

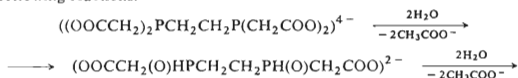
HYDROLYSIS OF ETHYLENEDIPHOSPHINETETRAACETATE ANIONS*

Jana PODLAHOVÁ and Jaroslav PODLAHA

*Department of Inorganic Chemistry,
Charles University, 128 40 Prague 2*

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The anions of ethylenediphosphinetetraacetic acid are hydrolyzed in aqueous solutions at 80°C in the two following reactions:



$(\text{O}(\text{O})\text{HPCH}_2\text{CH}_2\text{PH}(\text{O}))^{2-}$. Both reactions are acid and base catalyzed so that, at $\text{pH} < 12$, the first reaction is much faster than the second. The reaction course was studied by ^1H NMR spectroscopy and by isolation and characterization of the products. The effect of both reactions on the stability of solutions of ethylenediphosphinetetraacetic acid and their salts is negligible at laboratory temperature.

Ethylenediphosphinetetraacetic acid^{1,2}, a phosphorus analogue of EDTA, behaves very selectively towards metal ions³, leading to its usefulness as specific complexing agent. For its use in analytical chemistry or in homogeneous catalysis, it is important to know the stability of the ligand in water, the most common solvent. Tertiary phosphines are mostly insoluble in water and thus no systematic data are available on their hydrolytic stability. The P—C bonds in some tertiary phosphines with electronegative substituents are hydrolytically cleaved⁴⁻⁶, indicating possible instability of aqueous solutions of ethylenediphosphinetetraacetic acid. This work is concerned with the course and the products of its hydrolysis in aqueous solutions.

EXPERIMENTAL

The preparation of the tetrasodium salt and of the bis(hydrochloride) of ethylenediphosphinetetraacetic acid has already been described^{1,2}. Hydrolysis was carried out by heating 0.2M solutions in water or in HCl and NaOH at $80 \pm 0.5^\circ\text{C}$ under anaerobic conditions (glass ampoules sealed in an argon atmosphere). After quenching the reaction by cooling, the samples were stored at -10°C before spectral measurements. As the chemical shifts of the substances are dependent on the degree of protonation, the solutions were alkalinized prior to measurement of the NMR

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spectra so that the measured solution was 1.0M in NaOH. The NMR spectra were measured at 80 MHz on a Tesla BS 487 A instrument using sodium 2,2'-dimethylsilapentanesulphonate as an internal standard. The chemical shifts were recalculated to tetramethylsilane, $\delta_{\text{TMS}} = 0.015$ ppm. The precision and reproducibility of the intensity measurements were checked using a mixture of t-butanol and dioxane under the same conditions and equalled $\pm 3\%$ rel. The ^{31}P NMR spectra were measured on a Varian XL-200 instrument with addition of c. 30% D_2O , which provided an external deuterium lock. A solution of 85% H_3PO_4 was used as an external standard. Chemical shifts to lower fields are defined as positive.

Preparation of Ethane-1,2-bis(P-phosphinylacetic Acid) *I* and Ethane-1,2-bis(phosphinic Acid) *II*

