

An Analysis of Consecutive First-Order Reactions: Protodeacetylation of Diacetylmesitylene

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Abstract In 89.8% sulphuric acid 1,3-diacetyl-2,4,6-trimethylbenzene undergoes two successive protodeacetylation stages and a final sulphonation to give 2,4,6-trimethylbenzenesulphonic acid. A kinetic analysis of the component reactions has been realised.

There have been many theoretical studies¹⁻⁴ of the model kinetic system of consecutive, irreversible, first-order reactions. Few actual examples have been investigated, however, because complete analysis for the components of such a mixture is normally very difficult. We have now found a system of this type, which can be examined experimentally. The kinetic analysis is made possible because the component reactions could be studied individually.

In 89.8% sulphuric acid 1,3-diacetyl-2,4,6-trimethylbenzene (diacetylmesitylene) (**A**) is smoothly converted into 2,4,6-trimethylbenzenesulphonic acid (**D**) (see Figure 1). The reaction was followed spectrophotometrically at 315 nm; there was no spectroscopic evidence

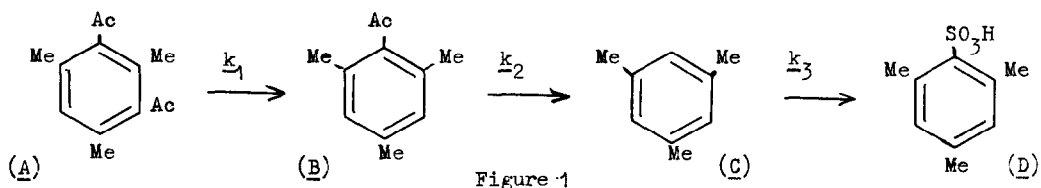


Figure 1

of the presence in the medium of the presumed intermediates 2,4,6-trimethylacetophenone (acetylmesitylene) (**B**) or 1,3,5-trimethylbenzene (mesitylene) (**C**). The kinetic data are presented in the Table. These reactions are characterized by high enthalpies of activation (ΔH^\ddagger) and high entropies of activation (ΔS^\ddagger), unusual for aromatic substitutions. The former accounts for the comparatively low reaction rates. High ΔS^\ddagger values can be explained as a gain in degrees of freedom (e.g. rotational) in proceeding from a highly strained initial state^{5,6} to a less strained transition state.

The sulphonation of mesitylene in 89.8% sulphuric acid could be estimated to have a high rate constant, $k_3 = 1.05 \text{ sec}^{-1}$ at 25°C.⁷

The stages involved, then, in the overall deacetylprotosulphonation, (**A**) \rightarrow (**D**), consist of three reactions, each being much slower than the subsequent one. Therefore, the chemical change as observed spectrophotometrically was essentially the formation of the acid (**D**) from the diketone (**A**). The only previously analysed cases of sequential first-order

reactions with increasing rate constants have been successive alkylations of alkylbenzenes, and these were complicated by the invariable formation of isomers.^{3,4,10}

Table
Protodeacylations of Mesityl Ketones in 89.8% Sulphuric Acid

<u>Substrate</u>	<u>k at 298.2K</u> (sec ⁻¹)	<u>ΔH[‡]</u> (kJmol ⁻¹)	<u>ΔS[‡]</u> (JK ⁻¹ mol ⁻¹)	<u>ΔG[‡]</u> (kJmol ⁻¹)
Acetylmesitylene (<u>B</u>)	4.68 X 10 ⁻³	82.0	- 14	86.3
Diacetylmesitylene (<u>A</u>)	9.88 X 10 ⁻⁶	102	+ 2.0	101.5
Benzoylmesitylene	1.92 X 10 ⁻⁵	107	+ 23	99.9

* Values of E_{Arr} are higher by 2.5 kJmol⁻¹

The concentrations of the components (A), (B), (C), and (D), relative to the initial concentration $[A]_0$, could be determined^{11,12} as a function of time, t , from the known rate constants of the component reactions, viz. k_1 , k_2 , and k_3 :

