

KINETICS AND MECHANISM OF THE NEUTRAL HYDROLYSIS OF 2, 4-DICHLOROPHENYL DIHYDROGEN PHOSPHATE

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ABSTRACT

Hydrolysis of 2, 4-dichlorophenyl dihydrogen phosphate has been studied in aqueous medium (*ca.* pH 7.0), at 98°. During the hydrolysis, the pH of the solution varies from pH 7.0 to pH 3.0. Agreement of the rate of neutral hydrolysis, with specific mononegative rate, shows that the reaction proceeds *via* mononegative species. The reaction proceeds with bimolecular nucleophilic attack of water on phosphorus of the reactive mononegative species involving phosphorus-oxygen bond fission. The effect of temperature, solvent and reagents on the reaction rate have been studied to give extra support to probable reaction mechanism.

THE well-acknowledged role and wide applicability of reactions of organic phosphates in various branches of chemistry, has inspired tremendous attention towards their reaction kinetics of hydrolysis during the last two decades¹. Almost no kinetic data of the neutral hydrolysis of phosphates are available. Thus investigation of the neutral hydrolysis of 2, 4-dichlorophenyl dihydrogen phosphate, which is a synthetic plant hormone², is undertaken with a view to finding the influence of the substitution of hydrogen atoms by chlorine atoms in ortho and para positions to the phosphate side chain of the ester on the reaction mechanism.

MATERIALS AND METHODS

2, 4-dichlorophenyl dihydrogen phosphate was prepared from the 2, 4-dichlorophenol and phosphorus oxychloride by the method devised by Maguire and Shaw². The product, 2, 4-dichlorophenyl phosphorodichloridate, b.p. 115°/1.5 mm, was slowly added to warm water with stirring; when cooled the solution deposited, 2, 4-dichlorophenyl

Neutral species $\xrightleftharpoons{\text{pH } 0.2 \text{ to } 4.5}$ Mononegative species + H⁺ $\xrightleftharpoons{\text{pH } 4.5 \text{ to } 7.46}$ Dinegative species + H⁺

dihydrogen phosphate which separated from toluene, m.p. 65° (Found C, 28.90; H, 2.50; P, 13.0. Required C, 29.65; H, 2.05; P, 12.74%).

PROCEDURE

Kinetic runs were carried out at 98° ± 0.05° employing 5.0 × 10⁻⁴ M solution of 2, 4-dichlorophenyl dihydrogen phosphate in aqueous medium (*ca.* pH 7.0). The estimation of reaction product (Inorganic phosphate) was carried out by Allen's

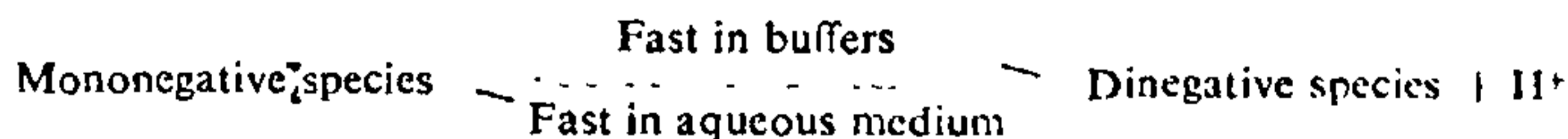
modified method³ using "Systronix" Photoelectric Colorimeter. All chemicals used were of A.R. quality. Dioxan was purified⁴.

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RESULTS AND DISCUSSION

The neutral hydrolysis (*ca.* pH 7.0) has been studied at 98° and the rate constant has been found to be 13.7 × 10⁻³ min.⁻¹. Identification of the reactive species has been done from the nature of the pH-log rate profile and pK values for various equilibria⁵. The hydrolysis of 2, 4-dichlorophenyl dihydrogen phosphate has also been studied in buffers in the range pH 1.24 to 7.46 at 98°⁶. The pH-log rate profile shows the maximum rate (14.74 × 10⁻³ min.⁻¹) in buffer of pH 4.5 and minimum rate (7.36 × 10⁻³ min.⁻¹) at pH 0.2 and these have been explained on the basis of reactive mononegative and neutral species respectively^{1,6}. The dinegative species in the buffer of pH 7.46 are found to be inert (0.2 × 10⁻³ min.⁻¹)⁶. The 2, 4-dichlorophenyl dihydrogen phosphate seems to be dissociated in two steps and the respective pK₁ (1.5) and pK₂ (7.5) have been calculated from the minimum rate at pH 0.2 and maximum rate at pH 4.5 respectively⁶.

