# The Heat of Hydrolysis of *i*-Propenyl Acetate and *m*-Cresyl Acetate and the Heat of Enolization of Acetone

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The heats of hydrolysis of *i*-propenyl acetate and of *m*-cresyl acetate were measured at 25°C in a reaction calorimeter. The experimental data yielded for the reaction
$$CH_2 = CMe . OAc(liq) + H_2O(liq) \rightarrow Me_2CO(liq) + HOAc(liq)$$
the value $\Delta H°_r = -14.39 \pm 0.06$ kcal.mole$^{-1}$ and for the reaction
$$m\text{-}MeC_6H_4 . OAc(liq) + H_2O(liq) \rightarrow m\text{-}MeC_6H_4OH(liq) + HOAc(liq)$$
the value $\Delta H°_r = -4.39 \pm 0.07$ kcal.mole$^{-1}$. A comparison between these two reactions yielded for the enolization reaction of acetone
$$Me_2CO(liq) \rightarrow CH_2 = CMeOH(liq)$$
a value of the enthalpy change of $\Delta H° = 7$ kcal.mole$^{-1}$ in excellent agreement with a value derived from the measurement of the equilibrium between acetone and *i*-propenol, made by Schwarzenbach and Wittwer [9].

## EXPERIMENTAL

*Apparatus, calibration and procedure* have been described elsewhere [1]. The calorimeter was charged with 90 ml of 60 % by volume ethanol containing 0.8 equiv. of sodium hydroxide per liter. The sample of the ester was enclosed in a sealed glass ampoule.

*Materials.* *i*-Propenyl acetate (Eastman Kodak) was purified by distillation through a 75 cm packed column; the main fraction had a b.p. of 96.7°C at 749 mm Hg (corr.). The equivalent weight was determined by hydrolysis in 90 % ethanol containing twice the required amount of NaOH. Equiv. wt found: 100.2, 100.2, 100.0 and 99.7; mean value 100.05 ± 0.10; calculated 100.11.

*m*-Cresyl acetate was synthesized [2] from *m*-cresol, distilled twice (b.p. 76° at 2 mm Hg and 102° at 22 mm Hg) and the resulting main fraction was frozen out four times (m.p. 9.8°, corr.). The purity was checked by alkaline hydrolysis. Neither the use of indicators and reference solutions nor of potentiometric titrations gave a sharp end point. The potentiometric titrations showed an equivalent weight 0.3 % too low.

Acetone, analytical reagent grade, was purified according to Vogel (method a) [3].

*m*-Cresol (B.D.H. Laboratory Reagent 98/100 %) was distilled and the main fraction (b.p. 71° at 3 mm Hg) was frozen out three times (m.p. 11.1°, corr.).

## RESULTS

*Calibration and heat of reaction measurements.* The determinations of the heat equivalent of the calorimeter and of the heat of hydrolysis of *i*-propenyl acetate and *m*-cresyl acetate are summarized in Tables 1, 2 and 3, respectively.

The first column in all tables gives the number of the experiment. In Table 1, the second column shows the temperature increase, expressed as $^{10}\log R_i/R_f$, where $R_i$ is the resistance of the thermistor at the initial temperature and $R_f$ that at the final temperature of the reaction period. The third column gives the input of electrical energy in calories and the fourth column shows the value obtained for the proportionality constant, $k$, in the expression $q(\text{cals.}) = k \times {}^{10}\log R_i/R_f$.

In Tables 2 and 3 the second column gives the number of mmoles of acetate hydrolyzed, the fourth column the amount of heat evolved and the last column the increase in enthalpy on a molar basis.

*Table 1.* The heat equivalent of the calorimeter. Initial temperature 24.5° and final temperature 25.5°C. The current was passed for 570 sec, the duration of the reaction period was 11 min.

| No. | $10^4 \times \log R_i/R_f$ | $q$, cal | $k \times 10^{-2}$ cal |
|---|---|---|---|
| 1 565 | 139.153 | 81.242 | 58.38 |
| 1 567 | 140.946 | 82.217 | 58.33 |
| 1 569 | 141.724 | 82.559 | 58.25 |
| 1 571 | 141.030 | 82.148 | 58.25 |

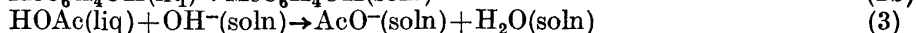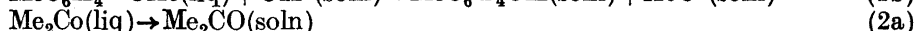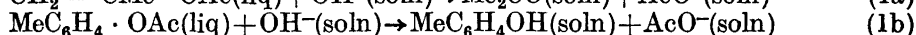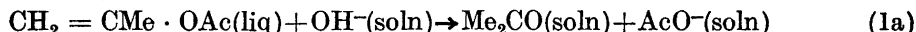Mean: $(58.30 \pm 0.30) \times 10^{-2}$

