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# Mineral Acid Catalyzed Hydrolysis of Synthesized Organic Phosphate Esters

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**Abstract-** The acid-catalyzed hydrolysis of mono-m-toluidine phosphate (1) and di-p-toluidine phosphate (2) esters were studied. The rate constants increase with increase in the concentration of perchloric acid due to protonation and decreases due to participation of water molecule in rate determining step. The bimolecular nature of hydrolysis was supported by different parameters such as Hammett, Zucker-Hammett, Bunnett, Bunnett-Olsen and Arrhenius.

**Keywords:** Mineral, Catalyzed, Hydrolysis, Synthesized, Phosphate.

**Introduction :** Organophosphorous esters are one of the most impor-tant classes of compound[1-5] They play a vital role in life process. It is used for protecting crops [6-7], linestock and hunan health. Organophosphorous (OP) nerve agents are organic esters of phosphorous[8-11] based acid derivatives that have uses in chemical warfare, terrorism, and pesticides &11, Detection and neutralization of major OPs to protect human life is a major challenge around the world. Phosphodiester bonding plays a vital role in biological chemistry by linking nucleoside units to nucleic acids. Numerous kinetic and mechanistic works on hydrolysis of simple mono-, di-, and triesters of phosphoric acid refer, in their introduction, to the importance of detailed understanding of the chemical behavior of this bond. However, surprising few attempts have been made to apply the results of these fundamental studies to hydrolytic reactions of compounds that would more closely mimic the nucleic acid[12]. General acid-catalysis plays a control role in many biological processes, such as the phosphoryl transfers of phosphate monoester or the cleavage of diesters (e.g. of RNA and DNA), where, in the absence of a catalytic metal, proton activation assists P-N bond breaking. General acid-base catalysis has been shown to be important in some simple models for phosphate transfer reactions, and the common feature of these efficient intermolecular model systems is a strong intermolecular hydrogen-bond in both the product and the activated complex [13,14].

**Experimental :** Mono-m-toluidine phosphate (1) and di-p-toluidine phosphate (2) were synthesized by literature method[15] in our laboratory. The method involves the reaction of m toluidine with phosphorylating agent phosphorous pentaoxide ($P_2O_5$) in 1: 1 mole ratio. The method involves the reaction of p-toluidine and phosphorous oxychloride in 2:1 mole ratio to give crude diester as a solid. The crude product so obtained was recrystallized by ammonia solution and hydrochloric acid to get a pure

sample. The melting point of diester noted is 195$^0$C All the chemicals used were of AR grade, and all solutions were prepared in triply distilled water.

**Kinetics:** The kinetic reactions were studied spectrophotometrically with Systronics (Type-105) spectrophotometer at 400 nm. All pH measurements were done using a Systronic pH meter. All kinetic reactions were conducted under pseudo-first order conditions in the presence of perchloric acid. For all of the kinetic runs, the absorbance/time result fits very well to the first order rate equation. 2.303 / t log a / a - x

**Results and discussion :** The kinetics of hydrolysis of mono-m-toluidine phosphate and di-p-toluidine phosphate were studied in 1.0 to 7.0 HCIO4, at 5$^0$ C and 60$^0$ C The di-p-toluidine phos-phate are not soluble in water; a 20/80 (v / v) 1,4-dioxanewater medium was used. The pseudo-first order rate constants have been summarized in table 1. from the results it can be seen that rate constants increases with increase in the concentration of perchloric acid ($HClO_4$) up to 4.0 mol $dm^{-3}$ for mono-m-toluidine phosphate and di-p-toluidine phosphate esters. The rate constants were found maximum at 4.0 mol $dm^{-3}$ perchloric acid due to maximum protonation. The decrease in the rate after 4.0 mol d $m^{-3}$ perchloric acid was attributed to the lowering of concentration of attacking nucleophile taking part in the reactio, ie. due to variation in water activity[16].

**Table-1 1. kinetic rate data for the acidic hydrolysis of mono-m-toluidine (1) and di-p-totuidine (2) phosphates**

| $HClO_4$ (mol dm-3) | $K_eX10^3$ (1) | log $K_e$ | $K_eX10^3$ (2) | Log $K_e$ |
|---|---|---|---|---|
| 1.0 | 10.4 | 1.02 | 8.86 | 0.95 |
| 1.5 | 17.3 | 1.24 | 11.2 | 1.04 |
| 2.0 | 26.4 | 1.42 | 16.9 | 1.23 |
| 2.5 | 37.2 | 1.57 | 20.4 | 1.31 |
| 3.0 | 50.5 | 1.70 | 26.6 | 1.42 |
| 3.5 | 64.4 | 1.81 | 43.5 | 1.64 |
| 4.0 | 72.6 | 1.86 | 44.6 | 1.65 |
| 5.0 | 63.0 | 1.79 | 38.2 | 1.58 |
| 6.0 | 50.7 | 1.70 | 28.0 | 1.45 |
| 7.0 | 36.6 | 1.56 | 16.9 | 1.23 |

Conditions: Substrate 5.0X10$^{-4}$, temp. 50$^0$ C (1), 60$^0$ C (2) .

