

TABLE I
 RESULTS OF VICINAL DIOL AND ALCOHOL OXIDATION WITH XENIC ACID^a

	pH							Products
	2 N H ₂ SO ₄	2.82	4.48	6.2	8.62	11.1	12.2	
Ethylene glycol	NR	V.S.	+	++	+++	++	+	CO ₂ ^b
2,3-Butanediol	NR	NR	+	++	+++	NR	+	Acetaldehyde, ^c acetate ^d
Sodium tartrate	NR	NR	+	++	+++	+	++	Oxalate and CO ₂
Sodium oxalate	NR	NR	+	++	+++	NR	NR	CO ₂
Pinacol hydrate	NR	NR	NR	+	++	++	+++	Acetone ^e and at high pH some acetate
Acetone	NR	NR	NR	NR	NR	NR	+	Only at high pH yields acetate
Acetate	NR	NR	NR	NR	NR	NR	NR	Acetate
<i>t</i> -Butyl alcohol	NR	NR	NR	NR	NR	NR	NR	<i>t</i> -Butyl alcohol
Acetaldehyde	NR	NR	+++	+++	+++	+++	+++	Acetate
Ethanol	V.S.	V.S.	+	+	+	++	++	Acetate
Isopropyl alcohol	NR	NR	NR	+	+	+	++	CO ₂ and acetone

^a Notations: NR—no reaction; V.S.—very slow; +—slow; ++—moderate; +++—fast. ^b Detected as CaCO₃ by Conway distillation method. ^c Detected by the nitroprusside spot test: Fritz, Fergl, and R. E. Oesper, "Spot Tests in Organic Analysis," Elsevier Publishing Company, Amsterdam, 1956, p. 334. ^d Detected by conversion to acetaldehyde. ^e Detected as the derivative of 2,4-dinitrophenylhydrazine.

of magnitude as that of periodic acid. Since periodate is highly specific for the oxidation of *vic*-diols as first observed by Malaprade⁵ and reviewed by Jackson,⁶ similar behavior of xenic acid toward *vic*-diols is expected. Thus, qualitative studies of *vic*-diol oxidation with xenic acid have been initiated and the results are reported.

Qualitative studies of xenic acid reactions with *vic*-diols were carried out by adding two drops of 0.02 *M* xenic acid to 3 ml. of 0.01 *M* *vic*-diol buffered solution. After 5 min. approximately 2.0 ml. of acid potassium iodide was added, and the absorbance of the triiodide was related to the apparent speed of the reaction at various pH's. The absence of the triiodide color indicates that all of the xenic acid was consumed by the organic compound while the presence of the triiodide color indicates an excess of xenic acid. The results of the xenic acid reaction with *vic*-diols and some selected organic compounds are summarized in Table I.

Xenic acid reacts readily with *vic*-diols and primary alcohols in neutral or basic solutions. However, no reaction is observed in acidic solutions. Periodic acid does not oxidize *vic*-diols in acid solutions as shown by the kinetic studies of Duke and Bulgrin,⁷ Buist and Bunton,⁸⁻¹⁰ and Zuman, *et al.*^{11,12} In fact, qualitative studies indicate that some *vic*-diols, for example, 2,3-butanediol, may react with xenic acid in a manner analogous to their reaction with periodic acid. An analysis of the oxidation products of xenic acid with *vic*-diols yields xenon gas and carboxylic acids or carbon dioxide from the terminal alcohol group. However, the periodic acid oxidation of *vic*-diols yields aldehydes, and the periodate is reduced to iodate. This marked difference in the reaction products of xenic acid and periodate with *vic*-diols can be attributed to the lack of stable intermediate oxidation states of xenon in aqueous solutions below

xenon(VI). Polarographic reduction of xenic acid at the dropping mercury electrode confirms this, as reported by Jaselskis.¹³

Xenic acid has potential not only as an analytical reagent for *vic*-diols but also as a preparative agent for certain organic acids.

