

Note

The solution of dimethyl oxalate and oxalic acid in water and alkali

The standard enthalpy of formation of dimethyl oxalate

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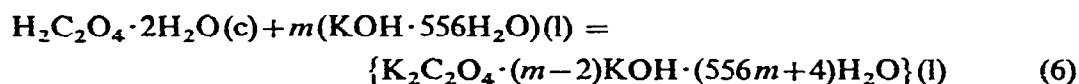
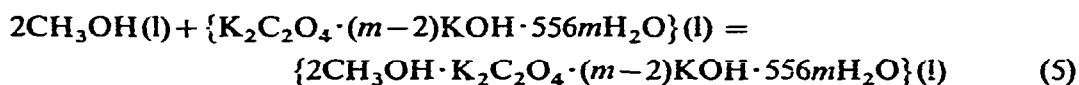
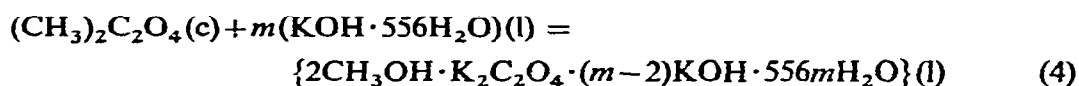
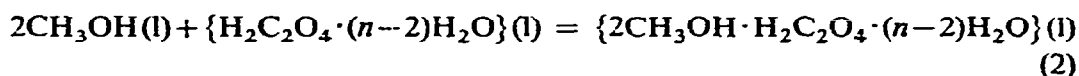
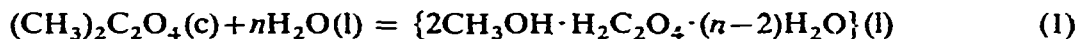
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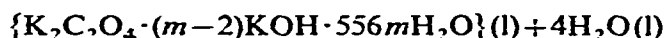
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Although it is easily prepared and purified, there are very few physical data available for dimethyl oxalate. The standard enthalpy of formation is given in only one¹ modern compilation, apparently derived from old oxygen-bomb calorimetry work²⁻⁴ for which it is impossible to quote error limits. The rate of hydrolysis in water or alkaline solution is known to be very fast^{5,6}, but although in general the hydrolysis of simple carboxylic esters may be assumed to go to completion under specified, particularly alkaline, conditions, due to the final protonation of the alkoxide ion, there appears to be no confirmation available for the specific case of dimethyl oxalate. In the present work, the enthalpies of reaction at 298.15 K have been measured for each of the following:



If hydrolysis is complete in both water and alkali, then $\Delta H(3) + \Delta H(2) - \Delta H(1) =$

$\Delta H(6) + \Delta H(5) - \Delta H(4)$, assuming the right-hand side of eqn (6) can be written



with negligible enthalpy change.

Two values for $\Delta H_f^\circ[(CH_3)_2C_2O_4, c, 298.15 \text{ K}]$ have been derived from each of the sets of reactions (1)–(3) and (4)–(6).

EXPERIMENTAL

Materials

Commercial dimethyl oxalate (BDH Ltd.) was refluxed for several hours with methanol, crystallised and pumped free from methanol. The process was repeated. Samples were analysed titrimetrically for oxalate using potassium permanganate solution previously standardised with potassium oxalate⁷. Three different batches of material gave, respectively, 74.58, 74.46 and 74.42% oxalate by mass (calculated value 74.53).

'AnalaR' grade oxalic acid dihydrate (BDH Ltd.) was dried very gently (323 K) in an oven, and analysed as above: 69.78% oxalate by mass was found (calculated value 69.83).

'AnalaR' grade methanol (BDH Ltd.) was used directly.

0.100 mol dm⁻³ potassium hydroxide solution was made up using 'AnalaR' grade (BDH Ltd.) pellets.

