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Preliminary note

Electrochemistry of organophosphorus compounds. III. Electroreduction of bis-(*p*-nitrophenyl) phosphate

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A previous paper[1] from this laboratory described the electroreduction of tris-(*p*-nitrophenyl) phosphate (TNP) and suggested a mechanism involving cleavage to give 4,4'-dinitrobiphenyl and 4-nitrophenyl phosphate. It is of interest to consider the case where one of the nitrophenyl groups is replaced by hydrogen, yielding bis-(*p*-nitrophenyl) phosphate (BNP) $[(NO_2C_6H_4O)_2(OH)P{=}O]$, to see whether reduction of this compound involves cleavage of both nitrophenyl ring systems in a manner similar to TNP or only one after electroreduction. Analysis of the products and electrochemical data for the electrochemical reduction of BNP provided a mechanism for the reduction generally in agreement with that proposed for TNP.

The polarographic half-wave potentials obtained for the three waves in the reduction of BNP at a dropping mercury electrode in N,N-dimethylformamide (DMF) containing 0.1 *M* tetra-*n*-butyl ammonium iodide (TBAI) were −0.94 V, −1.23 V, and −2.6 V *vs.* an aqueous saturated calomel electrode (SCE). By varying the height of the mercury column above the capillary, the first wave was found to be an adsorption wave (i_d/h = constant, where i_d is the diffusion current and h the head of the DME) and the second wave was shown to be a diffusion controlled process ($i_d/h^{1/2}$ = constant). Measurements on the third wave were obscured by maxima. The number of electrons involved in the reduction of BNP at the second wave was estimated to be about two with the calculated diffusion coefficient of BNP, 1.22×10^{-5} cm^2 s^{-1} (calculated from the known diffusion coefficient of TNP corrected for differences in molecular weights) and the measured diffusion current. The wave height of the third reduction was twice that of the second wave suggesting that the reduction involved twice the number of electrons in the second step and so corresponds to an n of about 4.

The reduction of BNP was also examined by cyclic voltammetry, typical results are given in Table 1 and Fig.1. The shape and position of the peak at −1.02 V was dependent on scan rate and shifted towards more cathodic values with increasing scan rate. This peak disappeared on repeated cycling between −0.83 V and −1.05 V. However, if the

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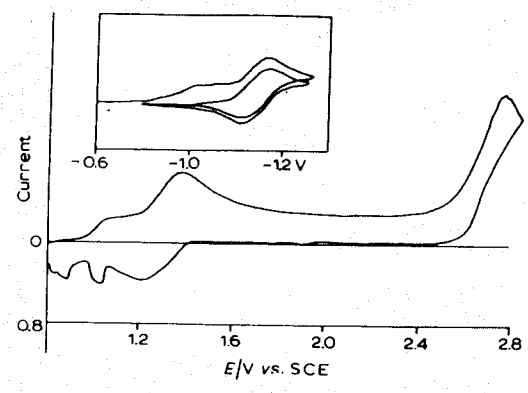

Fig. 1. Cyclic voltammogram of bis-(*p*-nitrophenyl) phosphate in DMF containing 0.1 *M* tetra-*n*-butyl ammonium iodide and 0.3 m*M* BNP. Insert: result of repeated cycling about the first and second peaks; the first and eighth scans are shown.

potential was held at −0.83 V for 1.5 s or more during the cycling, the peak reappeared. Moreover, the current function, $i_p/v^{1/2}$, (where i_p is the peak current and v is the scan rate) increased markedly with increasing scan rate. These results suggest that this peak is due to adsorption of the electroactive species.

The current function for the second peak decreased slightly with increasing scan rate, while that for the third peak was almost constant. The peak potentials showed a tendency to shift cathodically with increasing scan rate. On reversal of scan at −1.05 V, an anodic peak appeared but the measurements on a hanging mercury drop are complicated by the stirring phenomenon[2,3]. If a platinum electrode replaces the mercury drop, this anodic peak could be located at −1.27 V. The difference between the cathodic and anodic peak potentials of 80 mV for the second peak suggested an irreversible reduction or a reversible reduction followed by a fast chemical reaction[4].

