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Direct injection enthalpimetry and differential kinetic analysis—analytical and calorimetric possibilities [1]

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Abstract

The well-known AcOMe and AcOEt saponification reactions by NaOH were used to clarify the analytical, kinetic and calorimetric possibilities of direct injection enthalpimetry (DIE). The reaction rate range in which DIE can be efficiently used for kinetic measurements is specified. It is also shown that, by differential kinetic analysis of mixtures of two substances which slowly react with the same third substance, DIE enables the simultaneous determination of concentrations or the simultaneous determination of reaction rate constants and enthalpy changes. The results are good even if the reactions are fairly fast ($t_{1/2}$ is a few seconds) and the rate constants are almost identical.

INTRODUCTION

Although direct injection enthalpimetry (DIE) [1] is seldom used, it is a very good technique for studying solution reaction kinetics [2]. One aim of this work is to clarify the reaction rate range in which it can be efficiently used. Another aim is to specify the best conditions during the titration by differential kinetic analysis [3,4] of mixtures of two products that react with the same titrant, using a curve-fitting method to treat the experimental data, required to obtain both rate constants and enthalpy changes or the concentrations of the components of the sample.

For this study, the well-known methyl acetate (AcOMe) and ethyl acetate (AcOEt) saponification reactions by sodium hydroxide were used.

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Experimental

The 100 ml calorimeter used was built as recommended by Christensen et al. [5]; it is described, together with the injection pipette, in ref. 6. The temperature measurement device was composed of a VECO 31 A6 thermistor, a MacKee Pedersen (MP) voltage source (MP 1008 b), a Wheatstone bridge (MP 1010) and an operational amplifier (MP 1006 c). The output voltage passed directly to a highly sensitive millivoltmeter (Tacussel ISIS 20000) which digitized the signal and transferred it to a Hewlett–Packard HP 85 F computer and an $E = f(t)$ recorder (Tacussel EPL 1).

Product and solutions

The AcOMe and the AcOEt purities were monitored by gas chromatography ($> 99\%$). The stock solutions (0.5 M AcOMe, AcOEt or NaOH) were prepared with CO_2-free distilled water.

Enthalpogram recording and treatment

Using the injection pipette ($v \approx 1.25$ ml), the solution containing one or two esters was injected as quickly as possible into 90 ml of 0.5 M sodium hydroxide solution. The $\Delta T = f(t)$ curve was recorded and the data, in millivolts, were stored in the computer memory to be transformed into joules and corrected for the different parasitic thermal effects, e.g. solution stirring heat and heat exchange with the outside due to imperfect adiabatic properties of the calorimeter [7]. These corrected data were then treated by a curve-fitting method according to a non-linear least-squares process with which we can look for the set of parameters that minimizes the U function which is the sum of the weighted quadratic differences

$$U = \sum_{i=0}^{n} W_i (Q_{i,\mathrm{exp}} - Q_{i,\mathrm{calc}})^2 \tag{1}$$

where, for a given time t_i, $Q_{i,\mathrm{exp}}$ is the heat dissipated by the reaction recorded experimentally, $Q_{i,\mathrm{calc}}$ is the calculated heat from the tested set of parameters and W_i is a weighted factor, usually the inverse of the variance. The programs for data treatments were written in our laboratory [8]. In the last one, the data obtained for all the experiments (six or seven) were taken into account; the treatment of the pool of data allows the best estimate of the variances [9].

KINETIC MEASUREMENTS

Firstly, we determined the kinetic parameters of the AcOMe and AcOEt saponification reactions by NaOH. Although these reactions follow second-order kinetics, we studied them as pseudo-first-order, using a great excess of sodium hydroxide (×80). Under these conditions, the half-times $t_{1/2}$ were respectively 5 s and 8 s.

Pseudo-zero-time notion

During our first experiments it appeared that one aspect of the studies, important for its consequences, has rarely been mentioned and never taken into account by the few authors who have studied this subject [2,10–15]. This is the systematic error on the times t_i owing to a spurious assessment of the initial time $t = 0$, which is not negligible when the studied reactions are relatively fast ($t_{1/2} < 30$ s).

From time $t = 0$, the moment of substrate injection, three closely linked phenomena take place: the injection itself, during a time τ dependent on the shape and the volume of the pipette; the mixing of solutions, during a time τ' dependent on the stirring rate and the viscosity of the reagents; and the apparatus response time which is important at the beginning (thermal shock).

Two seconds are necessary to record 98% of the response during the neutralization of HCl by NaOH, and yet this is one of the fastest reactions.

For this purpose we introduced a "pseudo-zero-time" notion t_0^*. According to the different conditions from one experiment to another, t_0^* may vary and therefore it was introduced as an unknown in the calculations.

