Pyrolysis of Phenyl 2,2,2-Trideuterioacetate. Evidence Against a Concerted Mechanism

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Summary Pyrolysis of phenyl 2,2,2-trideuterioacetate yields phenol with no *ortho*-deuterium, indicating that the reaction does not involve a concerted sigmatropic rearrangement.

Two mechanisms have been proposed for the pyrolysis of phenyl acetate to phenol and keten. Hurd and Blunck, who first reported the reaction, suggested the radical-chain pathway shown in Scheme 1.[1] This mechanism has recently been questioned by Meyer and Hammond, who photolysed phenyl acetate in the gas phase.[2] They observed a number of products, including phenol, *o*- and *p*-cresol, *o*- and *p*-phenoxyphenol, and benzoquinone, but no keten. To account for these products, they suggested a different radical-chain mechanism involving attack of phenoxyl radical on phenyl acetate to yield, not phenol and keten, but the phenoxyphenols. Since the products were different from those obtained by Hurd and Blunck, Meyer and Hammond reasoned that the photolytic and pyrolytic decompositions must proceed by different pathways and suggested the concerted mechanism shown in Scheme 2. Not only did this mechanism provide an explanation for the different products observed in the thermal and photochemical reactions, but it also seemed consistent with the growing awareness of the role of concerted reactions in chemical transformations.[3]

$$\mathrm{PhO\cdot + MeCO_2Ph \rightarrow PhOH + \cdot CH_2CO_2Ph}$$

$$\mathrm{\cdot CH_2CO_2Ph \rightarrow CH_2{=}C{=}O + PhO\cdot}$$

Scheme 1

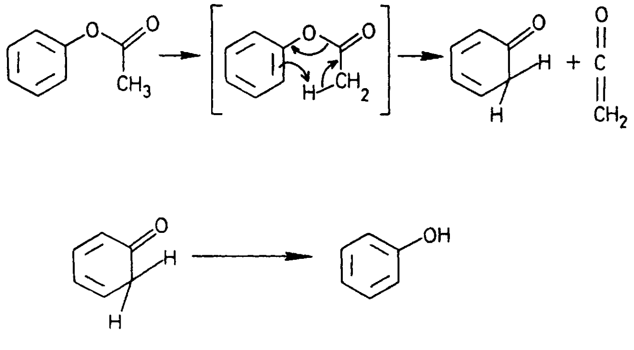
In order to determine which of the proposed thermal mechanisms actually operates, we have pyrolysed phenyl acetate and phenyl 2,2,2-trideuterioacetate (I). Pyrolysis of (I) would give phenol with no *ortho*-deuterium if the radical pathway operates, but the concerted pathway should give a mixture of phenol (II) and *o*-deuteriophenol (III). Although the ratio of (III) : (II) which would be obtained from the concerted reaction is difficult to predict because it would depend on the primary isotope effect for the dienone–phenol tautomerization, it should be greater than unity.

Table. Mass spectra of phenol from pyrolysis of phenyl acetate and of (I)

Source of phenol	Relative intensity[a] *m/e* 95	Relative intensity[a] *m/e* 96
Pyrolysis of PhOAc[b]	7·6 ± 0·5	1 ± 0·5
Pyrolysis of (I)[b]	9·4 ± 0·5	1 ± 0·5
Pyrolysis of PhOAc[c]	7·1 ± 0·3	0·5 ± 0·3
Pyrolysis of (I)[c]	7·6 ± 0·3	0·5 ± 0·3
Calculated[d]	6·6	0·4

[a] Relative to *m/e* 94 = 100%. [b] Spectra obtained at 16·18 eV on a Hitachi–Perkin Elmer RMU-6E spectrometer. [c] Spectra obtained at 18 eV on an AEI MS-902 spectrometer at the Research Triangle Centre for Mass Spectrometry. (Supported by the Biotechnology Resources Branch of the Division of Research Resources of the N.I.H.). [d] Calculated from isotopic abundance.[4]

Compound (I) was pyrolysed at 635° in a flow system designed so that 400 ml/min of nitrogen swept 1 g of (I) through a heated Vycor tube each 12 h. Unchanged phenyl acetate and some products were trapped in an ice-cooled flask, while an ice-cooled aniline trap was used to



Scheme 2

capture volatile products not condensed in the first trap. The aniline trap yielded acetanilide from the pyrolysis of phenyl acetate, indicating the presence of keten, and yielded 2,2-dideuterioacetanilide from the pyrolysis of (I).

The phenol [(II) and/or (III)] formed in each case was extracted with base from the unchanged phenyl acetate or (I) in the cold trap, then separated by the addition of hydrochloric acid. This treatment removed any deuterium present as PhOD. The phenol was then recrystallized from ether and sublimed. The mass spectra of the phenolic product from each pyrolysis are summarized in the Table. While in both cases the $M+1$ and $M+2$ peaks are slightly more intense than would be predicted on the basis of natural isotopic abundance, it is clear that pyrolysis of (I) does not give a significant amount of (III).

These results indicate to us that the pyrolysis of phenyl acetate to phenol and keten does not occur *via* the concerted sigmatropic rearrangement suggested by Meyer and Hammond. The possibility that a radical chain mechanism is operating in the thermal reaction is strengthened by g.l.c. analysis of the pyrolysis product mixture which shows peaks having retention times similar to those of the *o*- and *p*-cresols and *o*- and *p*-phenoxyphenols.

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