Electrochemistry of organophosphorus compounds. I. Electroreduction of tris(p-nitrophenyl) phosphate

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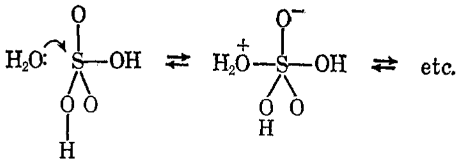
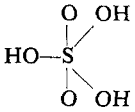


Since the acid constants for thiosulfuric and sulfuric acids are so similar, it is perhaps initially surprising that sulfate exchanges only as the free acid whereas thiosulfate exchanges as the monoanion. A reasonable explanation of this can be given in terms of the suggestion made by Branch and Calvin concerning the unexpectedly small value for pK_1 for sulfuric acid. If it is postulated that sulfate exists in aqueous solution as the hydrate, then the accessibility of its sulfur to a nucleophile, its value of β, and its acidity constant will all be reduced.



For thiosulfate, with its larger HS^- as an attached ligand, the ion may exist unhydrated as $HS_2O_3^-$; if so, thiosulfuric acid should have a larger value for pK_1 than does sulfuric acid and a larger value for β, and would be expected to be attacked by water faster as is observed.

Acknowledgment. We wish to thank Dr. Ennio Ciuffarin for the exploratory research on an analytical method, which he conducted several years ago in these laboratories, and the Atomic Energy Commission for the support of that initial work. We also thank the Conference Board of the Associated Research Councils of the Committee on International Exchange of Persons for a travel grant for Dr. Tonellato. We are pleased to acknowledge extremely helpful discussions with Professors Robert E. Davis, John O. Edwards, John Kice, Donald S. Noyce, V. J. Shiner, Henry Taube, and Frank H. Westheimer during the preparation of the manuscript.

Electrochemistry of Organophosphorus Compounds. I. Electroreduction of Tris(*p*-nitrophenyl) Phosphate

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Abstract: The electroreduction of tris(*p*-nitrophenyl) phosphate has been investigated by polarography, cyclic voltammetry, coulometry, and esr. A mechanism for the reduction based on an initial two-electron transfer followed by cleavage of the oxygen–carbon bond is proposed. The cleaved nitrophenyl rings condense to give 4,4′-dinitrobiphenyl as a product during controlled-potential reduction.

Although the electrochemical oxidation and reduction of organic nitrogen compounds have been widely investigated, relatively few studies have been concerned with phosphorus compounds. Because of the widespread use of organophosphorus compounds as biocides, plasticizers, and additives, and a fundamental interest in the mechanisms of oxidation and reduction of this class of compounds, for example, in biological systems, we have undertaken a systematic investigation of their electrochemical behavior. Tris(*p*-nitrophenyl) phosphate (TNP) [$(NO_2C_6H_4O)_3P{=}O$] was chosen as a model compound for an initial study, because of the well-known behavior of nitro aromatic compounds in aprotic media,[2] and because of the practical interest in nitro-substituted organosphorus compounds as insecticides. Recently Gulick and Geske[3] have reported the polarographic reduction of a number of nitrophenyl phosphates in nonaqueous media during a study of the electron spin resonance (esr) spectra of anion radicals derived from these compounds. No investigation of the mechanism of the reaction or of reactions following the electron transfer was reported.

A few electrochemical studies concerned with the development of polarographic methods for the analysis of such compounds as Malathion [S-(1,2-dicarbethoxyethyl) O,O-dimethyl dithiophosphate] and Parathion (O,O-diethyl O-*p*-nitrophenyl thiophosphate) have also been reported.[4–7]

Results

Polarography. The polarographic reduction of TNP in N,N-dimethylformamide (DMF) solution containing 0.1 *M* tetra-*n*-butylammonium iodide (TBAI) showed five waves (Figure 1): a small prewave followed by one well-defined and three ill-defined waves, with half-wave potentials ($E_{1/2}$) of −0.83, −1.07, −1.9, −2.2, and −2.5 v *vs.* an aqueous saturated calomel electrode (sce). The value of $E_{3/4} - E_{1/4}$ for the well-defined wave (wave 2) (Tômes criterion for reversibility) of 0.08 v suggested

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[1] To whom correspondence and request for reprints should be directed.

[2] See, for example, (a) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960); (b) J. Q. Chambers and R. N. Adams, *J. Electroanal. Chem.*, **10**, 400 (1965), and references contained therein.

