* alkenes.

With the development of a column for vapor phase chromatography which effected the complete separation of the stereoisomeric ozonides, it became possible to examine the relationship between alkene geometry and ozonide geometry. Typical data for 3-hexene and 2-butene are given in Table I. An interesting solvent effect which would appear to be dependent on nucleophilicity and not polarity is apparent in the data of Table I (n-C_5H_{12}, $\mu < 0.05$ D.; CH_2Cl_2, $\mu = 1.47$ D.; Et_2O, $\mu = 1.18$ D.; Me_2O, $\mu = 1.31$ D.).

Table I. Stereoisomeric Ozonides from *cis*- and *trans*-Alkenes[a]

Alkene	Reaction temp, °C	Solvent	Ozonide isolated, mmoles	% stereoisomeric ozonides[b] α form	% stereoisomeric ozonides[b] β form
cis-3-Hexene	−30	n-C_5H_{12}	44	52	48
	−30	Et_2O	40	62	38
trans-3-Hexene	−30	n-C_5H_{12}	11	59	41
	−30	CH_2Cl_2	12	54	46
	−30	Et_2O	22	66	34
	−70	Et_2O	21	67	33
	−110	Et_2O	18	66	34
cis-2-Butene	−30	n-C_4H_{10}	36	65	35
	−70	Me_2O	31	71	29
trans-2-Butene	−30	n-C_4H_{10}	18	66	34
	−70	Me_2O	17	70	30

[a] All data are calculated on the basis of 50 mmoles of ozone reacting with excess alkene. [b] Present information does not permit unambiguous assignment of configuration. The α form is the stereoisomer of shorter retention time.

The ozonation of 2-pentene, as reported earlier[3] for a *cis*–*trans* mixture of the alkene, becomes complicated by the fact that now three ozonides, *i.e.*, 2-butene ozonide, 2-pentene ozonide, and 3-hexene ozonide, are formed. The solvent has a much more striking effect on the relative amounts of these three ozonides than does alkene geometry, as is illustrated in Table II. It is clear that the formation of "crossed-ozonides" is much more pronounced in the ether solvent.

2-Pentene geometry does appear to influence the relative proportions of stereoisomeric ozonides more in the hydrocarbon solvent than in the ether solvent. This is evident from the data of Table III.

The above-described results were obtained by treating *ca.* 40 mmoles of alkene in 200–250 ml of solvent with 90–95% of the theoretical amount of ozone which was introduced at the rate of *ca.* 600 mg/hr. The solvent was removed *in vacuo* on a rotary evaporator with the reaction flask in a bath which was maintained at −50 to −70°, depending on the solvent. The ozonide was collected in a liquid nitrogen cooled trap *in vacuo* on the rotary evaporator by permitting the reaction flask to warm to 25°, and the ozonide subsequently was distilled *in vacuo*. All analyses were performed on the sample of distilled ozonide. The residue remaining in

(3) L. D. Loan, R. W. Murray, and P. R. Story, *J. Am. Chem. Soc.*, **87**, 737 (1965).

Table II. Ozonides from cis- and trans-2-Pentene[a]

Alkene	Reaction temp, °C	Solvent	2-Butene ozonide, mmoles	2-Pentene ozonide, mmoles	3-Hexene ozonide, mmoles
cis-2-Pentene	−30	n-C$_4$H$_{10}$	1.8	36	3.7
	−70	Me$_2$O	10	21	8.8
trans-2-Pentene	−30	n-C$_4$H$_{10}$	0.83	14	2.7
	−70	Me$_2$O	7.1	12	4.0

[a] Cf. footnote a, Table I.

Table III. Relative Amounts (%) of the Stereoisomeric Ozonides in the Ozonides from 2-Pentene

Alkene	Reaction temp, °C	Solvent	2-Butene ozonide[a] α form	β form	2-Pentene ozonide[a] α form	β form	3-Hexene ozonide[a] α form	β form
cis-2-Pentene	−30	n-C$_4$H$_{10}$	56	44	58	42	48	52
	−70	Me$_2$O	71	29	66	34	60	40
trans-2-Pentene	−30	n-C$_4$H$_{10}$	68	32	60	40	58	42
	−70	Me$_2$O	73	27	64	36	60	40

[a] Cf. footnote b, Table I.

the reaction flask was peroxidic oligomer. Authentic specimens of 2-butene ozonide and 3-hexene ozonide were established by carbon–hydrogen analysis, molecular weight, infrared absorption, and nmr spectra.