Comparative data of the hydrolysis of 2, 4-dichlorophenyl dihydrogen phosphate in neutral medium, *ca.* pH 7.0 (13.7 × 10⁻³ min.⁻¹) and in buffer of pH 7.46 (0.2 × 10⁻³ min.⁻¹) show that the rate of the neutral (pH 6.6) hydrolysis is 70 times more than the hydrolysis in buffer of 7.46. Such a big rise in rate seems to be due to fast shifting of equilibrium in the range pH 4.5 to 7.46, in the reverse direction.



Probably conversion of existing dinegative species (which are inert in buffers) to mononegative, by protonation is kinetically fast in aqueous medium. It has been confirmed by measuring the pH of the solution during hydrolysis, which decreases from 6.6 to 3.0.

Arrhenius parameters (Table I) for the neutral hydrolysis of 2, 4-dichlorophenyl dihydrogen phosphate were determined by carrying out kinetic runs at 80°, 90° and 98° in water. These results are consistent with bimolecular⁷ nature of the reaction. Agreement of these Arrhenius parameters with those calculated for mononegative species by carrying out kinetic runs at pH 4.17 (Table I) supports that the hydrolysis proceeds via mononegative species.

TABLE I

Arrhenius parameters for the hydrolysis of 2, 4-dichlorophenyl dihydrogen phosphate

Parameters	Medium	
	pH 4.17	Aqueous (ca. pH 7.0)
E	20.9 K.cal/mole	22.0 K.cal/mole
A	$4.8 \times 10^8 \text{ sec}^{-1}$	$2.3 \times 10^9 \text{ sec}^{-1}$
Δ_s^\ddagger	-21.2 e.u.	-18.2 e.u.

Study of the reaction in solvent mixtures has been carried out at 80° by Grunwald and Winstein^{8,9} method for supporting molecularity of the reaction. Data are summarised in Table II. Sensitivity constant (m) was found to be 0.10. Such a small magnitude of slope (much less than unity) is indicative of bimolecular^{8,9} nucleophilic attack of water on reactive species.

TABLE II

Solvent effect of neutral hydrolysis of 2, 4-dichlorophenyl dihydrogen phosphate in dioxan-water, v/v at 80°

Percentage of dioxan (v/v)	Dielectric constant at 25°	Ionising power Y	$k \times 10^3 \text{ min.}^{-1}$	k/k_0
60	27.00	0.715	2.30	3.28
50	35.60	1.361	2.49	3.55
40	44.30	1.945	2.71	3.87
20	62.20	2.880	3.00	4.28
00	78.50	3.493	2.70	3.85
80% Ethanol	0.70	1.00

Kinetic runs were carried out in aqueous medium (ca. pH = 7.0) for the further support to molecularity of the reaction of 2, 4-dichlorophenyl dihydrogen phosphate in presence of reagents of graded nucleophilic power (Table III). The change in rates

TABLE III

Hydrolysis of 2, 4-dichlorophenyl dihydrogen phosphate in aqueous medium at 98° in presence of nucleophiles

Nucleophilic reagent	Nucleophilicity ¹¹ constant n	Concentration of the reagent	$k_e \times 10^3 \text{ min.}^{-1}$	k_e/k_0
CH ₃ COO ⁻	2.72	0.1	1.63	0.12
CH ₃ COO ⁻	2.72	0.5	0.43	0.03
CH ₃ COO ⁻	2.72	1.00	0.27	0.02
H ₂ O	0.00	..	13.71	1.00
Cl ⁻	3.04	0.10	15.36	1.12
Br ⁻	3.89	0.10	16.21	1.18
I ⁻	5.04	0.10	18.26	1.33

with the change in reagents of graded nucleophilic power (Fig. 1) accounts for the bimolecular attack