[3] W. M. Gulick, Jr., and D. H. Geske, *J. Am. Chem. Soc.*, **88**, 2928 (1966).

[4] M. K. Saikina, *Uch. Zap. Kazansk Gos. Univ., Obshch. Sb.*, **116**, 121 (1956); *Chem. Abstr.*, **52**, 296 (1958).

[5] W. H. Jura, *Anal. Chem.*, **27**, 525 (1955).

[6] C. V. Bowen and F. I. Edwards, Jr., *ibid.*, **22**, 706 (1950).

[7] D. E. Ott and F. A. Gunther, *Analyst*, **87**, 70 (1962).

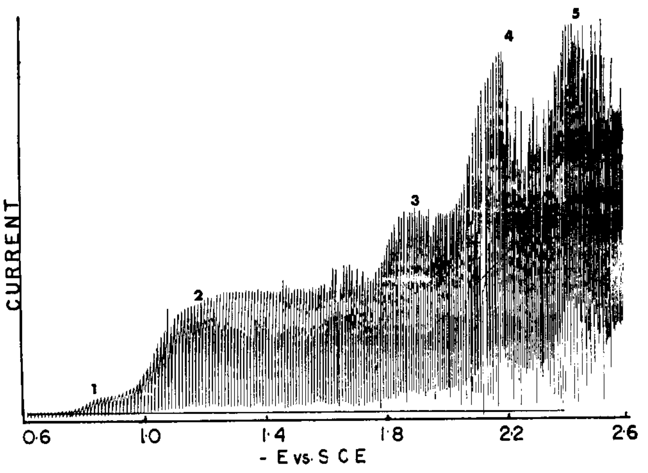

Figure 1. Polarogram for reduction of tris(*p*-nitrophenyl) phosphate. The solution contained 0.1 *M* TBAI in DMF with 2.8 m*M* TNP.

an irreversible reduction. To determine the type of processes responsible for the different waves, a study of the variation of the limiting currents with the head of the dropping mercury electrode (dme) was made (Table I). The wave height of the prewave varied directly with the height of the dme column, which is characteristic of an adsorption controlled process. The wave height of the second, well-defined wave varied with the square root of the head of the dme, indicating a diffusion-controlled process. Finally, the limiting current of the third wave was essentially independent of the head of the dme, suggesting an electrode reaction in which the magnitude of the current is determined by the rate at which the electroactive species is produced by a preceding chemical reaction (a kinetic current). Measurements on the third and fourth waves were difficult to make because of the occurrence of maxima.

Table I. Polarographic Data for Reduction of Tris-(*p*-nitrophenyl) Phosphate[a]

Height of dme, *h* (cor), cm	Wave 1 i_d/h, μa/cm	Wave 2 $i_d/h^{1/2}$, μa/cm$^{1/2}$	Wave 3 i_d, μa
110.9	0.0139	0.86	7.8
100.9	0.0139	0.87	7.8
90.9	0.0137	0.83	7.2
70.9	0.0127	0.92	7.8

[a] The solution was 0.1 *M* TBAI in DMF, and contained 1.47 m*M* TNP. At *h* = 110.9 cm, *m* = 1.70 mg/sec, and *t* = 2.74 sec.

The value of the diffusion current constant, *I*, for wave 2 ($I = i_d/m^{2/3}t^{1/6}C$) is 3.5. To estimate the number of electrons involved in wave 2 using the Ilkovic equation, an estimate of the diffusion coefficient, *D*, of TNP is required. The *D* of triphenyl phosphate can be estimated as 6.8×10^{-6} cm^2/sec by using the Stokes–Einstein equation and taking the density of triphenyl phosphate to be 1.202.[8] Assuming the *D* for TNP is about this value, we calculate an *n* of 2.0 for this wave. Gulick and Geske[7] found a value of *I* for the one-electron reduction of mononitro-substituted phosphates in DMF of about 2.2 (assuming their *m* and *t* values were about the same in DMF and acetonitrile); this value leads to an *n* of about 1.6. We conclude that the second wave probably involves a two-electron reduction of TNP.

