Kinetics of Sulphodeacylation of Dimesityl Ketone: a Dual-path Sequence of First-order Reactions

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The kinetics of the conversion in 89.8% (w/w) sulphuric acid of 2,2′,4,4′,6,6′-hexamethylbenzophenone (A) into 2,4,6-trimethylbenzenesulphonic acid (D) were measured, and analysed in terms of the dual-path first-order reaction sequence

$$\begin{tikzcd} & (B) \arrow[d] & \\ (A) \arrow[ur] \arrow[dr] & & \\ & (C) \arrow[r] & (D) \end{tikzcd}$$

, where (B) and (C) are, respectively, 2,4,6-trimethylbenzoic acid and 1,3,5-trimethylbenzene.

STERICALLY hindered aromatic ketones can undergo smooth protiodeacylation in the presence of concentrated sulphuric acid,[1] syrupy phosphoric acid,[2] or polyphosphoric acid.[3] The kinetics of protiodeacylation of certain substituted acetophenones have been studied by Schubert and Latourette,[1] and the reaction has recently been extended [4] to the diaryl ketone, benzoylmesitylene. The stepwise conversion of diacetylmesitylene into mesitylenesulphonic acid has been analysed kinetically as a sequence of three consecutive first-order reactions.[4] We report here a related but more complex system which involves a dual-path sequence of first-order reactions.

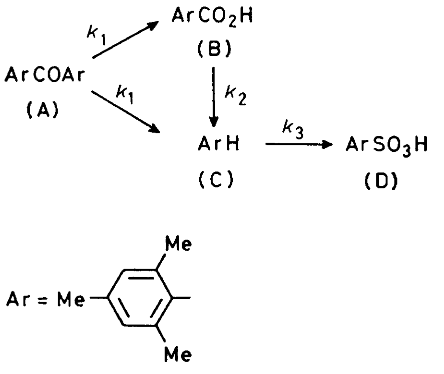
TABLE 1

Kinetics of protiodeacylation or protiodecarboxylation in 89.8% (w/w) sulphuric acid of substituted mesitylenes

Substrate	Reaction	k at 298.15 K/ s^{-1} *	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}	$\Delta G^‡$/ kJ mol^{-1}	Ref.
Dimesityl ketone (A)	k_1	3.24×10^{-5}	106	+24	98.5	This work
Mesitoic acid (B)	k_2	6.43×10^{-6}	96.7	−20	102.7	This work
Benzoylmesitylene		2.01×10^{-5}	106	+20	99.8	4; here revised
Acetylmesitylene		4.71×10^{-3}	82.9	−12	86.3	4

* Extrapolated.

Dimesityl ketone (A) in 89.8% (w/w) (16.6 mol dm^{-3}) sulphuric acid solution undergoes conversion into mesitylenesulphonic acid (D), involving protiodeacylation and decarboxylation, to mesitylene (C), and a final sulphonation, as summarised in the Scheme. The reaction sequence is thus made up of several pseudo-first-order reactions. The rate constant k_1 governs the simultaneous formation of the fragmentation products (B) and (C). In separate experiments, the conversion of mesitoic acid (B) into mesitylenesulphonic acid (D) was observed spectrophotometrically at 285 nm, and the conversion of ketone (A) into the product (D) was similarly measured at 390 nm, at which wavelength acid (B) does not absorb significantly. The conversion of mesitylene (C) into the product (D) occurs very rapidly (k_3 1.05 s^{-1} at 25 °C) in this medium.[5] The kinetic data obtained are summarised in Table 1, together with those of some related compounds.



SCHEME

The rate constant (k_1) of the initial reaction is comparable in magnitude with that for benzoylmesitylene, and is *ca.* 150 times slower than that for the sulphodeacylation of acetylmesitylene. The protiodeacylation reaction is promoted by the non-coplanarity of the carbonyl function with respect to the mesityl moiety.[6] The rate constant of the protiodecarboxylation step (k_2) is smaller than that of the initial reaction (k_1), and a build-up of mesitoic acid (B) is therefore to be expected in the reaction of ketone (A). This can be seen clearly in the Figure. The activation parameters are characterised by high enthalpies of activation ($\Delta H^‡$) and high, even positive, entropies of activation ($\Delta S^‡$); the significance of this will be discussed fully in a subsequent paper.