0.4 g of the bis(hydrochloride) of ethylenediphosphinetetraacetic acid (0.01 mol) was dissolved in 3 ml water and the pH was adjusted with 1M sodium hydroxide to a value of 2.5. The solution was heated in an ampoule in an inert atmosphere for 24 h to 80°C. Control ^1H NMR spectra indicated the formation of *I* and *II* in a ratio of 45 : 55%. The solution was evaporated *in vacuo* to dryness and reevaporated three times with small amounts of benzene to remove HCl and acetic acid. Then the components were separated by ion-exchange chromatography on a Dowex 50W X2 column (1.5 × 40 cm, 100–200 mesh, H^+ -form, elution with water at a flow-rate of 2 ml min $^{-1}$, conductivity detection) and two well-separated fractions were collected. Evaporation of the more mobile fraction to dryness *in vacuo* yielded a glassy substance that was recrystallized from anhydrous acetic acid to yield 115 mg (81%) of white crystalline substance with a m.p. of 119°C, with an ^1H NMR spectrum identical with that of substance *II**: NMR (1M-NaOH): ^1H : 1.63 ppm bd, $J = 3.5$ Hz, 4 H, CH_2CH_2 ; 6.96 d, $^1J(\text{PH}) = 514$, 2.1 H, P-H. $^{31}\text{P}\{^1\text{H}\}$: 30.68 s. IR (KBr disk and hexachlorobutadiene): 422 s, 460 w, 702, m, 768 m, 958 to 981 s, 1 020 m, 1 110 s, 1 183 vs, $\nu(\text{P}=\text{O})$, 1 420 w $\delta(\text{CH}_2)$, 2 410 m $\nu(\text{PH})$, 2 700 w, vb $\nu(\text{OH})$, 2 930 w, 2 970 w $\nu(\text{CH}_2)$. For $\text{C}_2\text{H}_8\text{O}_4\text{P}_2$ (158.0) calc. 15.20% C, 5.10% H, 1.28% H^+ , 39.20% P; found: 15.07% C, 5.14% H, 1.30% H^+ , 39.51% P. The same product was prepared by adding 1 g of bis(dichlorophosphine)ethane 1 dropwise to 3 ml methanol with cooling; the mixture was evaporated to dryness, boiled with 6M-HCl, evaporated several times with benzene and the residue was crystallized from acetic acid. The ^1H NMR spectrum of the product was identical with the spectrum of the above substance and the mixed melting point was undepressed.

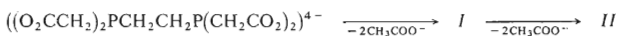
The less mobile chromatographic fraction was evaporated *in vacuo* to yield a solid substance. Crystallization from 1 ml of hot water yielded white crystals (192 mg, 73%) that melted at 197 to 198°C (decomp.) and had an ^1H NMR spectrum identical with *I*, present in the hydrolyzate of ethylenediphosphinetetraacetic acid. NMR (1M-NaOH): ^1H : 2.32 bd, $J = 3.0$, 4 H, CH_2CH_2 ; 3.0–3.3 m, 4.1 H, CH_2COO ; 7.14 d, $^1J(\text{PH}) = 528$, 0.9 H, P-H. $^{31}\text{P}\{^1\text{H}\}$: 37.73 s. IR (KBr disk and hexachlorobutadiene): 450 s, 595 w, 669 w, 762 m, 820 m, 900 w, 933 m, 975 m, 1 120 s, 1 170 vs $\nu(\text{P}=\text{O})$, 1 208 m COOH , 1 280 vs, 1 412 m $\delta(\text{CH}_2)$, 1 453 w $\delta(\text{CH}_2)$, 1 730 vs $\nu(\text{C}=\text{O})$, 2 435 w $\nu(\text{PH})$, 2 880–2 985 m $\nu(\text{CH}_2)$, 2 960 s, vb $\nu(\text{OH})$. For $\text{C}_6\text{H}_{12}\text{O}_6\text{P}_2$ (242.1) calculated 29.77% C, 5.00% H, 0.83% H^+ , 25.58% P; found: 29.22% C, 4.78% H, 0.83% H^+ , 25.69% P.

RESULTS AND DISCUSSION

The properties of aqueous solutions of ethylenediphosphinetetraacetic acid do not change in the range pH 2–12 (HCl or NaOH) during storage in an inert atmosphere for 1 month at laboratory temperature, as was demonstrated analytically, by ^1H NMR

* Present in a hydrolyzate of ethylenediphosphinetetraacetic acid.

spectra and thin-layer chromatography. A further study of the hydrolysis was therefore carried out at 80°C. Its time course was studied at various initial pH values by the ^1H NMR spectroscopic method. Because of the rapid exchange of the acetate protons for deuterium², all the measurements were carried out in H_2O . Fig. 1 gives the ^1H NMR and for illustration also the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a typical solution after hydrolysis. Changes in the intensities of the individual bands in dependence on the hydrolysis conditions can be unambiguously interpreted as formation of three products: acetate anion and components *I* and *II*, containing phosphorus. Measurement of the band intensities permitted quantitative evaluation of the contributions of the individual components. It has been found that the hydrolysis consists of the following reactions:



The dependence of the quantitative course of the reactions on the pH is given in Fig. 2. It is apparent that formation of *I* and *II* is acid and base catalyzed, where, except in strongly alkaline medium, the first reaction is much faster than the second.

