source for growth even at concentrations as high as for any other N-source regularly used in growth media. *C. lipolytica* and its variety may detoxicate HA by a lipase catalysed hydroxamate formation, and the hydroxamates formed may successively be hydrolysed and/or reduced by a HA reducing system during growth.

Thanks are due to Miss Birthe Jeppsson for skilful technical assistance.

1. Hayes, W. *The genetics of bacteria and their viruses*, Blackwells, Oxford 1964.
2. Allen, D. W. *Biochim. Biophys. Acta* **68** (1963) 418.
3. McNall, E. G. and Atkinson, D. E. *J. Bacteriol.* **74** (1957) 60.
4. Steinberg, R. A. *J. Agr. Res.* **59** (1939) 731.
5. Abadie, F. *Ann. Inst. Pasteur* **115** (1968) 197.
6. Hewitt, E. J., Hucklesby, D. P. and Betts, G. F. In Hewitt, E. J. and Cutting, C .V. *Recent aspects of nitrogen metabolism in plants*, 1968, p. 47.
7. Wallace, W. and Nicholas, D. J. D. *Biochim. Biophys. Acta* **171** (1969) 229.
8. Lundström-Eriksson, A. and Norkrans, B. *Arch. Microbiol.* **62** (1968) 373.
9. Czáky, T. Z. *Acta Chem. Scand.* **2** (1948) 450.
10. Zucker, M. and Nason, A. *J. Biol. Chem.* **213** (1955) 463.
11. Lipman, F. and Tuttle, L. C. *Biochim. Biophys. Acta* **4** (1950) 301.
12. Bernheim, M. L. *Arch. Biochem. Biophys.* **107** (1964) 313.
13. Virtanen, A. I. and Saris, N.-E. *Acta Chem. Scand.* **10** (1956) 483.
14. Peters, I. I. and Nelson, F. E. *J. Bacteriol.* **55** (1948) 581.
15. Sierra, G. *Antonie v. Leeuwenhoek* **23** (1957) 15.

Received May 14, 1969.

Comparison of Acid Strengths of Orthophosphoric Acid, Thiophosphoric Acid, Phenylphosphonic Acid, and Monophenyl Phosphate in Aqueous Potassium Chloride Solutions

OSMO MÄKITIE and VEIKKO KONTTINEN

Department of Inorganic Chemistry, University of Helsinki, Helsinki, Finland

In connection with an investigation of reactions of several phosphates in this laboratory, the values of the second dissociation constants of thiophosphoric acid (H_3PO_3S, phosphorothioic acid), phenylphosphonic acid ($PhPO_3H_2$), and monophenyl phosphate ($PhOPO_3H_2$, "phenyl phosphate") in aqueous solutions contain-

Table 1. pK_2 values of the acids at different ionic strengths (25°C).

	$\sqrt{I}$	pK_2
Orthophosphoric acid: H_3PO_4	0.098	7.042
	0.171	6.921
	0.328	6.742
	0.504	6.620
	0.993	6.443
	1.401	6.460
Thiophosphoric acid: H_3PO_3S	0.128	5.611
	0.187	5.517
	0.332	5.363
	0.500	5.228
	0.976	5.044
	1.373	5.053
Phenylphosphonic acid: $PhPO_3H_2$	0.095	7.264
	0.167	7.153
	0.320	6.994
	0.492	6.861
	0.970	6.712
	1.368	6.732
Monophenyl phosphate: $PhOPO_3H_2$	0.105	6.089
	0.145	6.040
	0.247	5.914
	0.333	5.823
	0.511	5.719
	0.715	5.629
	1.005	5.568
	1.418	5.606

Table 2. Computed values of the dissociation constants of phosphorus acids and the parameters of the Debye-Hückel equations (25°C).

	pK_2 ($I = 0.1$)	$pK_2°$	α	B
Orthophosphoric acid	6.76	7.21	1.19	0.16
Thiophosphoric acid	5.38	5.83	1.12	0.17
Phenylphosphonic acid	6.99	7.43	1.32	0.16
Monophenyl phosphate	5.85	6.28	1.41	0.15

