

TABLE 3—THERMODYNAMIC ACTIVATION PARAMETERS IN WATER-ACETONE

Acetone% (v/v)	$\Delta H^*$ , $\Delta G^*$ in kcal mol <sup>-1</sup> , $\Delta S^*$ in cal mol <sup>-1</sup> deg <sup>-1</sup>													
	15°			20°			25°			30°			35°	
$\Delta H^*$	$\Delta G^*$	$\Delta S^*$	$\Delta G^*$	$\Delta S^*$	$\Delta G^*$	$\Delta S^*$	$\Delta G^*$	$\Delta S^*$	$\Delta G^*$	$\Delta S^*$	$\Delta G^*$	$\Delta S^*$		
10	22.5	20.5	7.0	20.4	7.0	20.4	7.0	20.4	7.0	20.4	7.0	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	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	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	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	-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	-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	-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 increase with increasing percentage of acetone compared to the initial state. Naturally  $E_a$  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,  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$  were calculated by usual methods. They have been listed in Table 3. It is to be noted that  $\Delta G^*$  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  $\Delta S^*$  and  $\Delta H^*$  obeys the Barclay-Butler rule<sup>14</sup> resulting a straight line plot with slope equal to 750. This slope, also known as Glunwald<sup>15</sup> 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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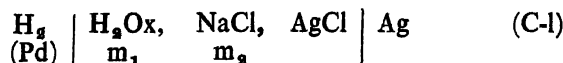
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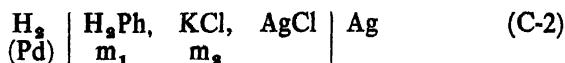
RECENTLY we have shown that the use of modified Davies equation gives as accurate values of  $pK_1$  and  $pK_2$  of *o*-phthalic acid as is obtained by the use of full Debye-Hückel equation<sup>1</sup>. Modified Davies equation (1) and the independence of  $\beta_1$ ,

$$\log \gamma_1 = -\frac{AZ_1^2 \sqrt{\mu}}{1 + \sqrt{\mu}} + \beta_1 \mu \quad (1)$$

therein on the composition of ionic atmosphere, at least upto  $\mu = 0.1$  mol kg<sup>-1</sup> was applied by Sinha *et al.*<sup>2</sup> 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.



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<sup>-1</sup>. For this, the cell (C-2) was set up.



Experimental

KCl (G.R.) free from Br<sup>-</sup> 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 buoyancy. The stoichio-

metric molalities of solutions prepared in double-distilled water were accurate upto a micro-mol kg<sup>-1</sup>. 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<sup>3</sup>. Palladised platinum electrodes used as hydrogen electrodes were prepared according to Britton<sup>4</sup>. Silver/silver chloride electrodes were prepared by thermal electrolytic method<sup>5</sup>. 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<sup>6</sup>. 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).

$$E = E^0 - k \log m_H \cdot m_{Cl} - k \log \gamma_H \cdot \gamma_{Cl} \quad (2)$$

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

$$-\log m_H = \frac{E - E^0}{k} + \log m_{Cl} - \frac{2A\sqrt{\mu}}{1 + \sqrt{\mu}} + \beta\mu \quad (3)$$

where,  $k = \frac{2.3026RT}{F}$ ,  $E^0 = E^0_{Ag/AgCl, Cl^-}$

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

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

$$m_H = m_{HPH} + 2m_{Ph} \quad (4)$$

and the ionic strength,  $\mu$  is

$$\mu = \frac{3}{2}m_H - \frac{1}{2}m_{HPH} + m_a \quad (5)$$

From second dissociation equilibrium, we have

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

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

From the e.m.f. values of Hamer, Pinching and Acree's cell<sup>1</sup> values of  $\beta_a$  could be calculated and are given in Table 1.

TABLE 1—VALUES OF  $\beta_a$

Temp. K	$\beta_a$ kg mol <sup>-1</sup>
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 ± 0.02

The values of  $k$ ,  $E^0$  and  $A$  are known from literature<sup>7-9</sup>. The values of  $\beta$  to be used in equation (3) have been recorded previously<sup>10</sup>. Now assuming an arbitrary value of  $\mu$  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  $\mu$ . The interaction is continued till we get constant and consistent values of  $\mu$ ,  $m_H$  and  $m_{HPH}$  correct to a micro-mol kg<sup>-1</sup>. Then  $m_{H,Ph}$  is obtained from equation (7).

$$m_{H,Ph} = m_H - m_{HPH} - m_{Ph} \quad (7)$$

Now,  $\log K_1 = \log \frac{m_H \cdot m_{HPH}}{m_{H,Ph}} + \log \frac{\gamma_H \cdot \gamma_{HPH}}{\gamma_{H,Ph}}$ , which

reduces to equation (8) on putting  $K_{A(1)} = \frac{m_H \cdot m_{HPH}}{m_{H,Ph}}$ ,

assuming  $\gamma_{H,Ph} = 1$  and introducing modified Davies equation.

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

Values of the molalities of various ionic species,  $\mu$

and  $(\log K_{A(1)} - \frac{2A\sqrt{\mu}}{1 + \sqrt{\mu}})$  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  $\mu$  at all the temperatures studied were linear, whose intercept

TABLE-2

Temp. = 303.15 K								
$m_1 \times 10^3$	$m_2 \times 10^3$	E abs. V	$m_H \times 10^3$	$m_{HPH} \times 10^3$	$m_{Ph} \times 10^3$	$m_{H,Ph} \times 10^3$	$\mu \times 10^3$	$\log K_{A(1)} - \frac{2A\sqrt{\mu}}{1 + \sqrt{\mu}} = q$
0.1652	0.3361	0.55341	0.946	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	0.48903	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	3.9751	$\bar{3}.0189$
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<sup>-1</sup>.

at  $\mu=0$  gave  $\log K_1$  and the slope  $\beta_1$ . 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.	From cell (U-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.*<sup>8</sup> are fairly accurate.

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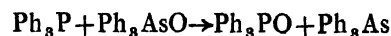
## Kinetics of Oxygen Transfer from Triphenylarsine Oxide to Triphenylphosphine in Molten State Monitored by Infrared Spectroscopy

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TERTIARYPHOSPHINES/arsines as well as their chalcogenides are known to form vast number of coordination compounds with different metal ions<sup>1-6</sup>. 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



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

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