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THE BEHAVIOUR IN ACID OF 4,4-DIMETHYL-, AND 4-DICHLOROMETHYL-3,4,5-TRIMETHYL-CYCLOHEXA-2,5-DIENONES

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The available kinetic data on dienone-phenol rearrangements cover limited ranges of acidity (1). We supplement results (2) on 4,4-dimethylcyclohexa-2,5-dienone (I), and report accurate basicity data for (I) and 4-dichloromethyl-3,4,5-trimethylcyclohexa-2,5-dienone (II).

Dienone (I) rearranges, with pseudo first-order kinetics in aqueous sulphuric or perchloric acid, to 3,4-dimethylphenol (70% isolated yield from 52% H_2SO_4 or $HC\ell O_4$). Observed rate constants in sulphuric acid (Table), and optical densities at zero time were derived from u.v. spectra of the acid solutions. Standard procedures (3) give $[B]/[BH^+]$ for (I) and (II). Both dienones follow the amide acidity scale H_A (4), with pK and m values (Eqn. 1) (-2.37 ± 0.03; 1.03 ± 0.01) for (I) and (-2.31 ± 0.10; 1.07 ± 0.03) for (II); amide bases have m close to 1.0. These pK's are the closest estimates of thermodynamic values; Bunnett and Olsen's method (5) gives pK (-2.06 ± 0.08) for (I) and (-2.10 ± 0.13) for (II).

Values of k_1 derived using Eqn. 2 are correlated by the straight lines of Eqn. 3 and by linear Bunnett and Olsen plots ($\phi = -0.28$). Combining Eqn. 4 (from transition state theory) with Eqn. 3 shows that $\log f_{\ddagger}/f_{BH^+}$ changes with the medium just half as fast as does H_A.

Both dienones show significant medium effects at some wavelengths. These must be allowed for in the pK studies and may explain differences between our values and the estimates in Refs. 2b and 6. Our plot of log k_1 against log(water activity) shows the graph in Ref. 2b to have incorrectly labelled axes, but agrees with Eqn. 5 of Ref. 2b.

$$\underset{[B]}{\text{(I)}} + H^+ \rightleftharpoons \underset{[BH^+]}{\text{O-Protonated dienone}} \rightleftharpoons \underset{[\ddagger]}{\text{Transition state}} \longrightarrow \text{Product}$$

Eqn. 1 $\log_{10} [B]/[BH]^+ = m(H_A - pK)$

Eqn. 2 Rate $= k_{obs}$ [Total dienone] $= k_1[BH^+]$; $k_1 = k_{obs}(1+[B]/[BH^+])$

Eqn. 3 $-\log k_1 = 0.27\ H_o + 3.33 \pm 0.03 = 0.52\ H_A + 3.72 \pm 0.06$

Eqn. 4 $\log k_1 = \log k_o - \log f_{\ddagger}/f_{BH^+}$ (f = activity coefficient)

Table Kinetics for (I) in aqueous H_2SO_4 at 25°C (min^{-1} units)

H_2SO_4 (molar)	5.92	6.72	7.17	7.44	7.79	8.37	8.56	9.18
$k_{obs} \times 10^4 (\pm 1\%)$	8.76	13.8	23.1	24.6	33.1	48.1	52.6	63.4
H_2SO_4 (molar)	10.17	10.74	11.06	11.74	11.80	12.76	13.56	
$k_{obs} \times 10^4 (\pm 2\%)$	101.6	130.4	163.4	223	201	269	332	

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