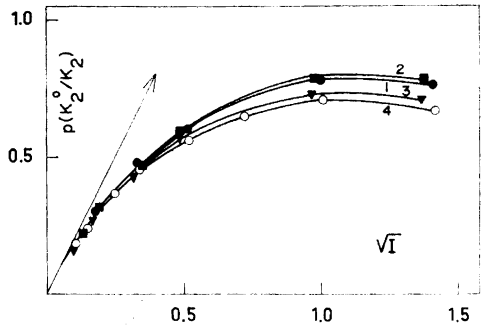


Fig. 1. $p(K_2°/K_2)$ as function of the square root of ionic strength. Curves for orthophosphoric acid (1), thiophosphoric acid (2), phenylphosphonic acid (3), and monophenyl phosphate (4).

ing potassium chloride as neutral salt, at 25°C, were potentiometrically determined. For comparison, the dissociation of orthophosphoric acid was also studied.

The results are given in Tables 1 and 2. Fig. 1 shows the dependence of the pK_2 values on ionic strength.

The thermodynamic value $pK_2° = 7.211$ (25°C) obtained for orthophosphoric acid in the present work is in accordance with previously reported values.[1] Thiophosphoric acid is a somewhat stronger acid; the value 5.83 obtained for $pK_2°$ can be compared with the value 5.75 at relatively low ionic strength reported by Neumann *et al.*[2] Several pK_2 values have been reported for phenylphosphonic acid in the literature; Lesfauries and Rumpf gave the value 6.85 (17°C, 0.02 M),[3] Polestak and Zimmermann the value 7.07 (10^{-3} M),[4] and Jaffe *et al.* the same value at ionic strength ~0.1 (the temperature was not, however, given).[5] Our values for phenylphosphonic acid at 25°C are $pK_2° = 7.43$ and $pK_2 = 6.99$ ($I = 0.1$). The second dissociation constant of phenylphosphonic acid is thus slightly lower than that of phosphorous acid ($pK_2° = 6.79 \pm 0.1$ at 25°C [6]). The values $pK_2° = 6.28$ and $pK_2 = 5.85$ ($I = 0.1$) evaluated for monophenyl phosphate show that this ester is a slightly stronger acid than orthophosphoric acid.

Experimental. The reagents used were potassium monohydrogen orthophosphate (K_2HPO_4, a reagent from The British Drug Houses Ltd.), trisodium monothiophosphate Na_3PO_3S prepared from thiophosphoryl chloride (a "pure" reagent from Koch-Light Laboratories Ltd.) and sodium hydroxide,[7] phenylphosphonic acid ($C_6H_5PO_3H_2$, a reagent from Aldrich Chemical Co., Inc.), and phenylphosphate, disodium salt $C_6H_5OPO_3Na_2$, a reagent from Eastman Organic Chemicals). Dried potassium chloride was used as neutral salt to adjust the ionic strengths of the solutions.

A Radiometer PHM 4d potentiometer connected to a Beckman glass electrode and an open liquid junction calomel electrode filled with saturated potassium chloride solution was used for EMF measurements. A 0.1 M hydrochloric acid solution was added in the titrations, which were carried out in a nitrogen atmosphere in a thermostated system. The hydrogen ion concentrations of the solutions were calculated with the aid of the apparent hydrogen ion activity coefficient values of Näsänen *et al.*[8]

The Debye-Hückel equation

$$pK_2 = pK_2° - 0.509 \cdot z^2 \sqrt{I}/(1 + \alpha \cdot \sqrt{I}) + B \cdot I$$

was fitted by the method of least squares to the data obtained from titrations carried out at different ionic strengths. The computed values of the constants and parameters are given in Table 2.