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(13) B. Jaselskis, *Science*, **143**, 1324 (1964).

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One-Electron Transfer from an Olefin to a Dicarbanium Ion

Sir:

Most electron-transfer reactions that involve aromatic π -systems fall into one of two kinetic categories; either the rates are extremely fast as measured by e.s.r. techniques, or they are too slow to fall within this measurement range.¹ We wish to report an electron transfer from an olefin to a dicarbanium ion in which the net reaction is some 10⁵ to 10⁷ slower than previously measured exchange rates.

Some years ago, Weitz and Schmidt² observed that when a solution of tetraphenyl-*p*-xylylene (I) and its dichloride were mixed in liquid SO₂, the solutions, originally yellow, became an intense reddish brown.

(1) Examples of rapid rates (10⁷ to 10⁹ l. mole⁻¹ sec.⁻¹) are between naphthalene and naphthalene anion [R. L. Ward and S. Weissman, *J. Am. Chem. Soc.*, **79**, 2086 (1957)], sodium benzophenone ketyl and benzophenone [this reaction involves sodium atom transfer: F. C. Adam and S. I. Weissman, *ibid.*, **80**, 1518 (1958)], tris-*p*-nitrophenylmethyl radical and the corresponding carbanion [M. T. Jones and S. I. Weissman, *ibid.*, **84**, 4269 (1962)], ferrocene and ferrocenium cation [D. R. Stranks, *Discussions Faraday Soc.*, **29**, 73 (1960)]. Other very fast exchanges for which rate constants are less accurately known are cyclooctatetraene radical-anion and dianion [H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 2360 (1963); T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, **32**, 1873 (1960)] and certain monocyclic aromatics and their radical-anions [T. R. Tuttle, Jr., and S. Weissman, *J. Am. Chem. Soc.*, **80**, 5342 (1958)]. Although rates are not reported, many other disproportionations must be very rapid [see, e.g., G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **84**, 4155 (1962)]. The rates of these reactions are often complicated by solvent and metal ion effects.

Examples of slow exchange rates are between cyclooctatetraene and its radical-anion [H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *ibid.*, **85**, 2360 (1963)] and naphthalene radical-anion and the corresponding dianion [S. I. Weissman, quoted in footnote 32 of the previous reference].

(2) E. Weitz and F. Schmidt, *Ber.*, **75**, 1921 (1942); see also the review article by E. Weitz, *Angew. Chem.*, **66**, 658 (1954).

(4) E. V. Appelman and J. G. Malm, private communication.

(5) M. L. Malaprade, *Bull. soc. chim. France*, **43**, 683 (1928).

(6) E. L. Jackson in R. Adams, Ed., "Organic Reactions," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 341.

(7) F. R. Duke and V. C. Bulgrin, *J. Am. Chem. Soc.*, **76**, 3803 (1954).

(8) J. G. Buist and C. A. Bunton, *J. Chem. Soc.*, 1406 (1954).

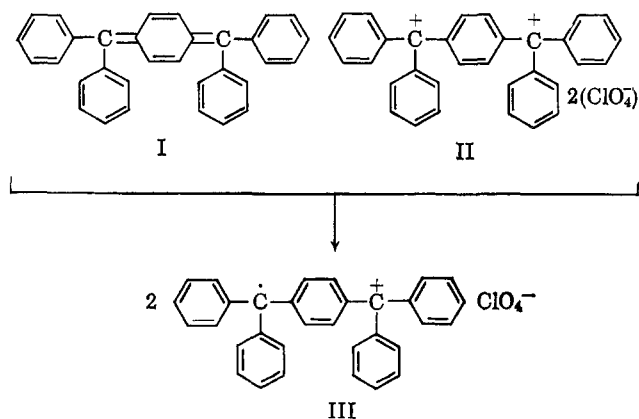
(9) J. G. Buist, C. A. Bunton, and J. H. Miles, *ibid.*, 4567, 4575 (1957).