Calorimetry

A commercial isoperibol solution-reaction calorimeter (L.K.B. Ltd., Model 8700) was used, containing 100 ml of liquid, and operated at $298.15 \pm 0.002 \text{ K}$. The output from the resistance bridge incorporating the temperature-measuring thermistor was connected across a chart recorder (Bryans Ltd., Model 27000) such that the resistance changes (normally of the order of 10 Ω) could be read to $\pm 0.001 \Omega$.

Dimethyl oxalate and oxalic acid dihydrate were contained in thin glass ampoules (L.K.B. Ltd., Type 8727-1), each sealed with a silicone rubber bung and wax. Methanol, for the first five experiments to determine $\Delta H(5)$, was contained in all-glass ampoules sealed with the special torch provided, but due to difficulty in sealing caused by the vapour pressure of methanol, later runs were performed using Type 8727-1 ampoules sealed with a silicone bung and 'Torr-seal' epoxy resin (Varian Ltd.); no difference in results was apparent.

The performance of the calorimeter was checked by determining the enthalpy of neutralization of 2-amino-2-hydroxymethylpropane-1,3-diol (THAM) in aqueous 0.100 mol dm⁻³ hydrochloric acid. The mean result (six determinations) was $\Delta H(298.15 \text{ K}, 1464 > r > 1285) = -29.719 \pm 0.029 \text{ kJ mol}^{-1}$, where r is the mole ratio of water to THAM. For this reaction, Hill et al. report⁸ $\Delta H(298.15 \text{ K}, 1574 > r > 1170) = -29.744 \pm 0.006 \text{ kJ mol}^{-1}$.

In calculating the results, weights were corrected to vacuo using densities⁹ of 1.15 g cm⁻³ for dimethyl oxalate, 1.65 g cm⁻³ for oxalic acid dihydrate and 0.791 g cm⁻³ for methanol. Corrections were made¹⁰ where appropriate for the evaporation of water and the condensation of vapour on breaking the ampoule. Uncertainties are expressed as \pm two standard deviations of the mean.

RESULTS

Table 1 reports the enthalpy of hydrolysis of dimethyl oxalate in water (eqn 1). The second series of experiments was performed to investigate the apparent trend of $\Delta H(1)$ with mass in the first series. However, this would seem to be mere coincidence from the second series. A combined value for $\Delta H(1)$ from the two series was obtained by weighting the mean value for each series according to the inverse of the respective variance.

TABLE 1

ENTHALPY OF HYDROLYSIS OF $(\text{CH}_3)_2\text{C}_2\text{O}_4$ IN H_2O AT 298.15 K
 $(\text{CH}_3)_2\text{C}_2\text{O}_4(\text{c}) + n\text{H}_2\text{O}(\text{l}) = \{2\text{CH}_3\text{OH} \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot (n-2)\text{H}_2\text{O}\}(\text{l})$
 $\Delta H(1) = 17.428 \pm 0.065 \text{ kJ mol}^{-1}$; $\langle n \rangle = 6941$.

1st series			2nd series		
mass $\{(\text{CH}_3)_2\text{C}_2\text{O}_4\}(\text{g})$	n	$\Delta H(1)$ (kJ mol ⁻¹) ^a	mass $\{(\text{CH}_3)_2\text{C}_2\text{O}_4\}(\text{g})$	n	$\Delta H(1)$ (kJ mol ⁻¹) ^a
0.04936	13290	16.677	0.16231	4042	17.413
0.12527	5237	17.384	0.17616	3724	17.474
0.09555	6865	17.311	0.13271	4934	17.446
0.09398	6980	17.330	0.07261	9034	17.328
0.08998	7290	17.268	0.05889	11139	17.487
0.12819	5117	17.620	0.11639	5634	17.448

^aAs used in eqn. (1).