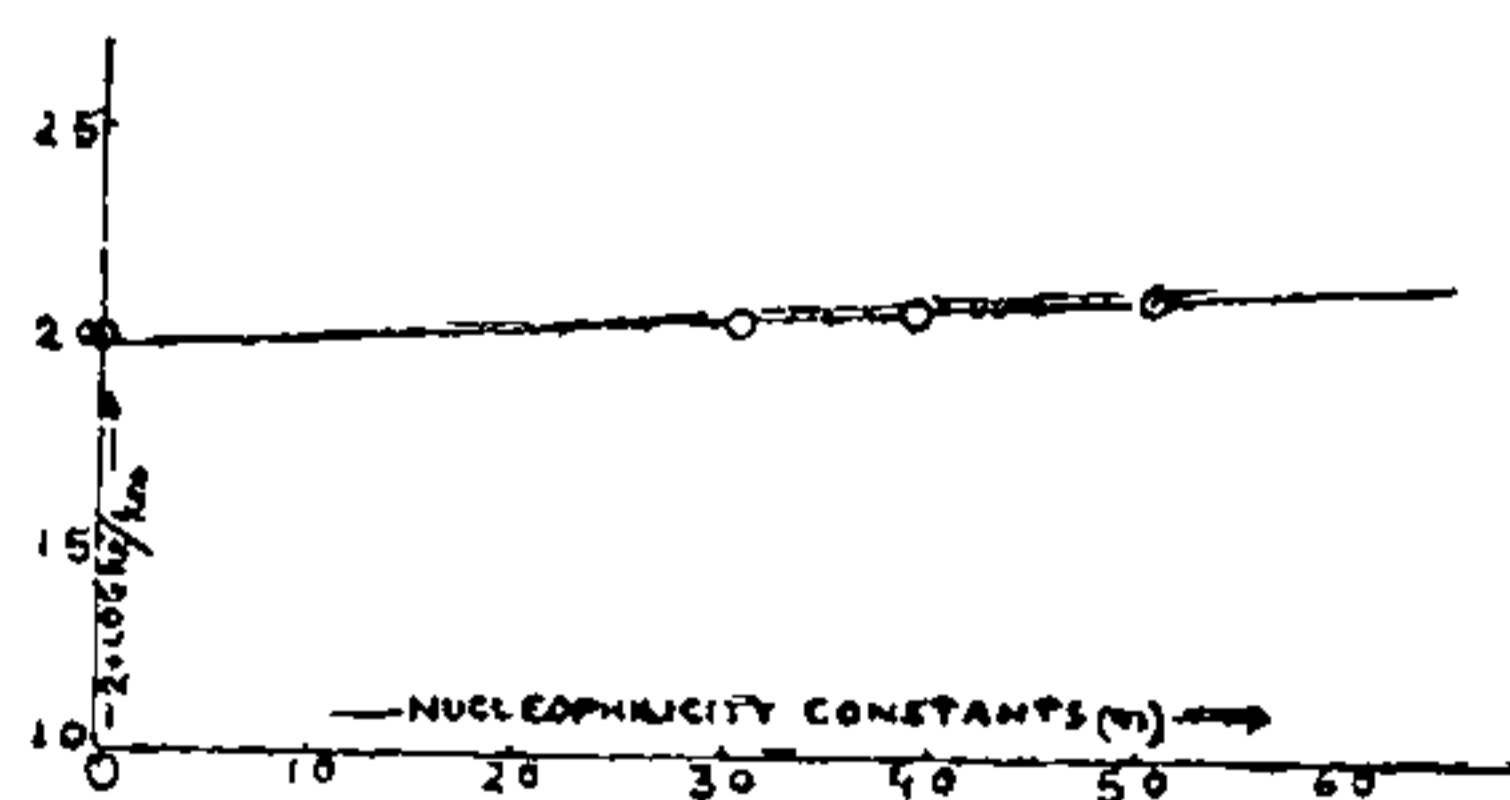


FIG. 1. Hydrolysis of 2, 4-dichlorophenyl dihydrogen phosphate in aqueous medium at 98° in presence of nucleophiles (Swain-Scott relationship).