(10) C. A. Bunton and J. G. Buist, *ibid.*, 4580 (1957).

(11) P. Zuman and J. Krupicka, *Collection Czech. Chem. Commun.*, **23**, 598 (1958).

(12) P. Zuman, J. Sicher, J. Krupicka, and M. Svoboda, *ibid.*, **23**, 1257 (1958).

The latter color was presumably due to the formation of radical-ion III.³



Tetraphenyl-*p*-xylylene (I)⁴ in methylene chloride has a single absorption at 424 $m\mu$ ($\log \epsilon$ 4.68), whereas crystalline perchlorate II,⁵ in the same solvent, has maxima at 424 $m\mu$ ($\log \epsilon$ 4.50) and 463 $m\mu$ ($\log \epsilon$ 4.57). Upon mixing carefully degassed equimolar solutions of I and II, one obtains a dark red solution which has a new band at 580 $m\mu$, as well as maxima at 467 and 424 $m\mu$. If one assumes that this spectrum is due to III only, $\log \epsilon$ is 3.64, 4.23, and 4.17,⁶ respectively. The e.s.r. spectrum is shown in Fig. 1.⁷ Although a

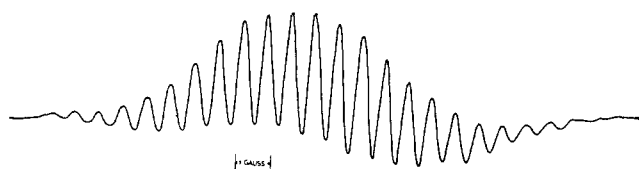


Fig. 1.—The e.s.r. spectrum of III at -90° ($4 \times 10^{-3} M$ solution in methylene chloride).

good signal was obtained at ambient temperature, resolution was improved by lowering the temperature. It is hoped that further experimentation with dilution, solvents, and temperature will improve the resolution, but 23 equally spaced lines with ΔH of 0.69 gauss are clearly visible.

Two syringes of equal size connected to separate arms of a capillary Y-tube were filled (argon atmosphere) with $10^{-3} M$ solutions of I and II. At this dilution, the solutions appeared pale yellow in the arms of the capillary tube. The plungers on the syringes were simultaneously and rapidly depressed; at the Y-juncture and 5 cm. beyond, the solution remained pale yellow, although it was dark red in the collection syringe attached to the third arm of the Y. When flow was

(3) In the nomenclature of the time, III was referred to as a meriquinoid salt. Presumably the same species was produced when the dichloride was treated with silver perchlorate or zinc chloride and I in benzene-chloroform. Other significant results in the earlier report² are (a) the solution is rapidly decolorized by oxygen; (b) it is converted by chlorine to the dichloride; and (c) the dichloride and I do not react in a nonpolar solvent.

(4) H. Staudinger, *Ber.*, **41**, 1355 (1908).

(5) Prepared from the dichloride and silver perchlorate in methylene chloride, and recrystallized at dry ice temperature from this solvent.

(6) Since I and II do not absorb at 580 $m\mu$, it is easy to show that the amount of species which absorbs at this wave length must be present at least to the extent of 64%; any concentration less than this would be meaningless in that it would require that the same species have a negative absorbance at 424 $m\mu$. It seems likely that the equilibrium between I + II and III lies largely, if not entirely, to the right.

(7) We are indebted to H. Kuska for assistance in obtaining this spectrum. The instrument was a Varian Model V-4500-10A e.p.r. spectrometer. Neither I nor II gives an e.s.r. signal.

stopped, the solution in the capillary beyond the juncture became dark red within 3 sec. Thus the half-life for production of the radical-ion is approximately 3 sec. and, if the reaction is bimolecular, its rate constant is roughly 300 l. mole⁻¹ sec⁻¹ at room temperature. Kinetic studies are therefore possible and are being undertaken.