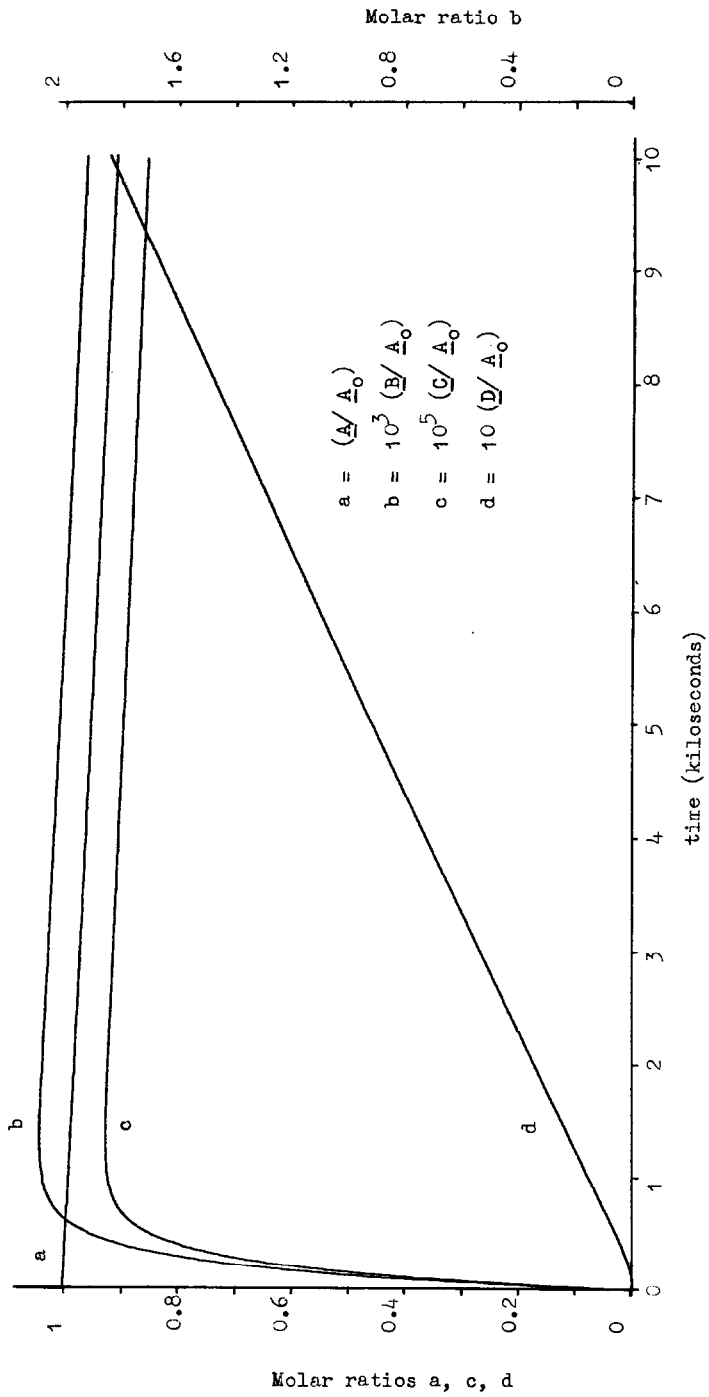
$$\begin{aligned} \text{It follows from the mechanism that:} \quad & -\frac{d[A]}{dt} = k_1[A] \\ & -\frac{d[B]}{dt} = k_1[A] - k_2[B] \\ & -\frac{d[C]}{dt} = k_2[B] - k_3[C] \\ & \frac{d[D]}{dt} = k_3[C]. \end{aligned}$$

From these equations it will follow that:

$$\begin{aligned} \frac{[B]}{[A]_0} &= \frac{k_1}{k_2 - k_1} \left[e^{-k_1 t} - e^{-k_2 t} \right] \\ \frac{[C]}{[A]_0} &= \frac{k_1 k_2}{(k_2 - k_1)(k_3 - k_1)} e^{-k_1 t} + \frac{k_1 k_2}{(k_1 - k_2)(k_3 - k_2)} e^{-k_2 t} + \\ & \quad \frac{k_1 k_2}{(k_1 - k_3)(k_2 - k_3)} e^{-k_3 t} \\ \frac{[D]}{[A]_0} &= 1 - \frac{k_2 k_3 e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)} + \frac{k_1 k_3 e^{-k_2 t}}{(k_1 - k_2)(k_3 - k_2)} + \frac{k_1 k_2 e^{-k_3 t}}{(k_1 - k_3)(k_2 - k_3)} \end{aligned}$$

From these equations it was calculated that maximal concentrations are present for $[B]/[A]_0 = 2.1 \times 10^{-3}$ and for $[C]/[A]_0 = 9.3 \times 10^{-6}$, both at $t = 22$ min. The sum of concentrations $[A] + [D]$ are therefore $> 99.7\%$ throughout the sequence of reactions, and this explains why good rate constants were here obtainable for the conversion of $A \rightarrow D$ by the spectrokinetic technique.

Figure 2



Plots of concentrations vs. time could be displayed (see Figure 2) by the use of an analogue computer method.¹¹

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