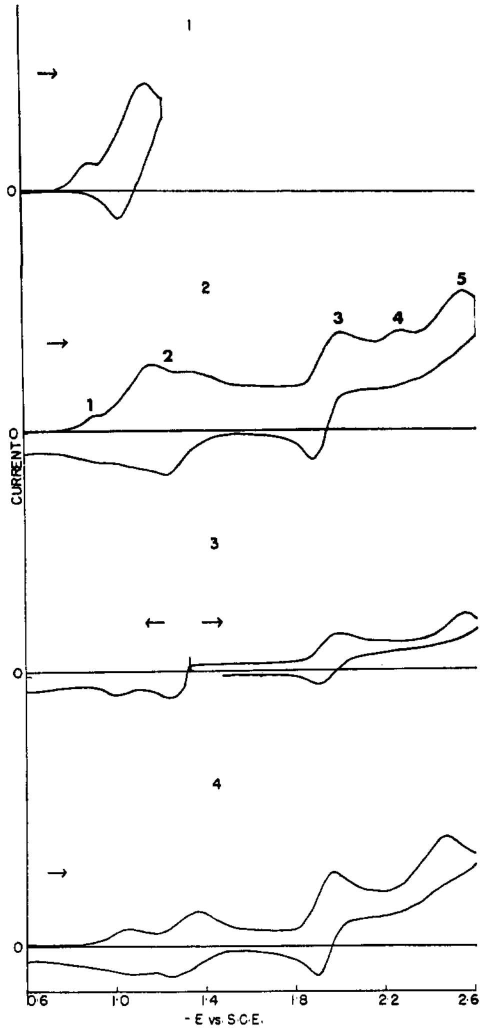

Figure 2. Cyclic voltammetry of tris(*p*-nitrophenyl) phosphate. The solution contained 0.1 *M* TBAI in DMF and (1) TNP before reduction when the scan is reversed at the first peak; (2) reduction of TNP past the first peak (the numbers on the peaks correspond to the waves in Figure 1); (3) TNP after reduction at −1.30 v *vs.* sce; (4) TNP after oxidation of the reduced species at −0.80 v *vs.* sce.

Cyclic Voltammetry. A cyclic voltammogram of TNP in DMF containing 0.1 *M* TBAI, at a platinum electrode, is shown in Figure 2, curve 1. Results are summarized in Table II. Essentially the same results were obtained with a hanging mercury drop electrode (hmde), but the stirring phenomenon[9] complicates the measurements of peak currents and potentials. The shape and position of the prepeak was dependent on the scan rate, shifting to more negative potentials with an increase in scan rate and tending to merge with the main peak. The effect of scan rate on the main process (wave 2) is to shift the peak potential to more negative potentials with increasing scan rate, a shift of 30 mv for a tenfold change in the scan rate. This indicates that the reduction process is irreversible.[10] A clear

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[8] J. W. McBain, C. E. Harvey, and L. E. Smith, *J. Phys. Chem.*, **30**, 312 (1926).

[9] K. S. V. Santhanam and A. J. Bard, *J. Am. Chem. Soc.*, **88**, 2669 (1966).

[10] R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

Table II. Cyclic Voltammetric Data for Second Peak in the Reduction of Tris(*p*-nitrophenyl) Phosphate[a]

Sweep rate, mv/sec	i_{pc}, μa	i_{pa}, μa	E_{pc}, v *vs.* sce	E_{pa}, v *vs.* sce
67	26.8	16.8	−1.13	−1.04
153	38.2	35.0	−1.14	−1.02
222	44.2	42.4	−1.14	−1.02
312	52.4	46.2	−1.15	−1.01
476	64.2	55.0	−1.16	−1.01

[a] The solution contained 0.1 *M* TBAI and 2.85 m*M* TNP in DMF. The working electrode was a platinum disk electrode with area of 0.031 cm².

Table III. Cyclic Voltammetric Data for the Reduction of Tris(*p*-nitrophenyl) Phosphate[a]

Sweep rate (v), mv/sec	Peak 2		Peak 3		Peak 4		Peak 5	
	E_{pc}, v[b]	$i_p{}^c/v^{1/2}$	E_{pc}, v[b]	$i_p{}^c/v^{1/2}$	E_{pc}, v[b]	$i_p{}^c/v^{1/2}$	E_{pc}, v[b]	$i_p{}^c/v^{1/2}$
67.1	−1.13	3.27	−1.96	3.12	−2.24	0.81	−2.51	6.11
153	−1.14	3.08	−1.96	2.27	−2.30	2.01	−2.55	3.39
222	−1.14	2.96	−1.99	1.93	−2.34	2.47	−2.59	1.98
312	−1.15	2.97	−1.99	1.24	−2.34	2.91	−2.61	...
476	−1.15	2.94	−2.00	0.91	−2.41	3.27	...	...
712	−1.16	2.96	−2.01	0.75	−2.49	3.27	...	...

