

OXIDATION OF ETHYLENEDIPHOSPHINETETRAACETATE ANIONS*

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Received November 22nd, 1982

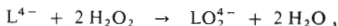
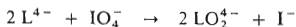
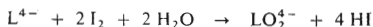
The oxidation of the ethylenediphosphinetetraacetate anion and its protonated forms by iodine, periodate, hydrogen peroxide, and oxygen has been studied in aqueous solution. The oxidation by the first three reagents is fast and yields a single product, bis(phosphine oxide), which has been isolated and characterized as ethylenebis(phosphinyl)tetraacetic acid. The oxidation by molecular oxygen proceeds considerably more slowly; in weakly acid solutions its rate is determined by the properties of the oxygen rather than by the electronic structure of the various protonated substrate species. The inhibiting effect of the phosphonium structures takes place only in strongly acid solutions.

Because of the potential use of ethylenediphosphinetetraacetic acid^{1,2} as a selective complexing reagent³, its stability towards usual reagents is of importance. The hydrolysis of the acid and its anions has been the subject of our previous study⁴. Another reaction of practical importance is oxidation of the trivalent phosphorus by molecular oxygen or other oxidants. Tertiary phosphines are usually oxidized to the corresponding phosphine oxides as the final products^{5,6}; the thermodynamics and kinetics of the reaction involved depend not only on the kind of the oxidant, but also on the phosphine type concerned, as the substituents at the phosphorus atom affect its steric accessibility⁷ as well as the electron density⁸. For the ethylenediphosphinetetraacetate anion, additional complications arise from the fact that its protonation proceeds partly through species containing quaternized phosphorus². In principle, oxidation of a single phosphorus atom giving rise to a phosphine-phosphine oxide mixed product should be considered; such partial oxidation, however, is not very likely, since analogous substances, if known at all⁹, have been synthesized by other, indirect methods.

In the present work, oxidation of the ethylenediphosphinetetraacetate anion (L^{4-}) and its protonated forms by various chemical agents, *viz.* iodine, hydrogen peroxide, potassium periodate, and molecular oxygen has been studied. The curves of potentiometric titrations of a Na_4L solution with the first three reagents in

* Part XXII in the series Compounds Structurally Related to Complexones; Part XXI: Polyhedron 2, 349 (1983).

various acidity conditions (I_2 and KIO_4 in a range from 4M- $HClO_4$ to 2M- $NaOH$, H_2O_2 at $pH < 7$) exhibit a single marked inflection, corresponding to the reactions



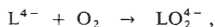
The first reaction has been utilized previously for a quantitative determination¹. The potentials establish quickly indicating that the reactions proceed rapidly. The course of the oxidation was investigated by the 1H NMR spectroscopy using a titration technique: aliquots of a concentrated solution of the oxidant were added to the Na_4L solution directly in an NMR tube and the spectral changes were monitored. The measurements were carried out in H_2O to prevent interferences from the rapid exchange of the acetate protons for deuterium under certain acidity conditions². The pH value was kept constant, since the chemical shifts depend markedly on the degree of protonation². A single product of the oxidation was invariably found to form without observable intermediates. Typical spectra are shown in Fig. 1.