Rate constant for hydrolysis of the compound in given anion; k_{e0} , Rate constant for the hydrolysis of the same compound in water; n , Nucleophilicity constant.

of the reagent on the substrate^{12,13,14} as has been observed by Swain and Scott¹⁴. The rate constants in the presence of the acetate ion (Table III) have been found to be an exception because of its dominating basicity¹⁵. The decrease in rate constants with the

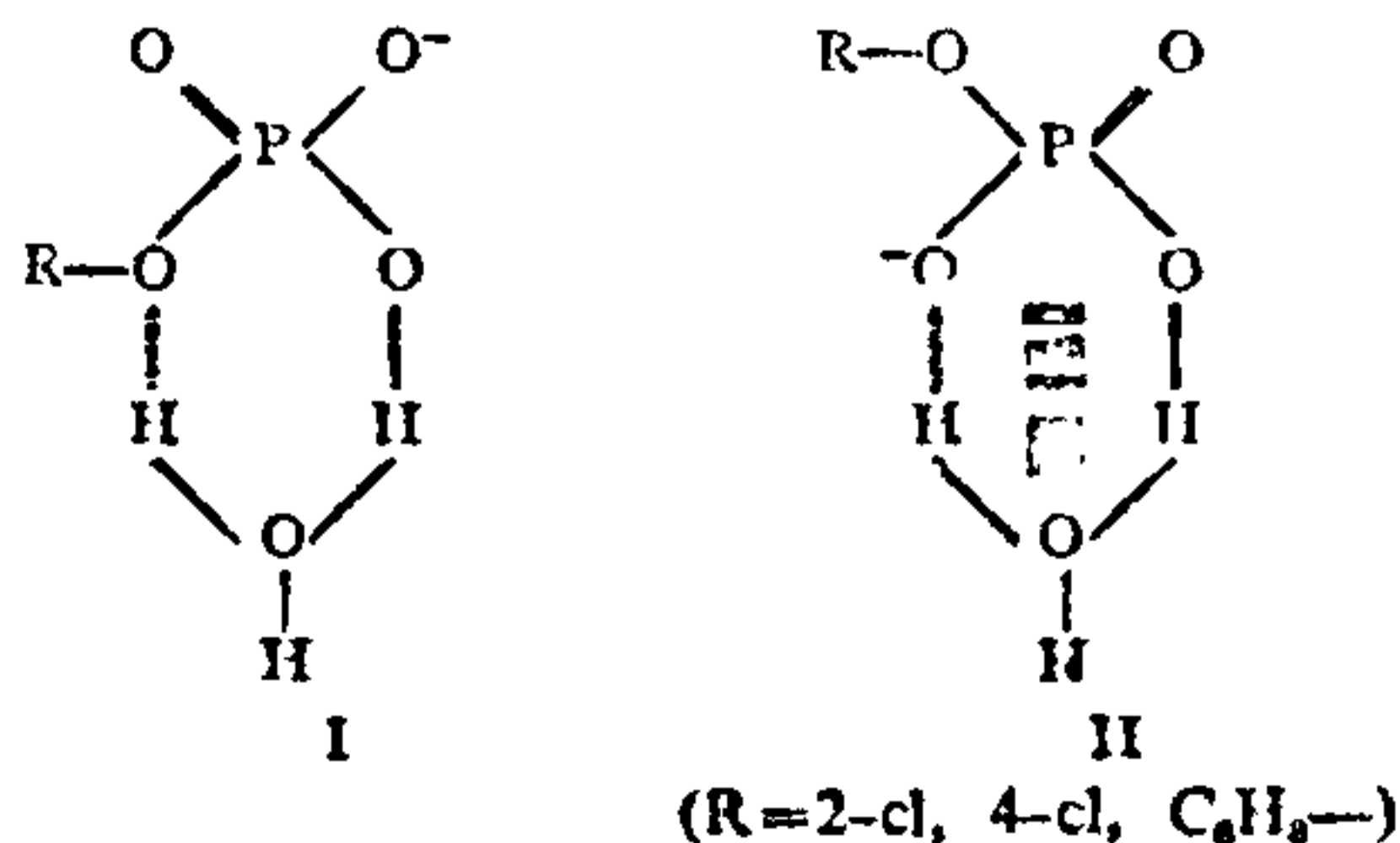
increase in ionic concentration of the acetate ions, as shown in Table III, is expected to be due to decrease in the concentration of the mononegative species in the pH range 4.5 to 7.46^{6,16,17}.