[a] The solution contained 0.1 *M* TBAI and 2.85 m*M* TNP in DMF. The working electrode was a Pt disk electrode of area 0.031 cm² [b] Potentials *vs.* aqueous sce. [c] In μa sec$^{-1/2}$ mv$^{-1/2}$.

anodic peak on the reverse scan is obtained, with a difference between cathodic and anodic peak potentials of more than 100 mv. The ratio of the anodic peak current to cathodic peak current is less than one, increasing with increasing scan rates. These results suggest that wave 2 involves a chemical reaction following the charge transfer.

If the scan is continued past the second peak (Figure 2, curve 2), three other cathodic peaks appear on the cyclic voltammogram. Data for these peaks are given in Table III. The current function (proportional to $i_p/v^{1/2}$) for the second and third peaks decreased, while the current function for the fourth peak increased substantially, as the scan rate increased. These data, compared with the diagnostic criteria reported by Nicholson and Shain,[11] suggest that TNP is involved in an ece-type reaction with the species produced by the intervening chemical reaction being reduced as or more easily than TNP. The large increase in the current function in peak 4 (as compared to changes in peaks 2 and 3) probably is due to a higher number of electrons involved in that electrochemical process. The data suggest that the third and fifth peaks in cyclic voltammetry and the third and fifth wave in polarography can be ascribed to the reduction of products of the chemical reaction.

Controlled-Potential Coulometry. Coulometric experiments at a platinum gauze electrode at a potential on the diffusion plateau on the second wave (−1.30 v *vs.* sce) were undertaken to examine the nature of the reduction products. The reduction of TNP consumed 4.0 (TNP concentration 2.85 m*M*) and 3.94 (TNP concentration 1.47 m*M*) faradays of electricity per mole of TNP. Electrolysis products were examined by cyclic voltammetry and esr. The cyclic voltammetry of the reduced solution is shown in Figure 2, curve 3. On an initial cathodic scan, a peak at −1.96 v *vs.* sce, with a corresponding anodic peak on reversal appeared. The cathodic current function for this wave was fairly constant, suggesting that the process is diffusion controlled.

Controlled-potential oxidation of the reduced solution at −0.80 v *vs.* sce consumed 0.90 faraday per mole of TNP and yielded a cyclic voltammogram with peaks at −1.06, −1.36, −1.96, and −2.47 v *vs.* sce (Figure 2, curve 4). The latter two peaks were also present in the reduced solution. If no complications due to chemical reaction were present, controlled-potential oxidation would lead to the original cyclic voltammogram. The change in the cyclic voltammetric behavior after reduction and oxidation is persuasive evidence for chemical reactions following the electron-transfer reaction. To determine the identity of the intermediates in the electroreduction of TNP, the peak potentials found during various stages in the reduction of TNP were compared with those obtained with various known nitro compounds under the same conditions. The results are shown in Table IV. Dinitrobiphenyl appears to be one of the products of the chemical reaction; this evidence is also confirmed by esr studies (see below). The other product could not be identified by potentials alone, but it may be 4-nitrophenyl phosphate or a system closely related to it.

Electron Spin Resonance. Examination of the solution by esr spectroscopy after coulometric reduction proved very helpful in elucidating the mechanism of the reaction. The esr spectrum of the solution after reduction (transferred to an esr cell without contact with air) was 36 gauss wide and not fully resolved. The variation of the relative intensities of lines in the middle and on the outside of the spectrum with varying klystron power levels, and with time upon the introduction of a small amount of air, suggested that this spectrum was caused by two different radicals. With time the outer lines of the spectrum decreased in intensity until a spectrum 16 gauss wide and fully resolved at low power levels was obtained (Figure 3a). When air was rigorously excluded from the solution in the esr cell, the combined spectrum of both radicals persisted. This 16-gauss wide spectrum was attributed to 4,4′-dinitrobiphenyl anion radical and can be fit with the following coupling constants: a_N = 2.69 (2 N), a_H = 1.21 (4 H), and a_H = 0.21 (4 H) gauss; a computer-simulated spectrum using these values is shown in Figure 3b. The spectrum for 4,4′-dinitrobiphenyl anion radical in DMF has been previously reported by Rieger and Fraenkel[12] with a_N

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(11) R. S. Nicholson and I. Shain, *Anal. Chem.*, 37, 178 (1965).

