

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
<i>cis</i> -2-Pentene	-30	<i>n</i> -C ₄ H ₁₀	1.8	36	3.7
	-70	Me ₂ O	10	21	8.8
<i>trans</i> -2-Pentene	-30	<i>n</i> -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		2-Pentene ozonide ^a		3-Hexene ozonide ^a	
			α form	β form	α form	β form	α form	β form
<i>cis</i> -2-Pentene	-30	<i>n</i> -C ₄ H ₁₀	56	44	58	42	48	52
	-70	Me ₂ O	71	29	66	34	60	40
<i>trans</i> -2-Pentene	-30	<i>n</i> -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 Schröder² 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.

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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 Å, with a mean of 65 Å. 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. Bills, 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 communication¹ 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-

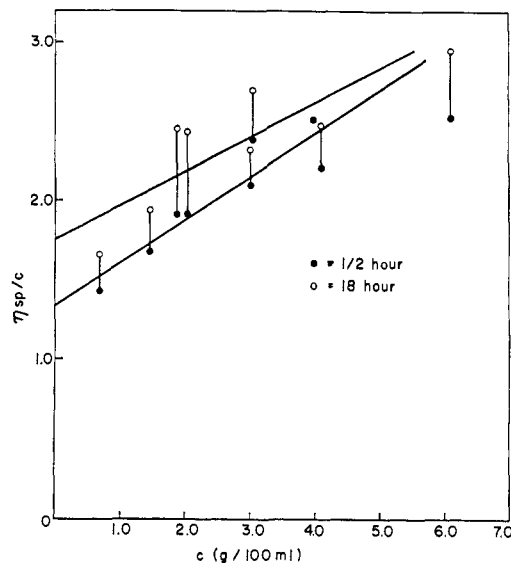


Figure 1. The reduced specific viscosity, η_{sp}/c , as a function of concentration of polymer, c . The limiting viscosity numbers are $[\eta] = 1.32$ and 1.75 ml/g for the freshly prepared and aged solutions, respectively. The lines were obtained by analyzing the data in the concentration range from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

(NO₃)_{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

preparation of the solution; 16 to 18 hr later, the viscosities were measured again. It will be noted from the figure that the viscosity had increased appreciably. The increase in viscosity observed with time appears to arise from formation of aggregates of polymer as well as hydration and change of configuration. Observation by electron microscopy of the aged preparations revealed aggregated particles with a spongy appearance.

The density increment, k_D , was found to be independent of concentration in the range from 0 to 5 g/100 ml. Its measured value was 0.53. Since $k_D = 1 - \bar{v}\rho_0$ (ρ_0 is the density of the solvent, 1.03393 g/ml), \bar{v} is equal to 0.456. It is known that $[\eta] = \nu\bar{v}$, where ν is the viscosity increment. From our data, ν equals 2.9. Einstein demonstrated² that ν for a nonhydrated sphere equals 2.5, and deviations from this value are indicative of either hydration or asymmetry. It follows therefore that the iron polymers in freshly prepared solution are behaving as spheres with approximately 7% bound water, by weight. Using the more accurate values for \bar{v} obtained in this work, the molecular weight of the iron hydroxy nitrate polymer from ultracentrifugation measurements is 1.5×10^5 , and by direct visualization with electron microscopy is 2.1×10^5 . The concentration dependence of reduced specific viscosity observed in Figure 1 is anomalous and is suggestive of polymer-polymer interaction. However, the agreement of molecular weights obtained by sedimentation equilibrium studies on solutions containing 4 g/100 ml of polymer and by electron microscopy of very dilute solutions suggests that the dependence does not arise from aggregation of polymer units.

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(2) A. Einstein, "Investigations on the Theory of the Brownian Movement," Dover Publications, Inc., New York, N. Y., reprinted 1956, pp 49-56.