Derivation of Kinetic Equations.—Consideration of the reactions in the Scheme leads to equations (1)—(4).

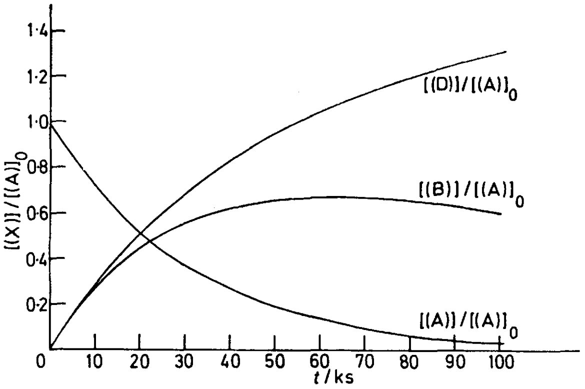
$$d[(A)]/dt = -k_1[(A)] \qquad (1)$$

$$d[(B)]/dt = k_1[(A)] - k_2[(B)] \qquad (2)$$

$$d[(C)]/dt = k_2[(B)] + k_1[(A)] - k_3[(C)] \qquad (3)$$

$$d[(D)]/dt = k_3[(C)] \qquad (4)$$

On solving these equations one obtains concentrations of the components (A)—(D), relative to the initial concentration $[(A)]_0$ of dimesityl ketone, as shown by equations (5)—(8). Since one molecule of ketone (A) gives two molecules of reaction products, the total number N_t of molecules present at any time t, relative to the initial number, is given by equation (9).



Ratios of reactant, $[(A)]/[(A)]_0$, and products, $[(B)]/[(A)]_0$, and $[(D)]/[(A)]_0$, as a function of time

$$[(A)]/[(A)]_0 = e^{-k_1 t} \qquad (5)$$

$$[(B)]/[(A)]_0 = \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \qquad (6)$$

$$[(C)]/[(A)]_0 = k_1\left[\frac{(2k_2 - k_1)}{(k_2 - k_1)(k_3 - k_1)}\, e^{-k_1 t} - \frac{k_2}{(k_2 - k_1)(k_3 - k_2)}\, e^{-k_2 t} + \frac{(2k_2 - k_3)}{(k_3 - k_1)(k_3 - k_2)}\, e^{-k_3 t}\right] \qquad (7)$$

$$[(D)]/[(A)]_0 = 2 - \left[\frac{k_3(2k_2 - k_1)}{(k_2 - k_1)(k_3 - k_1)}\, e^{-k_1 t} - \frac{k_1 k_3}{(k_2 - k_1)(k_3 - k_2)}\, e^{-k_2 t} + \frac{k_1(2k_2 - k_3)}{(k_3 - k_1)(k_3 - k_2)}\, e^{-k_3 t}\right] \qquad (8)$$

$$N_t = \frac{[(A)] + [(B)] + [(C)] + [(D)]}{[(A)]_0} = 2 - e^{-k_1 t}\Big] \qquad (9)$$

RESULTS

Using rate constants extrapolated for 298.15 K concentration ratios were calculated using equations (5)—(8).

TABLE 2

Concentration maxima and half-times of dimesityl ketone and its reaction products, in 89.8% (w/w) sulphuric acid at 298.15 K

Component	Ratio R at maximum [a]	$t_{\text{max.}}$/s	$R_{\frac{1}{2}}$ [b]	$t_{\frac{1}{2}}$/s
(A)	1.000	0	0.500	2.14×10^4
(B)	0.670	6.23×10^4	0.335	2.04×10^5
(C)	3.08×10^{-5}	10.1	1.54×10^{-5}	2.90×10^4
(D)	2.000	∞	1.000	5.53×10^4

[a] R = [Component]/$[(A)]_0$. [b] Of the two half-values possible for components (B) and (C), the decay half-values are given.