When equal volumes of $10^{-3} M$ methylene chloride solutions of I and II were mixed and evaporated to dryness, a dark red residue was obtained which had an infrared spectrum (KBr pellet, prepared in an inert atmosphere) with several bands different from those of I or II. In particular, III had a sharp, intense band at 7.94 μ and a strong broad band at 12.25–12.50 μ .⁸ The solid gave a broad e.s.r. signal, but dissolution in methylene chloride led to e.s.r. and visible spectra identical with those described above.^{9–11}

(8) Also present were numerous sharp bands approximately common to I and II in the 3–4 and 6–7.4 μ regions and a broad intense band at 8.7–9.8 μ (perchlorate) present in II but not I.

(9) This work is being extended to various combinations of the 30–34 electron system on the tetraphenylxylyl framework. It is anticipated that suitable substitution should vary the electron-transfer rate and, in certain cases, lead to the transfer of more than one electron.

(10) It has recently been recognized (S. Hunig, H. J. Friedrich, D. Scheut-zow, and W. Brenninger, *Tetrahedron Letters*, 181 (1964)) that similar one-electron transfers can be accomplished in π -systems of the cyanine type; no rates are reported.

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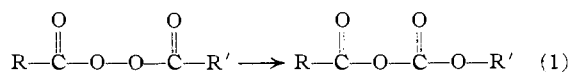
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Mechanisms of Decomposition of Diacyl Peroxides¹

Sir:

Thermal decomposition of diacyl peroxides is normally considered to proceed by a homolytic mechanism.² Exceptions are the rearrangement of unsymmetrical diaroyl peroxides in polar solvents³ and decomposition catalyzed by Lewis acids⁴ (eq. 1).



The large body of detailed experimental work on aliphatic diacyl peroxides has been interpreted^{2,5} principally in terms of homolytic decomposition and/or direct conversion of peroxide to ester (frequently a major product).

We have ascertained that the *major* path of decomposition of the *symmetrical* aliphatic diacyl peroxide

(1) This work was supported in part by the Atomic Energy Commission under contract No. AT(30-1)-905.

(2) A. G. Davies, "Organic Peroxides," Butterworths, London, 1961; E. G. E. Hawkins, "Organic Peroxides, Their Formation and Reactions," E. and F. Spon Ltd., London, 1961; C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

(3) J. E. Leffler and C. C. Petropoulos, *J. Am. Chem. Soc.*, **79**, 3068 (1957); D. B. Denney, *ibid.*, **78**, 590 (1956); J. E. Leffler, *ibid.*, **72**, 67 (1950); D. B. Denney and D. Z. Denney, *ibid.*, **79**, 4806 (1957); W. Honsberg and J. E. Leffler, *J. Org. Chem.*, **26**, 733 (1961).

(4) (a) D. Z. Denney, T. M. Valega, and D. B. Denney, *J. Am. Chem. Soc.*, **86**, 46 (1964); (b) J. T. Edwards, H. S. Chang, and S. A. Samad, *Can. J. Chem.*, **40**, 804 (1962); (c) R. Huisgen and W. Edl, *Angew. Chem.*, **74**, 588 (1962); (d) J. K. Kochi, *J. Am. Chem. Soc.*, **85**, 1958 (1963).

(5) (a) M. S. Kharasch, J. Kuderna, and W. Nudenberg, *J. Org. Chem.*, **19**, 1283 (1954); H. J. Dauben, Jr., and H. T. Liang, *Hua Hsueh Hsueh Pao*, **25**, 136 (1959); *Chem. Abstr.*, **54**, 4365f (1960); (b) F. D. Greene, *J. Am. Chem. Soc.*, **77**, 4869 (1955); (c) D. F. DeTar and C. Weis, *ibid.*, **79**, 3045 (1957); (d) H. H. Lau and H. Hart, *ibid.*, **81**, 4897 (1959); (e) H. Hart and F. J. Chloupek, *ibid.*, **85**, 1155 (1963); (f) R. C. Lamb and J. G. Pacifici, *ibid.*, **86**, 914 (1964).