This product was prepared by oxidation of $H_4L \cdot 2 HBr$ with hydrogen peroxide, and isolated as crystalline ethylenebis(phosphinyl)tetraacetic acid, H_4LO_2 . Its infrared and NMR spectra correspond to the expected structure. A significant feature of the infrared spectrum is the splitting of bands associated with the $P=O$ and $COOH$ groups: $\nu(C=O)$ at 1722 and 1659 cm^{-1} , $\nu(P=O)$ at 1166 and 1115 cm^{-1} , $\nu(OH)$ at 2750 and 2390–2625 cm^{-1} . This indicates a simultaneous existence, in the solid state, of relatively free $P=O$ and $COOH$ groups and groups involved in a strong hydrogen bonding interaction, probably of the $P=O \cdots HO-C$ type. The NMR spectra, except of $^{31}P\{^1H\}$, are deceptively simple: a detailed inspection of the multiplet structure reveals that, in fact, the spectra are second order. H_4LO_2 is a tetrabasic acid whose protonation constants $\beta_i^H = [H_iLO_2]/[H]^i [LO_2]$, determined conventionally³ at 25°C and $I = 0.1$ ($NaClO_4$), are $\log \beta_1 = 4.70(1)$, $\log \beta_2 = 8.59(1)$, $\log \beta_3 = 11.89(1)$, $\log \beta_4 = 14.15(2)$. The protons are attached consecutively to the carboxyl groups, as follows from the dependence of the chemical shifts of the non-labile protons on acidity (Fig. 2).

The behaviour of the LO_2^{4-}/L^{4-} redox system on a platinum electrode was studied in solutions of different acidity. Analogously to similar redox systems which require, in addition to the electron transfer, also the oxygen transfer between solvent and substrate, the LO_2^{4-}/L^{4-} system is irreversible. The potential that establishes after a prolonged time on the bright platinum electrode in the solutions containing equal concentrations of the two species at $pH < 8$ (both anions are deprotonated) is $190 \pm \pm 10$ mV, against hydrogen electrode. The potential, corrected for the protonation

of the two species, increases slightly on acidification, in agreement with an enhanced stabilization of the trivalent phosphorus by protonated carboxyl groups. The above potential value is qualitatively consistent with the shape of the potentiometric titration curves, and places L^{4-} among reductants of medium strength. For instance, ferric and cupric ions are reduced with excess L^{4-} to give ferrous and cuprous complexes of L^{4-} described previously³; because of its irreversible nature, however, the redox equilibrium cannot be utilized for a determination of the stability constants of extremely stable complexes, which in fact was the initial aim of this work.

The oxidation of the L^{4-} anion by molecular oxygen, the major product of which is also LO_2^{4-} ,



has quite a specific character. The oxidation rate is critically pH-dependent (Fig. 3), but this dependence does not correlate with the structure of the substrate, in particular, with the electron density at the phosphorus atoms of the various protonated species. On the other hand, the increasing oxidation rate up to pH about 1.5 corresponds with the change in the oxidation-reduction potentials of oxygen and the rate constants of its reactions^{10,11}; only in strongly acid solutions the decrease of the reaction rate can be explained as to be caused by protonation of the phosphorus

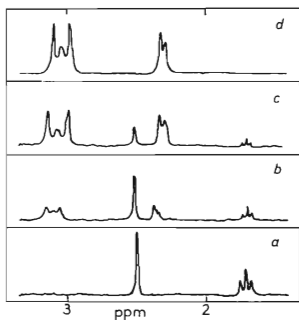


FIG. 1
Changes in the ¹H NMR spectrum of L^{4-} during its oxidation by iodine (pH 8.0). Molar ratio I_2/L^{4-} : a 0, b 0.7, c 1.4, d 2.1

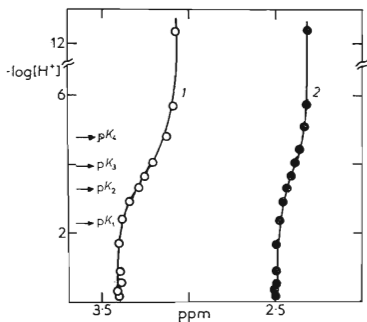
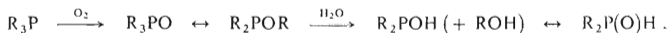


FIG. 2
Dependence of the chemical shifts of the nonlabile protons in H_4LO_2 on acidity. 1 $P(O)CH_2COO$, 2 $P(O)CH_2CH_2P(O)$

atoms². The course of the oxidation by oxygen appears to be complicated by additional processes, detectable particularly if the oxidation itself is slow. Similarly as for tributylphosphine¹², a competitive reaction is the hydrolysis of the P-CH₂-COO bonds, whose mechanism is presumably