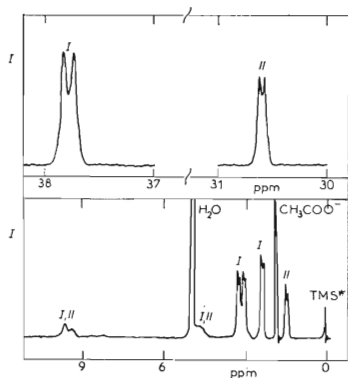


FIG. 1

NMR spectrum of the hydrolysis product after 24 h at pH 4. Top, $^{31}\text{P}\{^1\text{H}\}$, bottom, ^1H

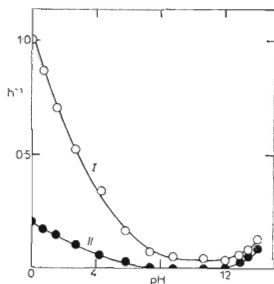
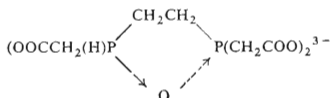


FIG. 2

Dependence of the half-time of the hydrolytic reactions producing *I* (A) and *II* (B) on pH

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the hydrolyzed product consists of two closely spaced doublets (separation ~ 0.1 ppm), whose relative intensities correspond to the contents of substances *I* and *II*. Thus substance *I* contains two very similar types of phosphorus atoms, as does substance *II*. It is highly improbable that a splitting of 0.1 ppm would correspond to two chemically different phosphorus atoms in a single substance, because the chemical shifts for the types of phosphorus atoms coming into consideration (tertiary phosphine, phosphine oxide, phosphinic acid) differ by tens of ppm⁷. The presence of a closely spaced doublet in the spectrum of a substance containing two chemically equivalent phosphorus atoms is frequent when both phosphorus atoms are chiral^{7,8}: the signals correspond to the racemate and to the *meso*-form, present in statistical ratio of 1 : 1. This structural type can be expected for substances *I* and *II*. No analogous effect was observed in the ^1H NMR spectra.

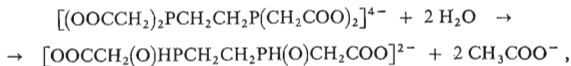
No further components were found in observable concentrations ($>2\%$) among the hydrolysis products, especially those that would contain an odd number of acetate groups. It can be expected that, if they are temporarily formed, the second phosphorus atom is affected by an intramolecular interaction of the type



leading to lability of the P—C bond on the “phosphine” atom and subsequent rapid splitting off of the second acetate group. The existence of this effect is demonstrated by the fact that oxidation of ethylenediphosphinetetraacetic acid⁹ and of other bis(tertiary) phosphines¹⁰ occurs at both phosphorus atoms simultaneously.

Compounds *I* and *II* were identified preparatively. The approximately equimolar mixture formed by hydrolysis under suitable conditions was separated chromatographically into two fractions, from which the crystalline products were obtained as the free acids. Analytical data, ^1H NMR, ^{31}P NMR and infrared spectra confirmed the following composition and structures of the products.

Compound *I*, ethane-1,2-bis(P-phosphinylacetic acid, $\text{HOOCCH}_2(\text{O})\text{HPCH}_2\text{CH}_2\text{.PH}(\text{O})\text{CH}_2\text{COOH}$ formed according to the equation