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A 4-Phenoxyphenoxy Radical and an Example of Hindered Aryl Ether Rotation

Sir:

The mechanism of the oxidative coupling of phenols has been under study in these laboratories.¹ One of the postulated mechanisms for this reaction involves the transfer of an electron across a diaryl ether bond.² This would appear unlikely in a radical reaction because a charge separation must be made with a conse-

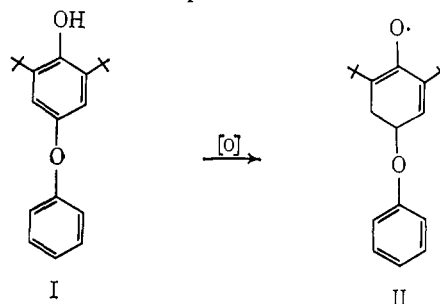
(1) A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, *J. Am. Chem. Soc.*, **81**, 6335 (1959); G. F. Endres and J. Kwiatak, *J. Polymer Sci.*, **58**, 593 (1962).

(2) H. L. Finkbeiner, G. F. Endres, H. S. Blanchard, and J. W. Eustance, *SPE Trans.*, **2**, 112 (1962); W. A. Butte, Jr., and C. C. Price, *J. Am. Chem. Soc.*, **84**, 3567 (1962).

quent expenditure of energy. It was with a view toward examining the possibility of such an electron jump that this work was undertaken.

The *o*-alkylation method of Kolka, *et al.*,³ was used to prepare 4-phenoxy-2,6-di-*t*-butylphenol (I) from *p*-phenoxyphenol and isobutylene. This reaction is slow and required the application of heat to achieve completion. White crystals of I were obtained by recrystallization from hexane, mp 132-133°, in 90% yield. *Anal.* Calcd for $C_{20}H_{26}O_2$: C, 80.5; H, 8.7; mol wt, 298. Found: C, 80.8; H, 8.8; mol wt, 286.

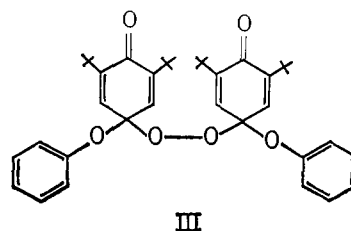
The phenol I could be oxidized to a stable free radical (II), in the absence of oxygen, with a variety of oxidizing agents. The method of choice is alkaline potassium ferricyanide. The esr spectrum of radical II (Figure



1) is a strong triplet due to the coupling of the electron spin to the two *meta* protons on the top ring as shown in the illustration. The splitting constant is 1.05 gauss, which is comparable with 1.8 gauss for *t*-butylphenoxy and 1.0 gauss for 4-*t*-butoxy-2,6-di-*t*-butylphenoxy.⁴ The radical is stable in the absence of air and a strong signal could still be obtained from the sample after 6-weeks storage at room temperature. The visible spectrum exhibited a broad maximum at $533 \text{ m}\mu$ ($\epsilon 150$).

Two factors argue against any appreciable electron density achieving a "jump" across the aryl ether linkage. There was no detectable interaction of the electron with the hydrogens on the phenoxy ring. The stability of the radical also means that the electron is localized on the hindered ring, otherwise dimerization reactions through the phenoxy ring would be expected.

The radical behaves normally by being converted to the peroxide III when the directions of Cook⁵ are followed. A white solid, mp 109-110°, is obtained which has the structure III. *Anal.* Calcd for $C_{40}H_{50}O_6$: C, 76.7; H, 8.0. Found: C, 76.4; H, 7.8.



Hydrolysis of this material in 95% ethanol yields phenol and 2,6-di-*t*-butylbenzoquinone. The hydrogen peroxide was not observed.

(3) A. J. Kolka, J. P. Napolitano, A. H. Filbey, and G. G. Eike, *J. Org. Chem.*, **22**, 642 (1957).

(4) E. Müller, H. B. Stegmann, and K. Scheffler, *Ann.*, **645**, 79 (1961).

(5) C. D. Cook, D. A. Kuhn, and P. Fianu, *J. Am. Chem. Soc.*, **78**, 2002 (1956).