(12) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 39, 609 (1963).

Table IV. Cyclic Voltammetric Data (v *vs.* sce) for Tris(*p*-nitrophenyl) Phosphate and Several Nitro Compounds[a,b]

Compound	E_{pc}	E_{pa}	E_{pc}	E_{pa}	E_{pc}	E_{pc}
Tris(*p*-nitrophenyl) phosphate	−1.14	−1.01	−1.96	−1.86	−2.24	−2.51
Reduced		−0.93 −1.17	−1.96	−1.86	...	−2.51
Reduced and oxidized	−1.06 −1.36	−0.92 −1.17	−1.96	−1.86	...	−2.47
4-Nitrophenyl phosphate	−1.28	...	−2.02	−1.86	...	...
4,4′-Dinitrobiphenyl	−1.05	−0.90	...	...	...	−2.50[c]
Nitrobenzene	−1.31	−1.01	...	...	...	...

[a] The solution contained 0.1 *M* TBAI and 2 m*M* electroactive compound in DMF. The working electrode was a Pt disk electrode of area 0.031 cm². [b] The cathodic limit for platinum in 0.1 *M* TBAI in DMF is −2.64 v *vs.* sce. [c] Broad peak.

= 2.69, a_H = 1.23, and a_H = 0.20 gauss. In one experiment involving the reduction of TNP in DMF with sodium perchlorate as supporting electrolyte, an esr spectrum was obtained which could be interpreted assuming coupling of the unpaired electron with one phosphorus (a_P = 11.4 gauss), one nitrogen (a_N = 8.1 gauss), and two pairs of hydrogens (a_H = 3.3 and a_H = 0.83 gauss) (Figure 4). This assignment suggests nitrophenyl phosphate anion radical. The coupling constants obtained are close to those reported by Gulick and Geske[3] for other nitro-substituted phosphorus radicals. These authors found, however, that essentially no coupling occurred from the hydrogens on the phenyl substituents in such compounds as diphenyl 4-nitrophenyl phosphate, so that it is possible that the anion radical observed is that of bis(*p*-nitrophenyl) phosphate or even of TNP. Attempts to generate the anion radical of nitrophenyl phosphate using the *intra muros* technique[13] and solutions of nitrophenylphosphoric acid or its disodium salt always produced the anion radical of nitrophenol. The esr spectrum of the radical in Figure 4 closely resembles that of the decaying radical in the previously described experiments. We conclude that two radicals are formed following the electron transfer; one is 4,4′-dinitrobiphenyl anion radical, and a second, that shown in Figure 4, which reacts rather rapidly with oxygen.

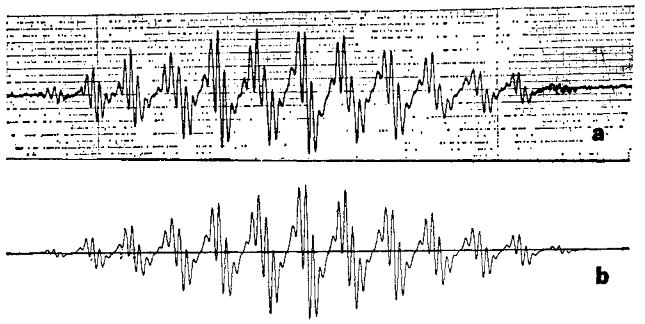


Figure 3. (a) Derivative esr spectrum of 4,4′-dinitrobiphenyl anion radical produced by electroreduction of 2.8 m*M* TNP solution containing 0.1 *M* tetra-*n*-butylammonium iodide in DMF. Spectrometer conditions: modulation amplitude, 0.05 gauss; power, 18 db; sweep rate, 1 gauss/min. (b) Calculated spectrum using constants in text.