*Table 2.* The heat of hydrolysis of $i$-propenyl acetate. Duration of the reaction period 7 min. $k = 0.5830$.

| No. | mmoles | $10^4 \times \log R_i/R_f$ | $q$, cal | $-\Delta H_1$ kcal.mole$^{-1}$ |
|---|---|---|---|---|
| 1 566 | 3.0262 | 131.157 | 76.464 | 25.27 |
| 1 568 | 3.1667 | 137.565 | 80.200 | 25.33 |
| 1 570 | 3.0230 | 131.277 | 76.534 | 25.32 |
| 1 572 | 3.2487 | 141.083 | 82.251 | 25.32 |

Mean: $25.31 \pm 0.015$ kcal.mole$^{-1}$

*Table 3.* The heat of hydrolysis of $m$-cresyl acetate. Duration of the reaction period 10 min. $k = 0.7219$ (1 577), 0.7207 (1 579), 0.6965 (1 588).

| No. | mmoles | $10^4 \times \log R_i/R_f$ | $q$, cal | $-\Delta H_1$ kcal.mole$^{-1}$ |
|---|---|---|---|---|
| 1 577 | 2.968 | 83.894 | 60.563 | 20.41 |
| 1 579 | 3.022 | 85.762 | 61.809 | 20.45 |
| 1 588 | 3.006 | 88.400 | 61.571 | 20.48 |

Mean: $20.45 \pm 0.02$ kcal.mole$^{-1}$

*Correction to standard states.* The actual reaction taking place in the calorimeter is represented by eqn. (1). In order to obtain the isothermal, ideal hydrolysis reaction (5), it is necessary to substract eqns. (2) and (3) from (1) and to add eqn. (4).

$$CH_2 = CMe \cdot OAc(liq) + OH^-(soln) \rightarrow Me_2CO(soln) + AcO^-(soln) \qquad (1a)$$
$$MeC_6H_4 \cdot OAc(liq) + OH^-(soln) \rightarrow MeC_6H_4OH(soln) + AcO^-(soln) \qquad (1b)$$
$$Me_2Co(liq) \rightarrow Me_2CO(soln) \qquad (2a)$$
$$MeC_6H_4OH(liq) \rightarrow MeC_6H_4OH(soln) \qquad (2b)$$
$$HOAc(liq) + OH^-(soln) \rightarrow AcO^-(soln) + H_2O(soln) \qquad (3)$$
$$H_2O(liq) \rightarrow H_2O(soln) \qquad (4)$$

$$CH_2 = CMe \cdot OAc(liq) + H_2O(liq) \rightarrow CH_3COCH_3(liq) + HOAc(liq) \qquad (5a)$$
$$MeC_6H_4 \cdot OAc(liq) + H_2O(liq) \rightarrow MeC_6H_4OH(liq) + HOAc(liq) \qquad (5b)$$
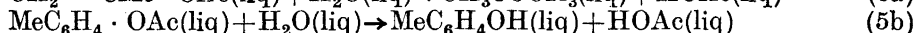
The heat of solution of acetone and $m$-cresol in a liquid phase of proper composition, eqn. (2), had to be determined in separate experiments. The heat of solution of glacial acetic acid, eqn. (3), and the heat of dilution of the liquid, eqn. (4), have been previously determined.

The heat of hydrolysis of the idealized reaction (5) at 25°C is then

$$\Delta H_r^\circ = \Delta H_1 - \Delta H_2 - \Delta H_3 + \Delta H_4$$

$\Delta H_2$ was determined to be $0.498 \pm 0.003$ kcal.mole$^{-1}$ (acetone) and $-4.643 \pm 0.007$ kcal.mole$^{-1}$ ($m$-cresol). $\Delta H_3$ and $\Delta H_4$ were found to be $-11.61 \pm 0.03$ and $-0.19 \pm 0.01$ kcal.mole$^{-1}$, respectively [4]. Thus

$$-\Delta H_r^\circ(liq) = 14.39 \pm 0.06 \text{ kcal.mole}^{-1} \qquad (5a)$$
$$-\Delta H_r^\circ(liq) = 4.39 \pm 0.07 \text{ kcal.mole}^{-1} \qquad (5b)$$

In order to calculate the heat of hydrolysis when both reactants and reaction products are in the gaseous state it is necessary to know the heats of vaporization for all the compounds at 25°C.