TABLE 2

ENTHALPY OF HYDROLYSIS OF $(\text{CH}_3)_2\text{C}_2\text{O}_4$ IN
 0.1 MOL DM⁻³ KOH AT 298.15 K
 $(\text{CH}_3)_2\text{C}_2\text{O}_4(\text{c}) + m(\text{KOH} \cdot 556\text{H}_2\text{O})(\text{l}) = \{2\text{CH}_2\text{OH} \cdot \text{K}_2\text{C}_2\text{O}_4 \cdot (m-2)\text{KOH} \cdot 556m\text{H}_2\text{O}\}(\text{l})$
 $\Delta H(4) = -102.24 \pm 0.14 \text{ kJ mol}^{-1}$; $\langle m \rangle = 15.3$.

mass $\{(\text{CH}_3)_2\text{C}_2\text{O}_4\}(\text{g})$	m	$-\Delta H(4)$ (kJ mol ⁻¹) ^a
0.05364	22.0	102.247
0.08432	14.0	102.257
0.11993	9.9	102.429
0.16935	7.0	102.415
0.03954	29.9	102.048
0.13069	9.0	102.027

^aAs used in eqn. (4).

Table 2 gives the results for hydrolysis in 0.100 mol dm⁻³ potassium hydroxide solution (eqn 4). All hydrolyses in water and alkali were smooth, fast reactions, equilibrium being re-attained within 100 sec of breaking the ampoule.

The enthalpy of mixing of methanol with oxalic acid solution, $\Delta H(2)$, (eqn 2), was determined as -14.33 ± 0.17 kJ mol⁻¹ (six experiments, $\langle n \rangle = 6202$). The enthalpy of mixing of methanol with 0.100 mol dm⁻³ potassium hydroxide solution, $\Delta H(5)$, (eqn 5) was -14.66 ± 0.13 kJ mol⁻¹ (nine experiments, $\langle m \rangle = 8.7$).

For the enthalpy of solution of oxalic acid dihydrate in water (eqn 3) we obtain $\Delta H(3) = 35.41 \pm 0.19$ kJ mol⁻¹ (six experiments, $\langle n \rangle = 7784$), and for the enthalpy of neutralization in potassium hydroxide (eqn 6), $\Delta H(6) = -83.20 \pm 0.92$ kJ mol⁻¹ (six experiments, $\langle m \rangle = 14.2$). For the last two reactions, it was found that smooth reaction only occurred when finely powdered crystals of oxalic acid dihydrate were used. Larger crystals led to uneven reactions and inconsistent results.

From the results given, we obtain

$$\Delta H(3) + \Delta H(2) - \Delta H(1) = 3.64 \pm 0.24 \text{ kJ mol}^{-1} \quad (7)$$

$$\Delta H(6) + \Delta H(5) - \Delta H(4) = 4.38 \pm 0.94 \text{ kJ mol}^{-1} \quad (8)$$

This agreement, within the limits of error, confirms the complete hydrolysis of dimethyl oxalate in both water and alkali.

Using the following ancillary data:

$$\Delta H_f^\circ(\text{CH}_3\text{OH}, l) = -238.53 \pm 0.21 \text{ kJ mol}^{-1} \text{ (ref. 11)}$$

$$\Delta H_f^\circ(\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}, c) = -1426.7 \pm 0.2 \text{ kJ mol}^{-1} \text{ (refs. 12 and 13)}$$

$$\Delta H_f^\circ(\text{H}_2\text{O}, l) = -285.830 \pm 0.042 \text{ kJ mol}^{-1} \text{ (ref. 14)}$$

we obtain

$$\Delta H_f^\circ(\text{CH}_3)_2\text{C}_2\text{O}_4, c, 298.15 \text{ K} = -756.80 \pm 0.32 \text{ kJ mol}^{-1} \text{ from eqn (7)}$$

$$-756.06 \pm 1.01 \text{ kJ mol}^{-1} \text{ from eqn (8)}$$

$$\text{or combining the two values, } -756.73 \pm 0.31 \text{ kJ mol}^{-1}.$$

This compares with the earlier value of -752.7 kJ mol⁻¹ derived from oxygen-combustion calorimetry¹⁻⁴.

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