This pseudo-zero-time t_0^* (Fig. 1 is similar to a fictitious time at which the reaction would begin if the injection, mixing and response times were quick (< 0.01 s, thermal equilibrium reached immediately), so that the

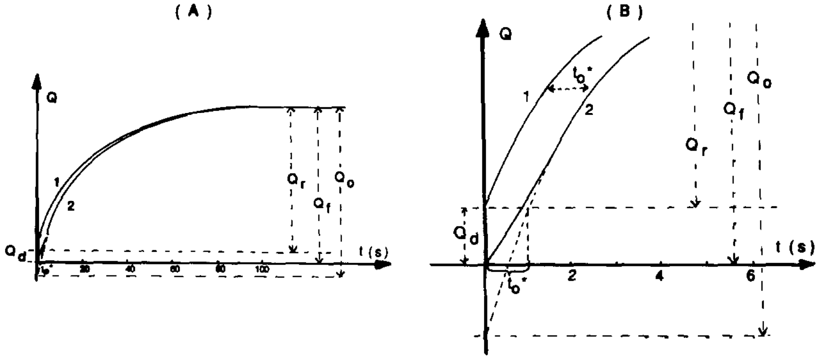

Fig. 1. Theoretical (curve 1) and experimental (curve 2) enthalpograms $Q_t = f(t)$ for a slow reaction. (A) complete curves and (B) detail of first 5 s: Q_r, heat dissipated by the reaction; Q_d, heat due to the substrate dilution; Q_f, total heat dissipated; Q_0, heat calculated from the intercept on the ordinate of the line $\ln(Q_f - Q_t) = f(t)$.

calculated theoretical curve 1 (Fig. 1) and the experimental real curve 2 (dotted extension of curve 2 in Fig. 1) would exactly superpose.

Determination of k, *Δ*H *and* t$_0^*$

The first-order or pseudo-first-order reaction rate constant k, the reaction enthalpy change ΔH and the pseudo-zero-time t_0^* were calculated in two different ways:
by following the concentration of species that had not reacted

$$Q_f - Q_t = VC^0\Delta H\ e^{-k'(t-t_0^*)} \tag{2}$$

and by following the concentration of species that had reacted

$$Q_t = VC^0\Delta H(1 - e^{-k'(t-t_0^*)}) + VC^0\Delta H_d \tag{3}$$

where $k' = kC_{NaOH}$, the pseudo-first-order rate constant, Q_f is the total heat dissipated by the reaction ($t = \infty$), Q_t is the heat dissipated at time t, V is the total volume of solution in the calorimeter, C^0 is the initial concentration of the substrate and ΔH_d is the dilution molar enthalpy of the injected substrate.

In the first case, we need not take into account either the heat due to the substrate dilution or a possible thermal effect due to the mixing of non-isothermal solutions or the presence of other products which would immediately react with the titrant. Conversely, it is necessary to know Q_f (the reaction must be completed) and to take into account the propagation error on the determination of Q_f.

The second calculation method is far more usual; a knowledge of Q_f is not necessary but titrant dilution or other possible effects must be taken into account.

Results and discussion

The values of k, ΔH and t_0^*, corresponding to the AcOMe and AcOEt saponification reactions, were determined at 298 K, according to the two calculation methods; the results are given in Table 1.

TABLE 1

Values of k (second order), ΔH and t_0^* for the AcOMe and AcOEt saponification reactions at 298 K according to the two calculation methods [a]

Substance	Calculated from	k (l mol^{-1} s^{-1})	σ_k	ΔH (kJ mol^{-1})	$\sigma_{\Delta H}$	t_0^* (s)	$\sigma_{t_0^*}$
AcOMe	$Q_f - Q_t$	0.212_3	0.002_6	−48.56	0.71	0.90	0.12
	Q_t	0.208_6	0.002_6	−48.87	0.21	0.84	0.04
AcOEt	$Q_f - Q_t$	0.131_9	0.001_8	−51.41	0.69	0.73	0.12
	Q_t	0.127_0	0.002_7	−52.31	0.52	0.66	0.07