**Table 2 : Hammett, Zucker-Hammett, Bunnett and Bunnett-Olsen rate data for the hydrolysls of mono-m-toluldine phosphate esters**

| $HClO_4$ (mol $dm^{-3}$) | log $C_H^+$ | log $k_e$ - log $C_H^+$ | $-H_o$ | log $k_e$ + $H_o$ | - log $C_H^+$ + $H_o$ | $-\log^a_{H_2O}$ |
|---|---|---|---|---|---|---|
| 1.0 | 0.00 | 1.02 | 0.20 | 0.82 | 0.20 | 0.02 |
| 2.0 | 0.30 | 1.12 | 0.69 | 0.72 | 0.39 | 0.04 |
| 3.0 | 0.48 | 1.22 | 1.05 | 0.65 | 0.57 | 0.07 |
| 4.0 | 0.60 | 1.26 | 1.40 | 0.46 | 0.79 | 0.11 |
| 5.0 | 0.70 | 1.10 | 1.76 | 0.04 | 1.06 | 0.16 |
| 6.0 | 0.78 | 0.92 | 2.12 | -0.62 | 1.34 | 0.21 |
| 7.0 | 0.84 | 0.72 | 2.53 | -0.97 | 1.69 | 0.28 |

**Table 3.** Hammett, Zucker-Hammett, Bunnett and Bunnett-Olsen rate data for the hydrolysis of di-*p*-toluidine phosphate ester

| $HClO_4$ (mol $dm^{-3}$) | log $C_H^+$ | log $k_e$ - log $C_H^+$ | $-H_o$ | log $k_e$ + $H_o$ | - log $C_H^+$ + $H_o$ | $-\log^a_{H_2O}$ |
|---|---|---|---|---|---|---|
| 1.0 | 0.00 | 2.91 | 0.20 | -0.20 | 2.75 | 0.02 |
| 2.0 | 0.30 | 2.93 | 0.69 | -0.39 | 2.54 | 0.04 |
| 3.0 | 0.48 | 2.95 | 1.05 | -0.57 | 2.37 | 0.07 |
| 4.0 | 0.60 | 3.05 | 1.40 | -0.80 | 2.25 | 0.11 |
| 5.0 | 0.70 | 2.88 | 1.76 | -1.06 | 1.82 | 0.16 |
| 6.0 | 0.78 | 2.67 | 2.12 | -1.34 | 1.33 | 0.21 |
| 7.0 | 0.84 | 2.38 | 2.53 | -1.68 | 0.70 | 0.28 |



**Table 4.** Kinetic solvent effects rate data for the hydrolysis of mono-*m*-toluidine (1) at 50 °C and di-*p*-toluidine (2) phosphate esters at 60 °C

| $HClO_4$ (*M*) | % of Dx | $k_e \times 10^3$ (1) | $HClO_4$ (*M*) | % of Dx | $k_e \times 10^3$ (2) |
|---|---|---|---|---|---|
| 1.5 | 10.0 | 26.3 | 4.0 | 20.0 | 44.6 |
| 1.5 | 20.0 | 25.5 | 4.0 | 30.0 | 51.8 |
| 1.5 | 30.0 | 31.6 | 4.0 | 40.0 | 58.3 |

**Molecularity of reaction:** The Zucker-Hammett hypothesis[17] is made up of two parts. In the first part, 17 Hammett postulated that the reac-tions that give a linear plot of log rate constants against the acidity function ($-H_o$) did not involve water molecules in the rate-determining step. The slope value 0.71 and 0.52 (figures not shown) of the plots is far from unity, indicating the absence of unimolecular hydrolysis. The second part of the hypothesis deals with a plot between the log rate constant and the log acid molarity. A unit or approximately unit slope of this plot was used as a criterion to predict the probable mechanism to be bimolecu-lar, i.e. the reaction involves the participation of water molecule in the transition state. The slope values 0.77 and 1.10 (figures not shown) clearly indicates the bimolecularity of the reaction. The slope values of $\omega$ = 7.04, 7.65, ω *= .43, 2.09 and $\theta$ = 1.23 1.36 for Bunnett and Bunnett-Olsen parameters[18] (figures not shown) for mono-m-toluidine phosphate and di-p-tolui-dine phosphate esters also indicates the positive effect of the ionic strength. The bimolecular nature of hydrolysis was supported by different parameters such as Hammett, Zucker-Hammett, Bunnett, Bunnett-Olsen and Arrhenius. The kinetic rate data for the hydrolysis of mono-m-tolui-dine phosphate and di-p-toluidine phosphate esters have been summarized in Tables 2 and 3.