1. *Stability Constants of Metal-Ion Complexes*, The Chemical Society, London, Special Publ. No. 17, 1964, p. 180.
2. Neumann, H., Steinberg, I. Z. and Katchalski, E. *J. Am. Chem. Soc.* **87** (1965) 3841.
3. Lesfauries, P. and Rumpf, P. *Compt. Rend.* **228** (1949) 1018; Jaffe, H. H., Freedman, L. D. and Doak, G. O. *J. Am. Chem. Soc.* **75** (1953) 2209; **76** (1954) 1548; Polestak, W. J. and Zimmerman, Jr., H. K. *J. Phys. Chem.* **60** (1956) 787.
4. Mäkitie, O. and Savolainen, M.-L. *Suomen Kemistilehti* **B 41** (1968) 242.
5. Yasuda, S. K. and Lambert, J. L. *J. Chem. Educ.* **31** (1954) 572.
6. Näsänen, R., Lumme, P. and Mukula, A.-L. *Acta Chem. Scand.* **5** (1951) 1199.

Received May 13, 1969.

The Cyclization of Some *cis*-Alkenynoic Acids to α-Pyrones

II. Lactonization of Dec-2*cis*-ene-4,6,8-triynoic Acid, and 5-(5-Methyl-2-thienyl)-pent-2*cis*-en-4-ynoic Acid

KÅRE HAUGE

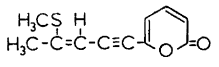
Institutt for organisk kjemi, Norges tekniske høgskole, Trondheim, Norway

In a previous note[1] the lactonization of dec-2*cis*-ene-4,6-diynoic acid (*cis*-lachnophyllum acid) (I), and of deca-2*cis*, 8*cis*-diene-4,6-diynoic acid (*cis*, *cis*-matricaria acid) (II) to the corresponding 6-substituted α-pyrones was described. The cyclization of two other *cis*-alkenynoic acids: dec-2*cis*-ene-4,6,8-triynoic acid (*cis*-dehydromatricaria ester) (III) and 5-(5-methyl-2-thienyl)-pent-2*cis*-en-4-ynoic acid (IV) to give the α-pyrones V and VI respectively, is now reported. The methyl esters of these acids are naturally occurring substances.[2,3]

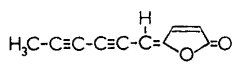
V

VI

The α-pyrone V has recently been synthesized by another method by Bohlmann *et al.*;[4] namely by cyclization of 1,1-dichlorodeca-1*trans*, 3*trans*-diene-6,8-diyn-5-one in a mixture of dioxane and 0.2 N HCl. Bohlmann also has reported the isolation of the naturally occurring acetylenic α-pyrone VII[5] and the synthesis of this by addition of methylmercaptan to V.[4]



VII



VIII

A sufficient quantity of *cis*-dehydromatricaria ester was obtained partly by isolation from *Artemisia vulgaris*[2] and partly by UV-isomerization of synthetic *trans*-dehydromatricaria ester.[6] Acid hydrolysis of the ester by the method given in the previous note[1] was then attempted. However, the acidic medium notwithstanding, the formed *cis*-dehydromatricaria acid showed a pronounced tendency toward formation of the corresponding butenolide VIII, and the yield of free *cis*-dehydromatricaria acid was small. No α-pyrone formation could be detected. Attempts were then made to combine the dehydromatricaria ester hydrolysis with Hg-catalysed ring closure to the C_5-carbon atom of the formed free acid. The best yield was obtained as follows: 100 mg *cis*-dehydromatricaria ester was dissolved in a mixture of 28 ml dioxane and 56 ml tetrahydrofuran, 30 ml sulfuric acid and 40 ml of water added together, and the mixture heated to reflux. After 9—10 min, a solution of 35 mg $HgSO_4$ in 25 ml 25 % H_2SO_4 was added slowly, addition time 45 min. The mixture was refluxed for another 15 min before work-up. After separation on an SiO_2-column, one main substance and smaller quantities of two others were isolated; all absorbed ultraviolet light.

The least polar of them was identified as the desired α-pyrone V. Initially this compound was contaminated by some of the butenolide VIII, but the pyrone was obtained pure after careful crystallization. Yield: 56 %, m.p. 108° (m.p. 110°, Bohlmann[4]). The UV, IR, NMR, and mass spectral data for the compound agree well with the data reported by Bohlmann.[4]

The most polar of the isolated compounds was identified as the Hg-containing bilactone derivative IX. Yield: 10 %. Solid, decomposes slowly on heating.