Discussion

Although the reaction appears to be quite complicated, the following mechanism appears to be consistent with the electrochemical and esr results. The first wave is probably an adsorption prewave such as

$$\mathrm{(NO_2C_6H_4O)_3PO\ (soln) + 2e \longrightarrow (NO_2C_6H_4O)_3PO^{2-}} \qquad (1)$$

or it might involve reduction of adsorbed TNP. The polarographic data indicate that wave 2 is a two-electron reduction and the cyclic voltammetric data suggest an ece mechanism such as eq 2–5, where HS is the solvent and all of these reactions occur at potentials near those of wave 2; reaction 4 occurs at potentials just a little more negative than that of reaction 2 and could barely be noticed as a small separate wave in cyclic voltammetry. Reaction 5 occurs at potentials more positive than that of reaction 2. During polarography, in the short lifetime of the drop (~3 sec), reaction 3 does not progress to a very large extent, and wave 2 is close to a two-electron reduction wave. During coulo-

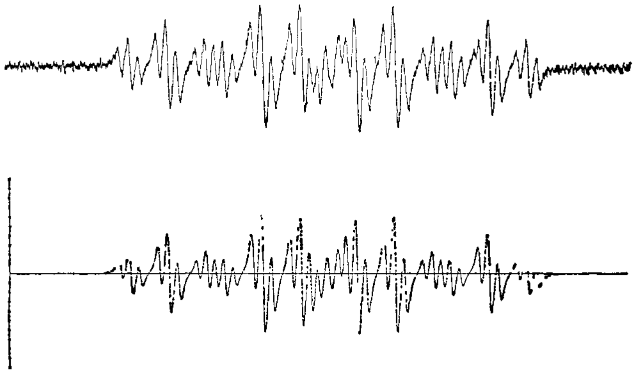
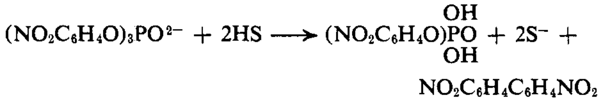
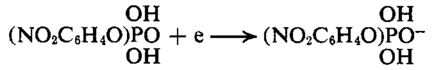


Figure 4. Top: Derivative esr spectrum of radical produced by electroreduction of TNP solution containing 0.1 *M* sodium perchlorate in DMF. Spectrometer conditions: modulating amplitude, 0.25 gauss; power, 10 db; sweep rate, 2 gauss/min. Bottom: Calculated spectrum using constants in the text.

$$\mathrm{(NO_2C_6H_4O)_3PO + 2e \longrightarrow (NO_2C_6H_4O)_3PO^{2-}} \qquad (2)$$



$$\mathrm{(NO_2C_6H_4O)_3PO^{2-} + 2HS \longrightarrow (NO_2C_6H_4O)\overset{OH}{\underset{OH}{PO}} + 2S^- + NO_2C_6H_4C_6H_4NO_2} \qquad (3)$$



$$\mathrm{(NO_2C_6H_4O)\overset{OH}{\underset{OH}{PO}} + e \longrightarrow (NO_2C_6H_4O)\overset{OH}{\underset{OH}{PO^-}}} \qquad (4)$$

$$\mathrm{NO_2C_6H_4C_6H_4NO_2 + e \longrightarrow NO_2C_6H_4C_6H_4NO_2^-} \qquad (5)$$

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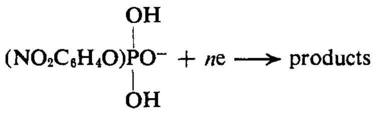
(13) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

metric reduction, which occurs over about 30 min, reduction 3 goes essentially to completion, and four electrons per molecule of TNP are consumed. This scheme also accounts for the esr results. It is also possible that reaction 3 involves the formation of bis-(nitrophenyl) phosphate liberating a nitrophenyl radical which then dimerizes. However, the absence of evidence for the formation of nitrobenzene, which would also probably form in this scheme, makes us prefer a mechanism in which both nitrophenyls come from the same TNP molecule.

Since the current function of wave 3 decreases with increasing scan rates, it probably involves a product of the chemical reaction, which follows the charge transfer (3), such as



$$(NO_2C_6H_4O)\overset{\displaystyle OH}{\underset{\displaystyle OH}{P}}O^- + ne \longrightarrow \text{products} \quad (6)$$

On the other hand, the current function of wave 4 increases with increasing scan rate, so that wave 4 can be ascribed to

$$(NO_2C_6H_4O)_3PO^{2-} + ne \longrightarrow \text{products} \quad (7)$$

Wave 5 can be ascribed to a reaction such as

$$NO_2C_6H_4C_6H_4NO_2^- + ne \longrightarrow \text{products} \quad (8)$$

since 4,4′-dinitrobiphenyl has a reduction wave at these potentials (Table IV).

