TABLE 3—THERMODYNAMIC ACTIVATION PARAMETERS IN WATER-ACETONE

ΔH^*, ΔG^* in k cal mol^{-1} , ΔS^* in cal mol^{-1} deg^{-1}

Acetone% (v/v)	ΔH^*	15°		20°		25°		30°		35°	
		ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*
10	22.5	20.5	7 0	20.4	7 0	20.4	7.0	20.4	7.0	20.4	7.0
20	22.0	20.6	5.0	20.6	5.0	20.6	4.9	20 5	5.0	20.5	5.1
30	21 6	20.7	3.1	20.7	3.1	20.7	3.1	20 6	3.2	20 6	3.2
40	21.1	20.8	0.8	20.8	0.7	20.8	0 8	20.8	0.8	20.8	0.8
50	20.9	20.9	−0.2	20.9	−0.3	20.9	−0.2	20.9	−0 2	20.9	−0.1
60	20.6	21.0	−1.3	21.0	−1 3	21.0	−1.2	21.0	−1.3	21.0	−1.2
70	20.2	21.0	−3.0	21.0	−2.9	21.1	−3.0	21.1	−3.1	21.1	−3.0

percentage of acetone. If the decrease is attributed to the solvation change then one of the states (reactant or transition state) is more prone to solvation than the other.

Since the transition state is a large dipolar anion with two units of negative charge on it, its solvation will ıncrease with increasing percentage of acetone compared to the initial state. Naturally E_0 value will decrease. However, it is important to note that the rate is not increasing. This may be on account of the fact that the reaction is entropy dependent.

Thermodynamic parameters : The thermodynamic activation parameters, ΔH^*, ΔS^* and ΔG^* were calculated by usual methods. They have been listed in Table 3. It is to be noted that ΔG^* increases very slowly as the proportion of acetone is increased. This shows that the stability of the transition state is very little affected by the addition of organic cosolvent. The variation in ΔS^* and ΔH^* obeys the Barclay-Butler rule[14] resulting a straight line plot with slope equal to 750. This slope, also known as Glunwald[15] solvent stabilisation operator, predicts, the absence of the strong interaction when the value is near about 800. This suggests that only little interaction when acetone is taking place.

Effect of ionic strength : The small effect of ionic strength suggests that the reaction is not of ion-ion but ion-molecule type.

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First Dissociation Constant of *o*-Phthalic Acid from 283.15 to 323.15 K

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Manuscript received 16 August 1983, revised 29 June 1984, accepted 15 February 1985

RECENTLY we have shown that the use of modified Davies equation gives as accurate values of pK_1 and pK_2 of *o*-phthalic acid as is obtained by the use of full Debye-Hückel equation[1]. Modified Davies equation (1) and the independence of β_i

$$\log \gamma_i = -\frac{AZ_i^2\sqrt{\mu}}{1+\sqrt{\mu}} + \beta_i\mu \tag{1}$$

therein on the composition of ionic atmosphere, at least upto $\mu = 0.1$ mol kg^{-1} was applied by Sinha *et al.*[2] to determine pK_1 of oxalic acid from 283.15 to 323.15 K in steps of 5 K and for this, cell (C-1) was used.

$$\underset{(Pd)}{H_2} \,\Big|\, \underset{m_1}{H_2Ox,}\quad \underset{m_2}{NaCl,}\quad AgCl \,\Big|\, Ag \qquad \text{(C-1)}$$

In this note an attempt has been made to test indirectly the accuracy of the pK_1 values of oxalic acid obtained by them. Simultaneously it has been shown that modified Davies equation gives the values of activity coefficient fairly accurately at least upto $\mu = 0.1$ mol kg^{-1}. For this, the cell (C-2) was set up.

$$\underset{(Pd)}{H_2} \,\Big|\, \underset{m_1}{H_2Ph,}\quad \underset{m_2}{KCl,}\quad AgCl \,\Big|\, Ag \qquad \text{(C-2)}$$

Experimental

KCl (G.R.) free from Br^- and *o*-phthalic acid (G.R.) on analysis by standard methods were found to be respectively 99.99 and 99.95% pure. All weighings were corrected for buoyency. The stoichiometric molalities of solutions prepared in double-distilled water were accurate upto a micro-mol kg^{-1}. The cell and its filling up with experimental solution, the thermostat and the potentiometric assembly and the measurement of the e.m.f. of the cells were the same as reported earlier[3]. Palladised platinum electrodes used as hydrogen electrodes were prepared according to Britton[4]. Silver/silver chloride electrodes were prepared by thermal electrolytic method[5]. Cells were set up in duplicate and the e.m.f. readings of the two cells agreed with one another within 0.06 mV. The recorded e.m.f. values in abs. volt are the mean of the two duplicate readings after making correction for the barometric pressure, vapour pressure and bubbler depth[6]. The molalities of the various ionic species were found as described below.

