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Note

Kinetic studies in a flow microcalorimeter

The acid-catalysed hydrolysis of methyl acetate at 25 °C

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In a flow microcalorimeter of the conduction type such as the LKB flow microcalorimeter (Type 10700-1, LKB Produkter, Bromma, Sweden), a reacting solution can be allowed to flow at a constant rate R through a small calorimeter cell of effective volume V_c. The instrument records the rate of heat production averaged over a residence time τ ($= V_c/\mathrm{R}$) as a function of time. If the reaction occurring in the solution is first order with respect to a component whose initial concentration in the reacting mixture is C^0 then the instrument response is a function of the time t which has elapsed since the reacting components were mixed. It has been shown[1] that, if ΔH_R is the enthalpy change in the reaction, and k_1 the rate constant, the instrument response is proportional to:

$$-C^0 \mathrm{R} \Delta H_\mathrm{R}(1-\exp -k_1 \tau) \exp -k_1 t$$

If $k_1 \tau$ is small, then $(1-\exp -k_1 \tau)$ can be replaced by $k_1 \tau$, and the instrument response is then proportional to:

$$-C^0 k_1 \Delta H_\mathrm{R} V_c \exp -k_1 t$$

This is equivalent to the assumption that the rate is constant over the residence time in the cell. Clearly, when this is valid, a plot of the logarithm of the instrument response as a function of time should give a straight line with slope proportional to the rate constant. The intercept at $t = 0$ can be used to calculate ΔH_R provided that the relationship between the energy dissipated per unit time within the cell and the instrument response can be obtained by, for example, electrical calibration.

In order to evaluate the utility of this technique of measuring rate constants the acid-catalysed hydrolysis of methyl acetate has been briefly examined. This well-known reaction is not kinetically simple but gives good first-order rate constants at constant acid concentrations. Griffith and Lewis[2], for example, found $k_1 = 7.54 \times 10^{-3}$ min^{-1} at an initial ester molarity of 0.7093 in 1 M HCl at 25 °C. Figure 1 shows plots of the logarithm of the instrument response against time for three different ester concentrations hydrolysed in aqueous 1.25 M HCl at 25 °C. Experiments were

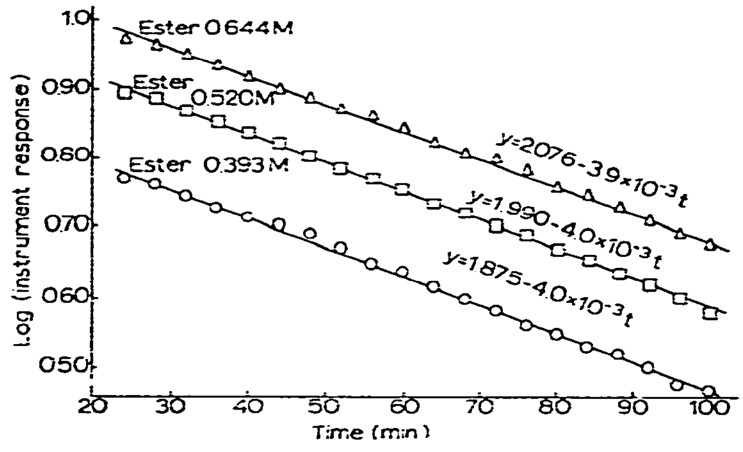

Fig. 1. First-order plots for methyl acetate hydrolysis in 1.25 M HCl.

repeated using 1.00 M HCl as catalyst, and the least-squares constants of the linear plots were calculated in each case. From the slopes, the rate constant k_1 could be calculated, and $(V_c \Delta H_R)$ could be obtained from the intercepts, the appropriate k_1 value, and an electrical calibration. The manufacturers' figure for the volume of the cell (0.45 ml) was accepted for V_c. For more refined calculations it would be desirable to obtain an effective value of V_c, appropriate to the experimental conditions, by calibration of the instrument with a slow first-order reaction for which ΔH_R is known. Results are shown in Table 1.

TABLE 1

THE ACID HYDROLYSIS OF METHYL ACETATE AT 25°C

Molarity of HCl	*Initial molarity of ester*	*Apparent first-order rate constant ($min^{-1} \times 10^3$)*	*ΔH[a] (kcal. (mole ester)$^{-1}$)*
1.25	0.394	8.9	0.483
	0.520	9.2	0.480
	0.644	9.2	0.472
1.00	0.330	6.9	0.478
	0.644	7.1	0.459
	0.644	6.9	0.519
	0.644	6.9	0.448

[a] Calculated assuming cell volume = 0.45 ml.

This is clearly quite an effective technique for measuring rate constants, which can provide, in addition, an accurate value of the enthalpy change in the reaction. In this case, the enthalpy change was small, yet good first-order rate plots were obtained because of the high sensitivity and stability of the instrument. Enthalpy changes in slow reactions of this kind cannot be measured by conventional calorimetry, yet very reproducible values were obtained in this case in an experiment of extreme simplicity. There is admittedly a difference of about 10% between our present value for k_1 and that of Griffith and Lewis[2] which can hardly be attributable to the difference in ester concentration, but we do not claim ours to be a definitive value. The small endothermic enthalpy change is consistent with the rather similar calorimetric values obtained indirectly by Wadsö[3] on other but similar esters.

We would draw attention to the fact that almost all reactions involve heat changes which are frequently larger than that found in this case, and the method should be of wide applicability. It could, for example, be used for reactions in which the reactant contains no chromophore.

REFERENCES

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3 I. Wadsö, *Acta Chem. Scand.*, 16 (1962) 487.