Kinetic runs have also been carried out in presence of cations of varying ionic radii as shown in Table IV. Increase in rates with the increase in ionic radii has been attributed to be due to specific salt effects⁶. Probably, electrostatic attraction of cation with -ve oxygen of reactive mononegative species reduces the -ve character of the reactive species. This effect also decreases with the decrease of the charge density, i.e., with increase of ionic radii^{19,20}.

TABLE IV
Hydrolysis of 2,4-dichlorophenyl dihydrogen phosphate in aqueous medium at 98° in presence of cations

Cations	Ionic ¹⁸ radii Å	Concentration of reagent (M)	$k_e \times 10^3$ min. ⁻¹
H ⁺	0.28	0.1 HCl	7.57
Li ⁺	0.60	0.1 LiCl	13.24
Na ⁺	0.95	0.1 NaCl	15.36
K ⁺	1.33	0.1 KCl	20.46

As regards bond fission during neutral hydrolysis, phosphorus-oxygen rather than carbon-oxygen is more probable, because resonance stabilised phenoxide ion²¹ is formed, while carbon-oxygen bond fission would have given rise to unstable cation intermediate. Electron attracting groups in the aryl part should facilitate phosphorus-oxygen bond fission²¹, whereas, carbon-oxygen bond fission should be inhibited.



The reaction paths of neutral hydrolysis via mononegative species may also be represented by

rapid formation of hydrogen bonded complexes (I) and (II) with water, which readily decompose with phosphorus-oxygen bond fission, (II) is preferred over (I) since the rate of hydrolysis increases with electron attracting power of the substituent²² which will not favour hydrogen bonding as shown in I.

The probable reaction paths of the neutral hydrolysis, consistent with the experimental data, may be formulated as in Chart I shown below:

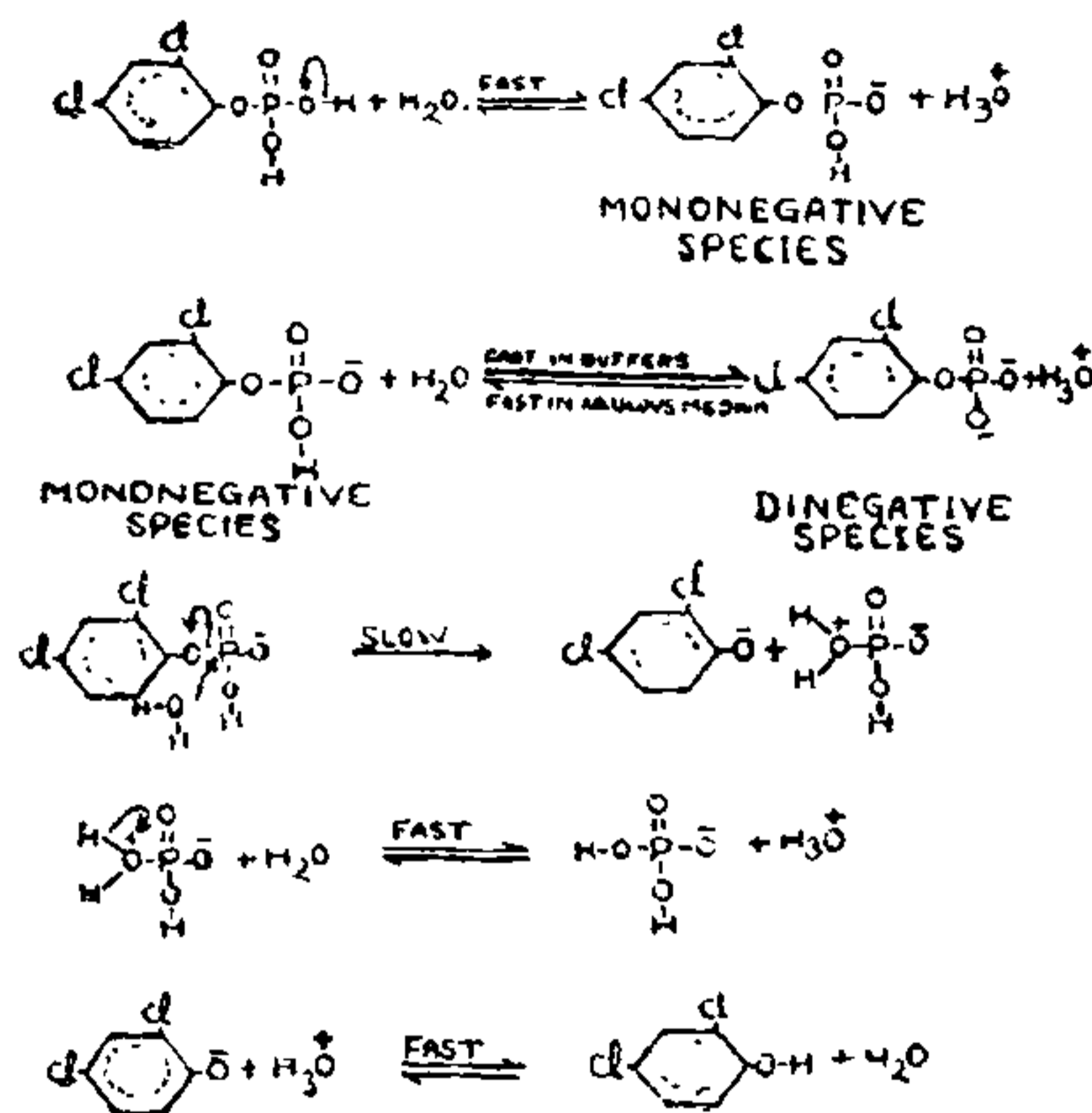


CHART 1. Mechanism of the neutral hydrolysis of 2,4-dichlorophenyl dihydrogen phosphate.

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DIELECTRIC CONSTANTS AND EFFECTIVE IONIC CHARGES OF SOME CUBIC NITRATES

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ABSTRACT

Low frequency dielectric constant measurements have been made on die-pressed powder samples of $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$. The dielectric constants (corrected to crystal density) are 5.17, 4.59 and 11.90 respectively. These dielectric constants yield the values 0.84, 0.71 and 1.04 respectively for the Szigetzi charges.

THE nitrates of Sr, Ba and Pb form an isomorphous group of crystals with cubic structure. Krishnan¹ has reviewed the data regarding several physical properties of these crystals. However there is meagre information about their dielectric constants. The few values that are available in literature show considerable scatter. Thus we have the values 5.33² and 5.83³ for $\text{Sr}(\text{NO}_3)_2$, 4.95² and 5.9⁴ for $\text{Ba}(\text{NO}_3)_2$ and 16.8², 15.9³ and 37.7⁴ for $\text{Pb}(\text{NO}_3)_2$. In view of these large differences between the values from different sources, a systematic redetermination of the dielectric constants of these materials has been carried out.

Pure chemicals obtained from B.D.H. were used for preparing die-pressed samples and measurements were made at various frequencies following the experimental technique described earlier⁵. Typical curves between the dielectric constant (ϵ_p) of the powder sample and the frequency (f) at which the measurement was made are given in Fig. 1. The implications of such curves have been discussed earlier⁵ as also, the procedure for obtaining the dielectric constant (ϵ) of the solid from the dielectric constant (ϵ_p) of a powder sample with packing fraction δ . The values of ϵ , thus obtained, are given in Table I.

The bonding in these crystals is of some interest. These crystals are essentially ionic. From electronegativity considerations the bonding in $\text{Ba}(\text{NO}_3)_2$ should be more ionic than that in $\text{Sr}(\text{NO}_3)_2$. From I.R. spectroscopic studies, Brooker *et al.*⁶ conclude that the bonding in these crystals is highly ionic.

TABLE I

Dielectric constants, input physical properties for eq. (1) and effective ionic charges of $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$

	r (Å)	v (Å ³)	$\frac{\beta}{10^{-12}}$ (cm ² dyne ⁻¹)	n^2	ϵ	q^*
$\text{Sr}(\text{NO}_3)_2$	3.54	117.7	2.95	2.53	5.17	0.84
$\text{Ba}(\text{NO}_3)_2$	3.73	133.3	4.26	2.47	4.59	0.71
$\text{Pb}(\text{NO}_3)_2$	3.62	121.1	3.21	3.17	11.90	1.04