The more significant values are collected in Table 2. Plots of concentration ratios $[(A)]/[(A)]_0$, $[(B)]/[(A)]_0$, and $[(D)]/[(A)]_0$ *versus* time are displayed graphically in the Figure.

Since the reaction leads to large proportions of the intermediate component (B), an attempt was made to estimate the ratio $[(B)]/[(A)]_0$ by an independent analytical method. The results (Table 4), though not of high precision, nevertheless confirm that maximal formation of (B) occurs at the time and to the extent predicted. The procedure strengthens the kinetic interpretations given above.

TABLE 3

Rate constants for the reactions in 89.8% (w/w) sulphuric acid of 2,4,6-trimethylbenzoic acid, 2,2′,4,4′,6,6′-hexamethylbenzophenone, and 2,4,6-trimethylbenzophenone

Reaction	10^2k/min^{-1} (K, in parentheses)
Protiodecarboxylation of 2,4,6-trimethylbenzoic acid	0.349 (315.4), 0.420 (317.3), 0.719 (321.7), 1.08 (325.3), 1.93 (330.5)
Sulphodecarbonylation of 2,2′,4,4′,6,6′-hexamethylbenzophenone	1.02 (309.7), 1.13 (310.6), 1.20 (311.2), 2.64 * (316.6), 3.21 * (318.0), 4.20 (320.4), 6.07 (322.4), 7.36 * (325.1), 11.5 * (327.6), 16.2 * (331.4)
Sulphodebenzoylation of 2,4,6-trimethylbenzophenone	0.238 (303.2), 0.258 (304.1), 0.593 * (309.1), 1.00 (313.1), 1.89 * (317.9), 4.22 * (324.1), 5.44 * (326.9)

* Mean of 2—6 determinations.

EXPERIMENTAL

2,2′,4,4′,6,6′-Hexamethylbenzophenone was prepared in earlier work.[6a,7] The kinetic procedure was similar to that reported earlier.[4] Silica cells (1 cm), fitted with PTFE stoppers, containing 89.8% (w/w) sulphuric acid, were thermally equilibrated in a thermostatted cell holder of a Perkin-Elmer model 402 spectrophotometer. A small quantity of the reactant was introduced into the solution cell (giving concentrations of *ca.* 10^{-4}—10^{-5} mol dm^{-3}) and, after thorough mixing, the light absorption was recorded at the chosen wavelength, either continuously, or at selected time intervals.

TABLE 4

Experimentally estimated concentration ratios $[(B)]/[(A)]_0$

	Concentration ratio $[(B)]/[(A)]_0$		
Time (ks)	Found	Computed	Error (%)
15	0.492	0.366	+25
56.4	0.626	0.668	−6.6
67.2	0.668	0.668	0
74.9	0.689	0.661	+4.1
79.2	0.679	0.654	+3.7
95.7	0.601	0.618	−2.8
171.5	0.444	0.409	+7.9

First-order rate constants were then computed, using estimates of E_0, E_∞, and k, which the iterative procedure used earlier[8] refined, in a rapidly converging manner, to give the 'best' values of k, *i.e.* those which minimised the quantity $\Sigma_i(E_i^{\text{calc.}} - E_i^{\text{obs}})^2$. Rate constants were obtained (replicates normally within ±3%) for 5—10 temperatures (Table 3). Activation parameters were then computed, and were also checked graphically.

Method of Estimation of 2,4,6-*Trimethylbenzoic Acid.*—A solution of 2,2′,4,4′,6,6′-hexamethylbenzophenone (39.6 mg) in 16.6 mol dm^{-3} sulphuric acid (100 ml) was kept at 25 °C. At selected intervals samples (10 ml) were taken of this solution, the solution quenched by pouring onto ice, the mixture extracted (3×) with ether, the combined extract shaken with portions of 0.1N-NaOH, and the alkali extract made up finally to 10 ml with more of this alkali. The organic acid was estimated from the absorbance at 267 nm (ε 313.9 dm^3 cm^{-1} mol^{-1}), where a maximum occurs. Typical values obtained by this procedure are given in Table 4.

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