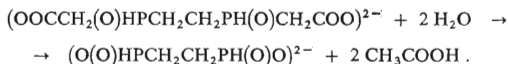


exhibits typical bands¹¹ for $\nu(\text{P}=\text{O})$ and $\nu(\text{PH})$ and also bands corresponding to undissociated carboxylic acid in the infrared spectrum. The ^1H NMR spectrum is

deceptively simple because of virtual coupling, which is common for this type of compounds^{8,12,13}. In addition to the apparent doublet at 2.32 ppm (its shape is strongly dependent on the pH), corresponding to the protons in the ethylene bridge, the spectrum contains a multiplet at 3.0–3.3 ppm, consisting mainly of two doublets. This feature is sometimes interpreted^{14,15} as a first-order spectrum with ${}^2J(\text{PCH}) \sim 14$ Hz and ${}^3J(\text{HPCH}) \sim 3.5$ Hz; at greater resolution, its shape is more complicated and also depends strongly on the pH, so that this multiplet apparently also reflects further long-range interactions in the molecule. The third typical feature in the spectrum is the widely separated doublet at 7.14 ppm (${}^1J(\text{PH}) = 528$ Hz), corresponding to the secondary phosphine hydrogen. The intensity of this band is not decreased by short action of D_2O , so that exchange for deuterium is slow compared to simple secondary phosphine oxides¹⁵. The high-field component of the doublet, measured at 80 MHz, is obscured partially by the water band; its exact position was revealed by the spectrum measured at 200 MHz. Both components of the doublet are broadened as a result of ${}^3J(\text{HPCH})$ interaction, but fine structure was not observed. The relative intensities of all the bands are in agreement with the composition of the compound.

The ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of *I* contains only a singlet whose position corresponds to the low-field component of the doublet in the original spectrum after hydrolysis. The isolated product will thus be either the racemate or the *meso*-form. As it was obtained in a yield greater than 50%, gradual isomerization of the mixture must have occurred during its precipitation, leading to formation of the less soluble form. Because of the existence of tautomeric equilibria for secondary phosphine oxides¹⁶, $\text{R}_2\text{P}(\text{O})\text{H} \leftrightarrow \text{R}_2\text{P}(\text{OH})$, it is probable that isomerization readily occurs through the tricoordinated phosphorus atom. It is, however, not clear from these properties whether the isolated substance is the *meso*-form or the racemate.

Compound *II*, ethane-1,2-bis(phosphinic acid) $\text{HO}(\text{O})\text{HPCH}_2\text{CH}_2\text{PH}(\text{O})\text{OH}$, is formed according to the equation



Its infrared spectrum contains bands of $\nu(\text{P}=\text{O})$, $\nu(\text{PH})$ and $\nu(\text{OH})$, typical for alkylphosphinic acid¹⁷. Similar to the previous case, the ${}^1\text{H}$ NMR spectrum is affected by virtual coupling and the ethylene hydrogen band is an apparent doublet at 1.63 ppm, whose shape and position change with the pH. A second feature of the spectrum is a widely spaced doublet at 6.96 ppm (${}^1J(\text{PH}) = 514$ Hz), that disappears in D_2O with a half-time of about 1 h, corresponding to hydrogens bonded to phosphorus. The components of this doublet are again broadened by ${}^3J(\text{HPCH})$ interaction. The relative intensities of the two doublets are in a ratio of 2 : 1.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum measured in D_2O immediately after dissolution again contains only a single band corresponding to a low-field component of the doublet in the original solution after hydrolysis. Leaving to stand in a D_2O solution led to gradual change of this band into a triplet with $^1J(\text{PD}) = 67.2$ Hz. It is apparent that the equilibria for this substance also shift in favour of the less soluble form, but it is not clear whether the racemate or the *meso*-form is involved.

The identity of *II* was also confirmed by independent synthesis from 1,2-bis(dichlorophosphino)ethane, yielding the same isomer as in the previous case.

It follows from the results that the mechanism of hydrolysis of ethylenediphosphinetetraacetic acid is completely different from that of EDTA which is hydrolyzed¹⁸ with splitting of the bond between the nitrogen and the bridging methylene group under drastic conditions. The relatively easy splitting of the $\text{P}-\text{CH}_2\text{COO}$ bond is apparently connected with its weakening as a result of the effect of the electro-negative carboxyl group and is in agreement with the similar behaviour of tertiary phosphines^{4-6,19,20}. The hydrolytic stability of ethylenediphosphinetetraacetic acid is thus less than that of EDTA but is quite sufficient for normal practical applications at laboratory temperature.

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