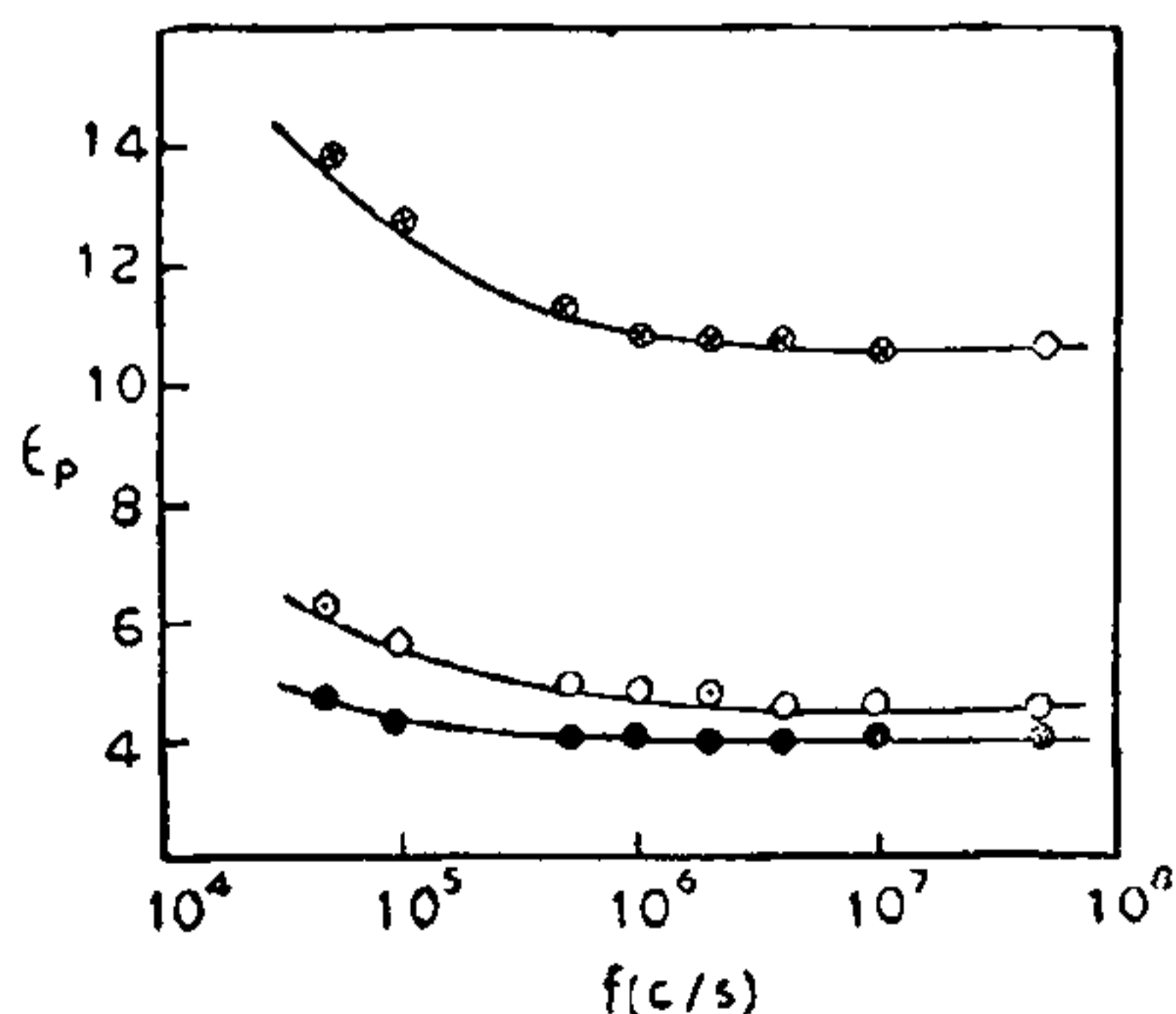


FIG. 1. Plot between the frequency (f) and the dielectric constant (ϵ_p) of the powder samples (with $\delta = 0.9$) of $\text{Sr}(\text{NO}_3)_2$ \odot , $\text{Ba}(\text{NO}_3)_2$ \bullet and $\text{Pb}(\text{NO}_3)_2$ \odot .