In agreement with this concept, glycolate and secondary phosphine oxides were detected by TLC and ¹H NMR in the oxidation products at pH 6. A comparison with the rate of hydrolysis of the substrate under anaerobic conditions⁴, which is negligible at pH 6, also supports the concept of an oxidized intermediate, which is readily hydrolytically cleaved,

EXPERIMENTAL

The procedures for the synthesis of Na₄L and H₄L.2 HBr, measurement of the spectra, and determination of the protonation constants have been reported previously¹⁻³. A PHM 64 instrument in conjunction with the system of a P 101 bright platinum electrode and a K 401 saturated calomel electrode (Radiometer, Copenhagen) was employed for the potentiometric measurements. The oxidation by molecular oxygen was monitored at 25°C by saturating 0.005M-Na₄L, in Britton-Robinson buffers or in HClO₄ or NaOH solutions, with oxygen gas freed from CO₂ and saturated with solvent vapours. Samples were withdrawn for the iodometric determination of the loss of trivalent phosphorus. The final product was subjected to TLC (Lucofol Quick, Kavalier; solvent: n-BuOH + MeOH + 5% NH₃ 1:1:1, detection with iodine) and ¹H NMR investigation.

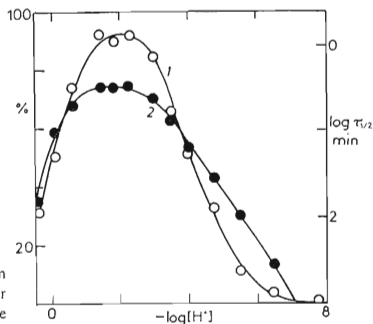


FIG. 3

The course of oxidation of L⁴⁻ by oxygen for various acidities. 1 reacted P(III) (per cent) in 10 min, 2 half-life of the substrate

Synthesis of ethylenebis(phosphinyl)tetraacetic acid (H₄LO₂): To a stirred and cooled solution of 2.0 g of H₄L.2 HBr in 10 ml of water was added 5 ml of 30% H₂O₂. The solution was vacuum-evaporated to dryness and repeatedly evaporated with small amounts of water. Crystallization from 80% acetic acid and drying at 80°C/0.2 kPa afforded 1.3 g (90%) of white crystals, m.p. 222–223°C, soluble in water and methanol and sparingly soluble in ethanol and acetone. For C₁₀H₁₆O₁₀P₂ (358.2) calculated: 33.53% C, 4.50% H, 17.29% P, alkalimetric equivalent 89.55; found: 33.43% C, 4.47% H, 17.38% P, alkalimetric equivalent 89.72. IR spectrum, cm⁻¹ (KBr disk and hexachlorobutadiene): 470 m, 607 w, 710 w, 744 m, 807 w, 862 s, 916 s, 1 021 w, 1 115 vs ν(P=O...HO), 1 166 vs ν(P=O), 1 225 s COOH, 1 291 vs COOH, 1 400 m, 1 421 s δ(CH₂), 1 659 vs ν(O=C—OH...O=P), 1 722 vs ν(C=O), 2 385–2 752 mb ν(OH...O=P) + + ν(OH), 2 923–2 996 w ν(CH₂). NMR spectrum (ppm, δ scale, D₂O): ¹H: 2.48, 4 H, distorted doublet, P(O)CH₂CH₂P(O); 3.40, 8 H, "filled-in-doublet", P(O)CH₂COO; ¹³C{¹H}: 18.62 m, P(O)CH₂CH₂P(O); 36.14 d, P(O)CH₂COO; 180.95 s, COO; ³¹P: 48.89 distorted quintet; ³¹P{¹H}: 48.88 s.

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Translated by P. Adámek.