The formation of 4,4′-dinitrobiphenyl indicated that the reaction occurs by the cleavage of the oxygen–carbon bond, while the energy-rich phosphorus–oxygen bond remains intact. A similar cleavage of oxygen–carbon has been proposed by Mitteil[14] in the reduction of diphenyl phosphate. Our results differ from his, however, in that we did not observe nitrobenzene as the cleavage product.

Experimental Section

The general experimental methods and purification techniques are the same as those previously described.[9] A multipurpose instrument employing operational amplifier circuitry with a three-electrode configuration was used in the voltammetric experiments. Controlled-potential coulometry was carried out using a previously described apparatus.[9] Cyclic polarograms were taken with a platinum disk working electrode (area = 0.031 cm²). The reference electrode was an aqueous sce connected *via* an agar plug and sintered-glass disk to a salt bridge containing the test solution and closed at the end by a fine porosity sintered-glass disk. A platinum gauze electrode was used in controlled-potential experiments. The auxiliary electrode was silver. The esr spectra were obtained with a Varian Associates V4502 spectrometer employing 100-kc field modulation. A Varian V-153C klystron (output 300 mw) was used; attenuation levels represent attenuation of the output of this klystron in a standard Varian bridge. Samples were contained in the flat Varian aqueous cell. Calculations were performed on a Control Data Corporation 1604 computer. Theoretical simulated spectra were plotted on a CDC 160 plotter.

Tris(*p*-nitrophenyl) phosphate (TNP) was obtained from Aldrich Chemical Co.; analysis by thin layer chromatography and mass spectrometry established that its purity was over 98%. 4-Nitrophenylphosphoric acid was prepared by passing an aqueous solution of the disodium salt through a cation-exchange resin solution and recrystallizing it twice from water (mp 105–107°). Other nitro compounds were obtained from Aldrich and were used without further purification. Tetra-*n*-butylammonium iodide (TBAI) was polarographic grade, obtained from Southwestern Analytical Chemicals (Austin, Texas).

Acknowledgment. This work was performed under Contract DA-18-035-AMC-715(A), U. S. Army Edgewood Arsenal.

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[14] I. Mitteil, *Ber.*, 72, 2129 (1939).

The Reaction of C_2O with Oxygen and Nitric Oxide

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Abstract: Products from the photolytic reaction of C_3O_2 with O_2 and NO have been measured for a variety of conditions. The reaction of C_2O with O_2 appears to form CO, CO_2, and oxygen atoms. The reaction of oxygen atoms with C_3O_2, producing mainly CO with only small amounts of CO_2 and C_2O, has a rate constant of $(4 \pm 2) \times 10^8$ l./mole sec. Two additional experiments confirm the presence of oxygen atoms in the C_2O–O_2 reaction. Nitric oxide is a very effective inhibitor of C_2O reactions, being more than 10^4 times as reactive with C_2O than is ethylene. The C_2O–NO reaction produces CO, N_2, N_2O, and CO_2. It has not been possible to construct a satisfactory mechanism to explain these products.

The existence of C_2O has now been established. Jacox, Milligan, Moll, and Thompson[1] have observed the infrared absorption of matrix-isolated C_2O. The observed isotope shifts and the modes of formation, either by photolysis of C_3O_2 or by the reaction of atomic carbon with CO, establish the structure as linear CCO. Flash photolysis of C_3O_2 in the gas phase produces a transient absorption between 5000 and 6350 A which is too complex to be a diatomic molecule.[2] A vibrational spacing of 1980 ± 20 cm^{-1} in the electronic spectrum, compared to 1978 cm^{-1} observed in the matrix-isolated C_2O, identifies the transient in the flash-photolysis experiments as ground-state C_2O. The matrix-isolated C_2O also has a broad absorption "near 5000 A."

Photolysis of C_3O_2 at 3000 A produces an intermediate which can insert a carbon atom into a carbon–carbon

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[1] M. E. Jacox, D. E. Milligan, N. G. Moll, and W. E. Thompson, *J. Chem. Phys.*, **43**, 3734 (1965).

[2] C. Devillers, *Compt. Rend.*, **262C**, 1485 (1966).