[a] For AcOMe, 1.264 ml pipette and for AcOEt, 1.230 ml pipette

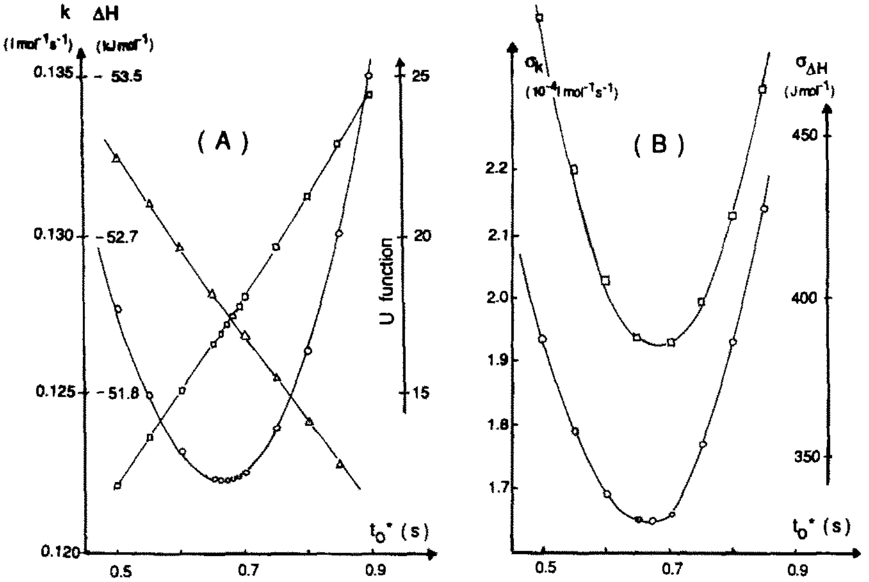

Fig. 2. (A) Variations of the U function (○), k (□) and ΔH (△), and (B) variations of σ_k (○) and $\sigma_{\Delta H}$ (□), versus different values of t_0^*.

There is good agreement between the pseudo-zero times obtained from the two calculation methods (differences between the times < 0.1 s): 0.90 and 0.84 s for the 1.264 ml pipette, and 0.73 and 0.66 s for the 1.230 ml pipette; t_0^* depends only on the experimental conditions. This confirms the physical reality of the pseudo-zero-time notion. In order to illustrate its influence on the results, we have plotted the evolution of k, ΔH and the U function, and the estimated errors σ_k and $\sigma_{\Delta H}$ versus the different values given to t_0^* (Fig. 2).

Comparison between our results and those found in the literature

The rate constants found (in l mol^{-1} s^{-1}) are identical to those given by other authors for similar experimental conditions: 0.206 [11] for AcOMe, and 0.134 [14], 0.130 [12] and 0.137 [11] for AcOEt. However, the enthalpy changes (in kJ mol^{-1}) for the two saponification reactions are smaller than those found in the literature: −62.7 [16], −45.83 [17] and −50.16 [11] for AcOMe, and −54.30 [12] for AcOEt. These differences result from the fact that the pseudo-zero-time was taken into account. Q_0, which is calculated from the intercept on the ordinate of the line $\ln(Q_f - Q_t) = f(t)$, is always greater than Q_f (Fig. 1).

Reaction rate range which can be studied by DIE

Assuming that substrate concentrations ranging from 10^{-3} to 2×10^{-2} M, $\Delta H \approx 40$ kJ mol^{-1} and that $t_{1/2}$ from 2 to 300 s have an exploitable thermal effect, we can determine a range of rate constants from 0.002 to 0.35 s^{-1} for first-order reactions and from 0.1 to 500 l mol^{-1} s^{-1} for second-order reactions, or from 2×10^{-4} to 0.7 l mol^{-1} s^{-1}, working in pseudo-first order with a titrant one hundred times more concentrated.

TITRATION OF TWO-ESTER MIXTURES BY DIFFERENTIAL KINETIC ANALYSIS: THERMOKINETIC ANALYSIS [2]

Equations yielding values for C_1^0, C_2^0 and t_0^*

We treated this problem, as before, according to two calculation methods: from Q_t and from $Q_f - Q_t$. In eqns. (4), (5) and (6) below, the symbols have the same meaning as in eqns. (2) and (3); subscript 1 corresponds to the product which reacts the fastest (AcOMe) and subscript 2 to that which reacts slowest (AcOEt):

$$Q_f = V\left[C_1^0(\Delta H_1 + \Delta HD_1) + C_2^0(\Delta H_2 + \Delta HD_2)\right] \tag{4}$$

$$Q_f - Q_t = V\{C_1^0 \Delta H_1 \exp[-k_1'(t - t_0^*)] + C_2^0 \Delta H_2 \exp[-k_2'(t - t_0^*)]\} \tag{5}$$

$$\begin{aligned} Q_t = V\big[&C_1^0(\Delta HD_1 + \Delta H_1\{1 - \exp[-k_1'(t - t_0^*)]\}) \\ &+ C_2^0(\Delta HD_2 + \Delta H_2\{1 - \exp[-k_2'(t - t_0^*)]\})\big] \end{aligned} \tag{6}$$

Results and discussion

The results, given in Tables 2 and 3, are very satisfactory whichever calculation mode is used, although the two esters react at very similar rates ($k_1/k_2 = 1.6$). Calculations carried out for "pure" solutions (first and last lines in Tables 2 and 3) show the reliability of the method. We note once

TABLE 2

Titration of the mixtures of esters: results from $Q_f - Q_t$ (concentrations in millimoles per litre) [a]

Mixtures (%)		Taken (mM)		Found (mM)				
AcOMe	AcOEt	AcOMe	AcOEt	C_1^0	$\sigma_{C_1^0}$	C_2^0	t_0^* (s)	$\sigma_{t_0^*}$
100	0	6.72	0	6.74	0.07	−0.02	0.88	0.03
80	20	5.47	1.37	5.52	0.04	1.32	0.85	0.02
50	50	3.40	3.40	3.43	0.07	3.37	0.94	0.04
33	67	2.30	4.59	2.34	0.04	4.53	0.88	0.02
20	80	1.42	5.30	1.60	0.07	5.16	0.81	0.04
0	100	0	6.74	−0.05	0.11	6.78	0.73 [a]	0.06

[a] 1.230 ml pipette.