The heat of vaporization of acetic acid to form monomer gaseous molecules was calculated by Parks and Huffman [5] to be 12.5 kcal.mole$^{-1}$. The heat of vaporization of acetone [5] and water [6] have been determined to be 7.59 and 10.52 kcal.mole$^{-1}$, respectively. For $i$-propenyl acetate and $m$-cresyl acetate, the heat of vaporization was estimated from Klages equation [7] to be 8.9 and 13.2 kcal.mole$^{-1}$, respectively. For $m$-cresol the heat of vaporization was calculated from Stull's vapor pressure data [8] to be 12.0 kcal.mole$^{-1}$.
Thus, for the reaction,

$$CH_2 = CMe \cdot OAc(g) + H_2O(g) \rightarrow CH_3COCH_3(g) + HOAc(g) \qquad (6a)$$
$$\Delta H_r^\circ(g) = -13.7 \text{ kcal.mole}^{-1}$$

and for the reaction

$$CH_3C_6H_4 \cdot OAc(g) + H_2O(g) \rightarrow CH_3C_6H_4OH(g) + HOAc(g) \qquad (6b)$$
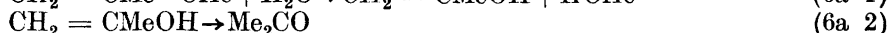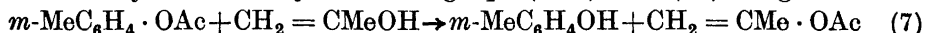$$\Delta H_r^\circ(g) = -3.6 \text{ kcal.mole}^{-1}$$

## THE HEAT OF ENOLIZATION OF ACETONE

The hydrolysis of $i$-propenyl acetate to acetone, (6a), may be split into two consecutive steps, $viz.$ the hydrolysis to $i$-propenol, (6a 1) and the protomeric isomerization of $i$-propenol to acetone, (6a 2):

$$CH_2 = CMe \cdot OAc + H_2O \rightarrow CH_2 = CMeOH + HOAc \qquad (6a\ 1)$$
$$CH_2 = CMeOH \rightarrow Me_2CO \qquad (6a\ 2)$$

A knowledge of the value of the heat of reaction (6a 1) makes it possible to obtain a value for the heat of reaction (6a 2), which is the reverse of the enolization reaction of acetone.

Reaction (6a 1) is of course not experimentally accessible; it is therefore necessary to estimate the accompanying change in enthalpy indirectly. This has been achieved by a comparison of the hydrolysis of $i$-propenyl acetate with that of $m$-cresyl acetate. By subtracting eqn. (6a 1) from (6b) one gets

$$m\text{-MeC}_6\text{H}_4 \cdot \text{OAc} + \text{CH}_2 = \text{CMeOH} \rightarrow m\text{-MeC}_6\text{H}_4\text{OH} + \text{CH}_2 = \text{CMe} \cdot \text{OAc} \quad (7)$$

The complete symmetry in eqn. (7) suggests that $\Delta H_7 = \Delta H_{6b} - \Delta H_{6a\ 1} = 0$. Thus $\Delta H_{6a\ 1} = -3.6$ kcal.mole$^{-1}$ and the heat of enolization of acetone in the gaseous state becomes $-\Delta H_{6a\ 2} = +10$ kcal.mole$^{-1}$.

The heat of vaporization of acetone [5] is 7.6 kcal.mole$^{-1}$ and that of $i$-propenol was estimated to 10.5 kcal.mole$^{-1}$ from a comparison between saturated and unsaturated compounds. The heat of enolization of acetone in the liquid state is therefore equal to 7.0 kcal.mole$^{-1}$.

Schwarzenbach and Wittwer [9] determined experimentally the equilibrium between acetone and $i$-propenol in solution and found the change in standard free energy to be about 8 kcal.mole$^{-1}$. The change in entropy accompanying the isomerization can be estimated in the following way.

For the dehydrogenation reaction

$$\text{Me}_2\text{CHOH(g)} \rightarrow \text{Me}_2\text{CO(g)} + \text{H}_2\text{(g)} \quad (8)$$
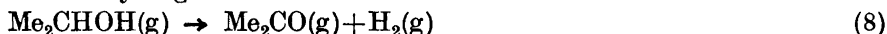
the entropy change at 25°C is $\Delta S_8° = 29.80$ e.u.[5] A comparison between different gaseous compounds of the two types RCH $=$ CMe . R' and RCH$_2$—CHMeR' and with known values of $\Delta S°$ shows that the unsaturated compound has an entropy value which is in average 0.3 kcal. less than that of the saturated compound. This value combined with the known $\Delta S°$ value for gaseous hydrogen [6], 31.2 e.u., gives $\Delta S° = -1$ e.u. for the isomerization $i$-propenol(g)→acetone(g). From estimated values of the vapor pressure (20 mm) and heat of vaporization (10.5 kcal.) of $i$-propenol at 25°C and those data of acetone [5], the entropy change for the isomerization in the liquid state was calculated to $+3$ e.u. Thus, the heat of enolization of acetone to $i$-propenol in the liquid state becomes 7 kcal.mole$^{-1}$ in excellent agreement with the result from the present thermochemical investigation.

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