It was Schröder[2] who, on the basis of stereochemical studies, first questioned the complete validity of the Criegee ozonolysis mechanism. This mechanism makes no provision for stereochemical effects, and it is obvious that a successful ozonolysis mechanism must do so. It is rather unrewarding to indulge in such speculation until the configurations of the stereoisomeric ozonides can be established unambiguously, and such experiments are now in progress.

Fred L. Greenwood

Department of Chemistry, Tufts University
Medford, Massachusetts

Viscosity Studies on the Behavior of Inorganic Iron Polymers in Aqueous Solution

Sir:

The isolation of a rather homogeneous polymer of iron hydroxy nitrate has recently been achieved.[1] Examination of this inorganic polymer by electron microscopy revealed that the dry polymer exists as discrete spheres whose diameters varied from 60 to 110 A, with a mean of 65 A. We wished to determine if the polymers also exist as spherical units in solution and therefore carried out a series of viscosity experiments to determine the specific viscosity, η_{sp}, over a range of concentrations. We also measured the partial specific volume, $\bar{v}$, of this polymer by means of density determinations. With these two results we have been able to demonstrate that freshly prepared inorganic iron hydroxy nitrate polymers behave as spheres with about a 7% hydration shell.

Viscosity measurements were carried out using a modified Fenske viscosimeter with an emptying time of 501.7 sec for water at 20.85°. All measurements were carried out in a water thermostat, regulated at 20.85 ± 0.01°. Flow times were such that kinetic energy corrections could be ignored. The density,

(1) T. G. Spiro, S. E. Allerton, J. Renner, A. Terzis, R. Bils, and P. Saltman, J. Am. Chem. Soc., 88, 2721 (1966).

and thus the $\bar{v}$, of the iron polymer was determined using a 25-ml pycnometer fitted with a thermometer and calibrated in the usual fashion. Iron polymer was prepared as described in a previous communication[1] from a solution in which the hydroxide/iron ratio was 2:1. The material was isolated by Sephadex gel filtration and dried by lyophilization. Independent determinations of iron, hydroxide, and nitrate ions were carried out as described previously and yielded values corresponding to an empirical formula [Fe(OH)$_{2.5}$-
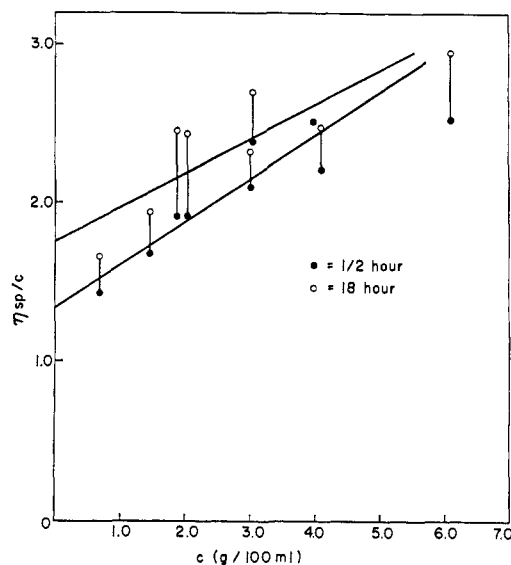

Figure 1. The reduced specific viscosity, η_{sp}/c, as a function of concentration of polymer, c, The limiting viscosity numbers are $[\eta] = 1.32$ and 1.75 ml/g for the freshly prepared and aged solutions, respectively. The lines were obtained by analyzing the data in the concentration range from 0 to 5 g/100 ml by the method of least squares.

(NO$_3$)$_{0.5}$]$_n$. Solutions for viscosity and density measurements were prepared by dissolving the dried solid in a solution 0.01 N in nitric acid and 0.6 M in potassium nitrate. Concentrations of iron in solution were determined analytically following both the viscosity and pycnometer measurements.

Figure 1 presents the results of the reduced specific viscosity, η_{sp}/c, as a function of concentration, c. The initial viscosities were measured 30 min after the