Results and Discussion

The e.m.f. of cell (C-2) is given by equation (2).

$$E = E^o - k \log m_H \cdot m_{Cl} - k \log \gamma_H \cdot \gamma_{Cl} \qquad (2)$$

It reduces to equation (3) on applying modified Davies equation.

$$-\log m_H = \frac{E-E^o}{k} + \log m_{Cl} - \frac{2A\sqrt{\mu}}{1+\sqrt{\mu}} + \beta\mu \qquad (3)$$

where, $k = \frac{2.3026RT}{F}$, $E^o = E^o_{Ag/AgCl,Cl^-}$

and $\beta = (\beta_H + \beta_{Cl})$.

For the cell solution, since $m_K = m_{Cl}$,

$$m_H = m_{HPh} + 2m_{Ph} \qquad (4)$$

and the ionic strength, μ is

$$\mu = \frac{3}{2}m_H - \frac{1}{2}m_{HPh} + m_2 \qquad (5)$$

From second dissociation equilibrium, we have

$$\log\frac{m_{Ph}}{m_{HPh}} = \log K_2 - \log m_H + \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}} - \beta_2\mu \qquad (6)$$

where, $\beta_2 = (\beta_H + \beta_{Ph} - \beta_{HPh})$.

From the e.m.f. values of Hamer, Pinching and Acree's cell[1] values of β_2 could be calculated and are given in Table 1.

TABLE 1—VALUES OF β_2

Temp. K	β_2 kg mol^{-1}
278.15	0.67±0.02
283.15	0.64±0.05
288.15	0.64±0.03
293.15	0.68±0.001
298.15	0.70±0.02
303.15	0 69±0.02
308.15	0.67±0.04
313.15	0.65±0.03
318.15	0.64±0.03
323.15	0.64±0.C2

The values of k, E^o and A are known from literature[7-9]. The values of β to be used in equation (3) have been recorded previously[10]. Now assuming an arbitrary value of μ in equation (3) we get a value of m_H, which when fed in equations (4) and (6) gives values of $(m_{HPh}+2m_{Ph})$ and $\frac{m_{Ph}}{m_{HPh}}$ and hence values of m_{HPh} and m_{Ph}, respectively. The values of m_H and m_{HPh} when fed in equation (5) gives a fresh value of μ. The interaction is continued till we get constant and consistent values of μ, m_H and m_{HPh} correct to a micro-mol kg^{-1}. Then m_{H_2Ph} is obtained from equation (7).

$$m_{H_2Ph} = m_1 - m_{HPh} - m_{Ph} \qquad (7)$$

Now, $\log K_1 = \log \frac{m_H \cdot m_{HPh}}{m_{H_2Ph}} + \log \frac{\gamma_H \cdot \gamma_{HPh}}{\gamma_{H_2Ph}}$, which reduces to equation (8) on putting $K_{A(1)} = \frac{m_H \cdot m_{HPh}}{m_{H_2Ph}}$, assuming $\gamma_{H_2Ph} = 1$ and introducing modified Davies equation.

$$\log K_{A(1)} - \frac{2A\sqrt{\mu}}{1+\sqrt{\mu}} = \log K_1 - \beta_1\mu \qquad (8)$$

Values of the molalities of various ionic species, μ and $\left(\log K_{A(1)} - \frac{2A\sqrt{\mu}}{1+\sqrt{\mu}}\right)$ are recorded in Table 2. The values at 303.15 K only have been given for brevity.

Plots of L.H.S. of equation (8) against μ at all the temperatures studied were linear, whose intercept

TABLE—2

Temp.=303.15 K

$m_1\times10^2$	$m_2\times10^2$	E abs. V	$m_H\times10^3$	$m_{HPh}\times10^3$	$m_{Ph}\times10^5$	$m_{H_2Ph}\times10^3$	$\mu\times10^2$	$\log K_{A(1)} - \frac{2A\sqrt{\mu}}{1+\sqrt{\mu}} = q$
0.1652	0.3361	0.55341	0.945	0.935	0.51	0.712	0.4311	$\bar{3}$.0306
0.3419	0.6850	0.52285	1.569	1.557	0.56	1.857	0.8424	$\bar{3}$ 0329
0.6031	1.2095	0.49947	2.281	2.269	0.61	3.756	1.4382	$\bar{3}$ 0294
0.9059	1.8168	0.48303	2.964	2.950	0.67	6.102	2.1138	$\bar{3}$ 0260
1.2057	2.4180	0.47169	3.543	3.528	0.72	8.521	2.7730	$\bar{3}$.0199
1.7110	3.4314	0.45774	4.429	4.413	0.78	12.689	3.8751	$\bar{3}$ 0189
2.5012	5.0443	0.44277	5.588	5.571	0.87	19.433	5.6040	$\bar{3}$ 0082