TABLE 3

Titration of the mixtures of esters: results from Q_t (concentrations in millimoles per litre) [a]

Mixtures (%)		Taken (mM)		Found (mM)					
AcOMe	AcOEt	AcOMe	AcOEt	C_1^0	$\sigma_{C_1^0}$	C_2^0	$\sigma_{C_2^0}$	t_0^* (s)	$\sigma_{t_0^*}$
100	0	6.72	0	6.71	0.19	0.015	0.21	0.84	0.04
80	20	5.47	1.37	5.53	0.06	1.29	0.07	0.83	0.02
50	50	3.40	3.40	3.41	0.19	3.36	0.21	0.91	0.04
33	67	2.30	4.59	2.55	0.08	4.27	0.09	0.87	0.03
20	80	1.42	5.30	1.50	0.09	5.27	0.10	0.74	0.02
0	100	0	6.74	−0.01	0.23	6.73	0.26	0.66 [a]	0.07

[a] 1.230 ml pipette.

more that the pseudo-zero-time values found are the same as those obtained in the kinetic study.

SIMULTANEOUS DETERMINATION OF k AND ΔH FOR TWO SUBSTANCES REACTING WITH THE SAME TITRANT AT DIFFERENT RATES

Because of the good results obtained, it was logical to proceed to study the question the other way round, i.e. to determine the rate constants and the enthalpy changes knowing the substrate concentrations C_1^0 and C_2^0. The major difficulty was a mathematical problem: rather than determining three parameters (C_1^0, C_2^0, t_0^*), we were determining five (k_1, k_2, ΔH_1, ΔH_2, t_0^*). It is known that in this kind of algorithm, the inaccuracy concerning each parameter increases with the number of parameters determined.

Once again, the problem was treated according to the two calculation methods. When calculations are carried out from Q_t, whatever the mixture, we obtain very satisfactory agreement for the rate constants and the pseudo-zero-time (Table 4). The results are less good for the enthalpy changes although they are fairly close to the expected values. The estimated error in the ΔH value is particularly important because the ΔH value is far from the theoretical value; this is probably due to low sensitivity of the cost function (U) to the enthalpies.

When calculations are carried out from $Q_f - Q_t$, only the values obtained for k_1 and k_2 are acceptable: for certain mixtures ΔH_1, ΔH_2 and t_0^* are too far from the expected values.

Lastly, if both studied substances have very similar structures, one can adopt in the first approximation an identical ΔH value, calculated from Q_f and $C_1^0 + C_2^0$, and the average value 0.85 for t_0^* found during the previous experiments for the two reactions. Under these conditions, only three parameters are determined, and the results are considerably better; only a significant variation in t_0^* influences the ΔH value.

TABLE 4

Rate constants (second order) and enthalpy changes obtained from the different ester mixtures when calculations are carried out from Q_t

	Expected theoretical values (Table 1)	Mixture (AcOMe–AcOEt) (%)			
		(80–20)	(50–50)	(33–67)	(20–80)
k_1 (l mol^{-1} s^{-1})	0.208	0.206 ± 0.003	0.199 ± 0.022	0.198 ± 0.004	0.197 ± 0.030
k_2 (l mol^{-1} s^{-1})	0.127	0.134 ± 0.007	0.150 ± 0.015	0.137 ± 0.003	0.140 ± 0.012
ΔH_1 (kJ mol^{-1})	−48.9	−51.3 ± 0.7	−38.2 ± 6.8	−49.1 ± 2.1	−30.6 ± 24.0
ΔH_2 (kJ mol^{-1})	−52.3	−41.2 ± 2.6	−61.2 ± 8.5	−50.6 ± 0.8	−56.7 ± 5.6
t_0^* (s)	0.84	0.83 ± 0.05	0.89 ± 0.05	0.84 ± 0.04	0.74 ± 0.14

CONCLUSION

All the results presented show that direct injection enthalpimetry is a convenient technique for the study of fairly fast reactions. The possibility of obtaining a good estimation of the reaction rate constants of both substances with the same third substance, without any anticipated resolution of the mixture, offers a field of application which appears interesting for further investigations.

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