Controlled potential reduction of BNP at a mercury pool electrode on the plateau of the second wave at −1.40 V consumed three (3.06) faradays of electricity per mole of BNP. The solution turns bluish green during reduction. Electrolysis products were examined by cyclic voltammetry and electron spin resonance spectrometry (e.s.r.). In the cyclic voltammetry of the reduced solution with the scan started at −1.50 V, a cathodic sweep produced two irreversible peaks at −2.2 V (broad) and −2.54 V. On an anodic sweep, a huge peak around −1.2 V, due to stirring at the hanging mercury drop, indicated the presence of an oxidizable species in solution. The reduction peak at −2.54 V could be matched with the second reduction peak of 4,4'-dinitrobiphenyl[1]. The reduction process at −2.2 V appears to be due to hydrogen ion reduction; this was confirmed by carrying out cyclic voltammetry with small concentrations (1 mM) of $HClO_4$ or H_3PO_4 IN DMF solutions, which showed an H^+ discharge peak at −2.2 V.

An e.s.r. examination of the electrolyzed solution further confirmed the presence of 4,4'-dinitrobiphenyl. A spectrum with 16 gauss width and fully resolved at low power levels was obtained with coupling constants a_N = 2.69, a_H = 1.29 and a_H = 0.21 G. The spectrum and the coupling constants agreed well with the spectrum of 4,4'-dinitrobiphenyl

TABLE I

CYCLIC VOLTAMMETRIC DATA FOR THE REDUCTION OF BIS-(*p*-NITROPHENYL) PHOSPHATE[a]

Sweep rate/mV s^{-1}	*First peak* E_{pc}/V^b	$i_{pc}/\mu A$	*Second peak* E_{pc}/V^b	$i_{pc}\nu^{-1/2}/\mu A\ s^{1/2}\ mV^{-1/2}$	*Third peak* E_{pc}/V^b	$i_{pc}\nu^{-1/2}/\mu A\ s^{1/2}\ mV^{-1/2}$
91.4	−1.02	2.2	−1.35	0.73	−2.54	2.40
203	−1.02	2.4	−1.35	0.70	−2.64	2.38
298	−1.03	3.8	−1.36	0.70	−2.67	2.60
430	−1.04	5.4	−1.36	0.69	−2.70	2.38
657	−1.05	6.4	−1.36	0.66	−2.74	2.63
943	−1.06	8.2	−1.37	0.65	−2.77	2.50

[a]The solution contained 0.1 *M* tetra-*n*-butylammonium iodide and 1.03 m*M* BNP in DMF. The working electrode was a hanging mercury drop electrode of area 0.022 cm^2.
[b]Potential *vs.* aqueous SCE.

anion radical obtained by Reiger and Fraenkel[5] and found also in our previous study of TNP[1].

The following mechanism is proposed for the reduction of BNP on the basis of the above data:

$$(NO_2C_6H_4O)_2\underset{\underset{OH}{|}}{P}{=}O + 2e \rightarrow (NO_2C_6H_4O)_2\underset{\underset{OH}{|}}{P}{=}O^{2-} \quad (1)$$

$$(NO_2C_6H_4O)_2\underset{\underset{OH}{|}}{P}{=}O^{2-} + SH \rightarrow NO_2C_6H_4{-}C_6H_4NO_2 + HO{-}\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{P}}{=}O + 2\,S^- \quad (2)$$

$$NO_2C_4H_6{-}C_6H_4NO_2 + e \rightarrow NO_2C_6H_4{-}C_6H_4NO_2^- \quad (3)$$

where HS is the solvent and all reactions occur at potentials near the second wave. The reduction of 4,4'-dinitrobiphenyl occurs at -1.04 V[1]. On the cyclic voltammetric time scale, reaction (1) predominates, the small contributions from (2) and (3) yielding the ECE-like behavior. On the coulometric time scale, (2) goes to completion, and three faradays per mole are consumed and the radical anion produced. The mechanism suggests that cleavage of both nitrophenyl rings from each reduced molecule of BNP occurs. If only one of the nitrophenyl groups was cleaved, formation of nitrophenyl phosphate, which has two reduction peaks $E_p = -1.28$ V and $E_p = -2.02$ V and an oxidation peak at -1.86 V would probably have occurred. The absence of these peaks in the cyclic voltammetry of the reduced solution also favors the above mechanism. The mechanism of BNP reduction, then, closely resembles that of TNP and provides further evidence of reactivity of the organophosphorus radicals.

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