Concentrations and ionic strengths in mol kg^{-1}.

at $\mu=0$ gave log K_1 and the slope β_1. The values of pK_1 thus found and those recalculated from Hamer, Pinching and Acree's data are given in Table 3.

TABLE 3—pK_1 OF REACTION, $H_2Ph \rightleftharpoons H^+ + HPh^-$

Temp. K	pK_1 Recalculated from H.-P.-A.	pK_1 From cell (C-2)
283.15	2.930±0.0007	2.930±0.002
288.15	2.934±0.0003	2.937±0 0007
293.15	2.942±0.0004	2.940±0.002
298.15	2.956±0.0025	2.955±0.002
303.15	2.962±0.0009	2.965±0.002
308 15	2.967±0.0021	2.967±0 001
313.15	2.979±0.0008	2 975±0.002
318.15	2.986±0.0004	2.987±0.002
323.15	2.996±0.0005	2.997±0.002

It will be seen from Table 3, that the two sets of pK_1 values at all the temperatures closely agree with each other, and only at 313.15 K the difference goes upto 0.004.

The linearity of the plots and the agreement in pK_1 values shown in Table 3 indicate that modified Davies equation fairly correctly represents the activity coefficient of ions at least upto $\mu=0.1$ mol kg^{-1}. Close agreement among the pK_1 values recorded in Table 3 may be taken to indicate that pK_1 value of oxalic acid reported by Sinha *et al.*[2] are fairly accurate.

Acknowledgement

The authors are thankful to Dr. B. Prasad for his interest. Thanks are also due to U.G.C., New Delhi for the grant of a Teacher Fellowship to one of the authors (A.K.S.).

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Kinetics of Oxygen Transfer from Triphenylarsine Oxide to Triphenylphosphine in Molten State Monitored by Infrared Spectroscopy

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Manuscript received 10 May 1984, revised 29 October 1984, accepted 15 February 1985

TERTIARYPHOSPHINES/arsines as well as their chalcogenides are known to form vast number of coordination compounds with different metal ions[1-6]. However, there is no attempt in studying atom transfer reactions between organophosphorus and organoarsenic compounds based on difference in bond strengths of P=X and As=X (X=O, S, Se). Since these types of ligands (as such or in complexed form) find great use in different catalytic processes, it may be useful to know how a tertiaryphosphine/arsine is undergoing change. In case there is oxidation of phosphine say, how will one monitor oxygen transfer to phosphorus kinetically ? For example, the reaction of manganese(II) chloride with triphenylphosphine yields $Mn(Ph_3PO)_2Cl_2$ and not $Mn(PPh_3)_2Cl_2$, mechanism of the oxidation is not known. In order to understand such atom transfer reactions, the system consisting of triphenylphosphine and triphenyl arsine oxide has been arbitrarily selected. The reaction

$$Ph_3P + Ph_3AsO \rightarrow Ph_3PO + Ph_3As$$

has been studied under nitrogen atmosphere (PO group absorbs at 1180 while AsO group at 880 cm^{-1}). This work reports our initial results.

In order to know the concentration of PO group, the area method has been employed. The intensity height method is not normally useful in infrared spectroscopy because the bands are usually broad. For conducting the experiment, a known weight, say 75 mg of 1 : 1 mixture of Ph_3P and Ph_3AsO was added to each vessel of a set of six or seven glass vessels immersed in oil-bath at temperatures of 215, 225 and 235° under nitrogen atmosphere. At regular intervals of 0,10, . 50 min, a sample tube was taken out and the reaction contents cooled immediately to stop the reaction. The ir spectrum of each sample was recorded in KBr pellets with KSCN as the internal standard (sample amount : 15 mg ; KBr 160 mg and KSCN 8 mg). The ir spectra were recorded with a Spectromom-2000 instrument. The areas of PO groups as a function of time, temperature and mole ratio were corrected with respect to the unit area of CN group and converted into the molar concentration with the help of a calibration curve prepared from Ph_3PO.

The rate of second order reaction was calculated using the relation

$$k = \frac{1}{at}\left(\frac{x}{a-x}\right) \quad (1)$$