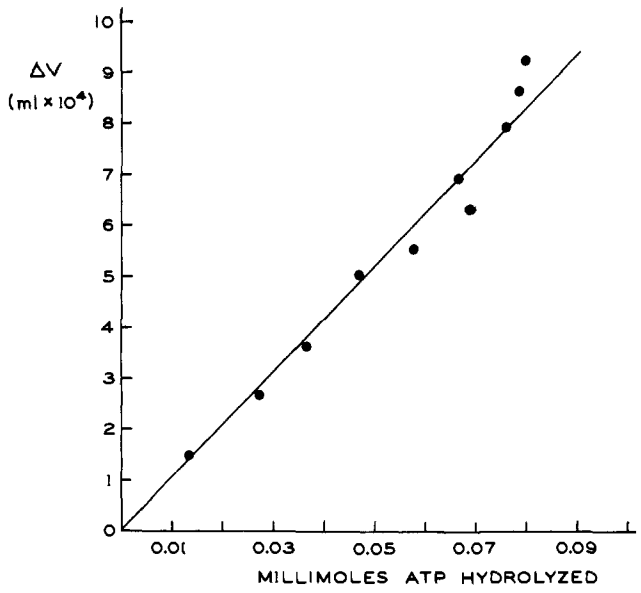

Figure 2.

where ϕ is the number of protons released per mole of P_i generated, R_i is the fraction of ϕ neutralized by buffer i, and ΔV_i is the molar volume change of ionization of said buffer, we have to evaluate also the contributions of the buffers. The buffer systems are tris(hydroxymethyl)aminomethane, maleate, and protein (roughly equivalent to 3 mmoles of histidine), and, in principle, the contribution from each is calculable. The buffer correction may be obtained *in toto*, however, by measuring ϕ and by measuring separately the volume change which occurs when ϕ moles of H^+ are added to the buffer mixture. From the simultaneous measurement of H^+ generated (pH stat) and P_i generated (colorimetric assay) under the aforesaid conditions we estimate $\phi = 0.60$. Under rather similar experimental conditions Green and Mommaerts[6] also obtained 0.6; ϕ calculated[4] from published ionization constants is about 0.67. By measuring the volume change when HCl is added to the buffer mixture (the protein buffer makes little difference in this measurement) we obtain $\sum_i R_i \Delta V_i = 12.8$ ml./mole of H^+. Therefore, under our ionic strength and pH conditions

$$\Delta V_{\text{dephosph}} = 10.9 \text{ ml./mole} + 0.6 \times 12.8 \text{ ml./mole} = 18.6 \text{ ml./mole of ATP split}$$

This value is not unreasonable, considering the ionic character of the dephosphorylation.[7] The only previous measurements[8,9] of this quantity we have found give a value of 10.5 ml./mole, a value close to our apparent (uncorrected) value. Evidently no buffer corrections were made on these earlier results which, in addition, were carried out with relatively crude enzyme preparations.

If the volume change due to the structural effect occurred instantaneously upon tilting the dilatometer (at $t = 0$), curves of Fig. 1 extrapolated to $t = 0$ should give an intercept which should be the "ΔV of superprecipitation."

With our technique the earliest measurement was made at 35 sec., so we cannot be sure of the instantaneous character of the reaction. However, when we make the extrapolation, the intercept found is not significantly different from zero.

The result of our experiments is a reasonable estimate of the ΔV of dephosphorylation. At face value our results indicate that the "ΔV of superprecipitation" might be zero; we conclude, however, that conventional dilatometry is probably inadequate to measure the ΔV of superprecipitation. The basic difficulty is that under the ionic conditions of superprecipitation myosin B is a viscous gel, so that if mixing with ATP is to be achieved within a minute or two, concentrations in excess of 1% are impractical. The minimum volume change detectable in these experiments was about 1×10^{-4} ml. This amounts to a volume change of about 350 ml./mole of protein [assuming a 1% suspension of protein having a molecular weight of 5×10^5 g. (myosin)]. To bring about a volume change of this magnitude entirely through the interaction of charges would require the neutralization of about 20 charges per mole of protein [assuming a ΔV/charge of 17 ml./mole[3]], which is probably a much larger charge effect than can be expected. Extensive conformational changes, however, could easily bring about a volume change of such a magnitude, and our results are an indication, though not a proof, that extensive conformational changes do not occur during superprecipitation.

The difficulties in measuring the ΔV of superprecipitation might be circumvented if much greater quantities of protein were used, but the use of large volumes introduces new experimental difficulties.

Acknowledgments.—The authors wish to acknowledge valuable discussions of this work with Dr. Manuel F. Morales. This work was supported by Grant HE-06285 from the U. S. Public Health Service, Grant G-19442 from the National Science Foundation, and Grant CI-8 from the American Heart Association.

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(6) I. Green and W. F. H. M. Mommaerts, *J. Biol. Chem.*, **202**, 541 (1953).
(7) W. Kauzmann, A. Bodanszky, and J. Rasper, *J. Am. Chem. Soc.*, **84**, 1777 (1962).
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Xenic Acid Reactions with *vic*-Diols

Sir:

Preparation of xenic acid by the hydrolysis of xenon tetrafluoride or hexafluoride as reported by Dudley, *et al.*,[1] and Williamson and Koch[2] has led to the investigation of physical properties and chemical reactivity of a hitherto unknown acid. In many respects the behavior of xenic acid is expected to resemble that of the neighboring periodic acid. In fact, Pauling,[3] years before the discovery of xenic acid, predicted that the structure of the then hypothetical xenic acid should be analogous to that of orthotelluric acid, H_6TeO_6. The oxidation potential of xenic acid has been estimated by Appelman and Malm[4] to be in the same order

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(2) S. M. Williamson and C. W. Koch, *Science*, **139**, 1046 (1963).
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TABLE I

RESULTS OF VICINAL DIOL AND ALCOHOL OXIDATION WITH XENIC ACID[a]

	pH						
	2 *N* H_2SO_4	2.82	4.48	6.2	8.62	11.1	12.2	Products
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
t-Butyl alcohol	NR	NR	NR	NR	NR	NR	NR	*t*-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 $CaCO_3$ by Conway distillation method. [c] Detected by the nitroprusside spot test: Fritz, Fergl, and R. E. Oesper, "Spot Tests in Organic Analysis," Elsvier Publishing Company, Amsterdam, 1956, p. 334. [d] Detected by conversion to acetaldehyde. [e] Detected as the derivative of 2,4-dinitrophenylhydrazone.

of magnitude as that of periodic acid. Since periodate is highly specific for the oxidation of *vic*-diols as first observed by Malaprade[5] 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.

Acknowledgments.—We thank J. G. Malm and E. H. Appelman from the Argonne National Laboratories for the provision of aqueous solutions of xenic acid.

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

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

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One-Electron Transfer from an Olefin to a Dicarbonium 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 dicarbonium ion in which the net reaction is some 10^5 to 10^7 slower than previously measured exchange rates.

Some years ago, Weitz and Schmidt[2] observed that when a solution of tetraphenyl-*p*-xylylene (I) and its dichloride were mixed in liquid SO_2, the solutions, originally yellow, became an intense reddish brown.

(1) Examples of rapid rates (10^7 to 10^9 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 ferrocinium 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).