**Solvent effect:** The kinetic solvent effect was studied at 1.5 mol $dm^3$ $HClO_4$ for mono-m-toluidine phosphate ester and at 4.0 mol $dm^{-3}$ $HClO_4$ for di-p-toluidine phosphate ester in 1,4-dioxane-water (v/v) medium. The rate constants gradually increase with increase the percentage of 1,4-dioxane (Dx). The

kinetic rate data have been summa-rized in Table 4. The effect of solvent on the rate of hydrolysis indicates the transition state in which charge is dispersed. This is in accordance with Chanley's observation19. The molecular structure of Dx may be related to ethanediol and methoxyethanol, but it is almost nonpolar, aprotic and protophilic solvent[20], It has no H-bond pair formation between two Dx molecules in pure liquid state [21-22], which is mainly due to the fact that in Dx molecule ether oxygens offer H-bond acceptor sites, but it cannot self-associate due to lack of H-bond donor posi-tions[23].

**Temperature effect:** The kinetic temperature effects were studied at 3.0 mol $dm^{-3}$ $HClO^4$, for mono-m-toluidine and di-p-tolui-dine phosphate esters. The rate constant increases with increase in the temperature due to collision of molecules. The Arrhenius parameters[24] was determined; $E_a$ = 19.2 14.3 kcal $mol^{-1}$, frequency factor A = 1.80, 1.57 X $10^{-5}$ $s^{-1}$ and entropy $\Delta S^*$=10.3 26.7 e.u. These values indicate the bimolecular nature of the hydrolytic reac-tion.

**Conclusion:** The acid-catalyzed hydrolysis of mono-m-toluidine phosphate (1) and di-p-toluidine phosphate (2) esters were studied. The rate constants increase with increase in the concentration of perchloric acid due to protonation and decreases due to participation of water molecule in rate determining step. The bimolecular nature of hydrolysis was supported by different parameters such as Hammett, Zucker-Hammett, Bunnett, Bunnett-Olsen and Arrhenius.

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**References :**

1. W. P. Staward and A. L. Thomas, Expert Opin. Invest. Drugs, 2000, 9, 2913.
2. M. Dubois, D. Canadas, A. G. D. Pernot, C. Coste and A. P. Leszkowicz, J. Agric. Food Chem., 2008, 56, 1116.
3. X. Hu, J. Zhu, S. Srivasthsan and D. Pei, J. Bioorg. Med. Chem, Lett., 2004, 14, 77.
4. W. L. Mock and H. Cheng, Biochem., 2000, 39, 13945.
5. S. Hashimoto, T. Inui and Y. Nakamura, Chem. Pharm. Bull., 2002, 48, 603.
6. A. Moulin, J. H. Bell, R. F. Pratt and D. Ringe, Biochem.. 2007, 46, 5982.
7. C. Indiani, A. Feis, B. D. Howes, M. P. Marzochi and G. Smulevich, J. Am. Chem. Soc., 2000, 122, 7368.
8. T. Dale and J. Rebek, J. Am. Chem. Soc., 2006, 128, 4500.
9. S. Bencic, T. Sternfeld and D. R. Walt, J. Am. Chem. Soc., 2006, 128, 5041.
10. J. Wang, J. Zima, N. S. Lawrence and M. P. Chatrapathi, Anal. Chem., 2004, 76, 4721.
11. S. D. Seferos, D. A. Giljohann, D. Hill and A. E. Progodich, J. Am. Chem. Soc., 2007, 129, 15477.
12. G. R. J. Thatcher and R. Kluger, Adv. Phys. Org. Chem., 1989, 25, 99.
13. A. J. Kirby, N. R. Dutta, D. Silva and J. M. Goodman, J. Am. Chem. Soc., 2007, 127, 7033
14. A. J. Kirby, J. C. Gesser and P. Nome, Can. J. Chem., 2005, 72, 3800.
15. Cavalier, Bull. Soc. Chim. France, 1895, 13,885
16. Debye and Hückel, J. Physic., 1923, 185, 305.
17. L. Zucker and L. P. Hammett, J. Am. Chem. Soc.. 1939, 6, 2791.

18. J. F. Bunnett and F. F. Olsen, Can. J. Chem., 1966, 44, 1917.
19. J. D. Chanley and E. J. Feageson, J. Am. Chem. Soc., 1958, 80, 2686.
20. F. Corradini, A. Marchetti, M. Tagliazucchi, L. Tassi and G. Tosi, Aust. J. Chem., 1995, 48, 1193.
21. A. L. McChellan, San Fransisco, CA, 1966.
22. S. Sudo, N. Oshiki, N. Shinyashiki, S. Yagihara, A. C. Kumbharkhane and S. C. Mehrotra, J. Phys. Chem. (A), 2007, 111, 2993.
23. S. Schrodle, G. Hefter and R. Buchner, J. Phys. Chem. (B), 2007, 111, 5946.
24. S. Arrhenius, J. Phys. Chem., 1889, 4, 226.