A Relaxation Study of the Isomerisation of 2,2,3-Trimethyl-levulinic Acid

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Temperature-jump measurements on buffer solutions of 2,2,3-trimethyl-levulinic acid have been used to determine the rate of interconversion of its ring and chain isomers, and the results have been compared with those for similar systems. The consistency of the results confirms the validity of the method previously used for estimating the position of ring–chain equilibria in solutions of these compounds, based on a comparison of conventional p*K* values with acid–base catalytic power. Some qualitative information was obtained for the isomerisation of 2-acetylbenzoic acid, but no relaxation process could be detected for 2,2-dimethyl-levulinic acid, probably because the relevant enthalpy change is too small.

A PREVIOUS paper [1] reported a temperature-jump study of the interconversion in aqueous solution of 2-formylbenzoic acid and its cyclic lactol tautomer. Although most aliphatic oxocarboxylic acids appear to exist mainly in the normal chain form in solution, there is good evidence [2,3] that aqueous solutions of 2,2,3-trimethyl-levulinic acid contain about 80% of lactol, presumably because of the well known effect of *gem*-dialkyl groups in favouring ring closure, and the present paper reports relaxation measurements on these solutions.

EXPERIMENTAL

The preparation and purification of 2,2,3-trimethyl-levulinic acid are described elsewhere.[3] Buffer solutions were prepared by adding weighed amounts of acid to standard solutions of sodium or potassium hydroxide. The enthalpy of ionization was determined by measuring the pH (glass electrode) of a solution 0.003M in both acid and anion at five temperatures. The derived thermodynamic dissociation constants increased from 1.64×10^{-6} at 18.0 °C to 2.62×10^{-6} at 50.5 °C, corresponding to $\Delta H = 11.6$ kJ mol^{-1}. Since ΔH for the ionization of simple carboxylic acids (including levulinic acid) is considerably smaller than this, a large part of the observed enthalpy change must result from the interconversion of the isomers.

The measurement of relaxation times followed closely the procedure described for 2-formylbenzoic acid,[1] but the present results are more accurate because the reactions are considerably slower and ΔH is larger. The change of pH was followed by using the indicator Bromocresol Purple (p*K* 6.4): at pH 6 a 4×10^{-4}% solution gave an absorbance of about 0.4 at 583 nm (due to the basic form) in the 2 cm cell of the temperature-jump apparatus. Most experiments utilized the decrease in absorbance at this wavelength, but in a few instances the increase in the less intense band at 430 nm, due to the acid form, was used. Separate experiments showed that the relaxation of the indicator equilibrium was too fast to be detectable on our time-scale, and the concentrations of indicator species were too low to play any appreciable catalytic role. All solutions contained 0.14M-potassium nitrate, and the initial solution temperature was 20 °C, so that the reaction temperature was close to 25 °C. Unless otherwise stated, the 10 μs filter was used. The results are given in Table 1.

Since 2,2-dimethyl-levulinic acid has a lactol content of about 50% in solution,[2,3] experiments were also carried out with this substance, prepared and purified as described elsewhere.[3] However, its dissociation constant (glass electrode) was found to vary only slightly with temperature, decreasing from 8.8×10^{-6} at 16.5 °C to 8.0×10^{-6} at 49.7 °C. Temperature-jump measurements were attempted, with Methyl Red as indicator, but the observed effects were small and difficult to interpret, probably because ΔH is too small.

TABLE 1

Relaxation constants for 2,2,3-trimethyl-levulinate buffers at 25 °C

Buffer ratio [acid]/[anion] = 0.5 unless otherwise stated

10^4[anion]	10^{-2} k(obs.)/s^{-1}	10^{-2} k(calc.) Uncatalysed	Catalysed	Total
0.60	24 *	28.4	0.3	29
0.60	26	28.4	0.3	29
1.0	30	32	1	33
2.0	35	35	1	36
4.1	38	38	3	41
6.1	44	38	4	42
6.1	40 †	38	4	42
8.2	46	39	6	45
10.2	47	39	7	46
15.2	49	39	11	50
20.0	53	40	15	55
40	76 ‡	40	30	70
40	70	40	30	70
40	77 §	40	30	70
80	101	40	59	99
160	145 ¶	40	119	159

* $t_{\frac{1}{2}}$ *ca.* 280 μs, filter 50 μs; hence observed rate may be too low. † Increase of absorbance followed at 430 nm, and value hence less certain. ‡ Buffer ratio 0.275. § Buffer ratio 1.0. ¶ $t_{\frac{1}{2}}$ *ca.* 48 μs, filter 10 μs; hence observed rate may be too low.

Slightly more information was obtained from experiments with 2-acetylbenzoic acid, which contains 80% of the cyclic isomer in solution.[4] Its dissociation constant was found to increase from 6.6×10^{-5} at 19.8 °C to 7.6×10^{-5} at 46 °C, corresponding to $\Delta H = 4.3$ kJ mol^{-1}, and temperature-jump measurements (indicator Bromophenol Blue) showed a change in the expected direction. However, the rate was too high to be measured quantitatively, even at anion concentrations of about 10^{-4}M, and it can only be stated that $k > 4 \times 10^5$ s^{-1} in these solutions.

DISCUSSION

The results in Table 1 indicate that the observed velocity consists of a ' spontaneous ' (or water-catalysed)

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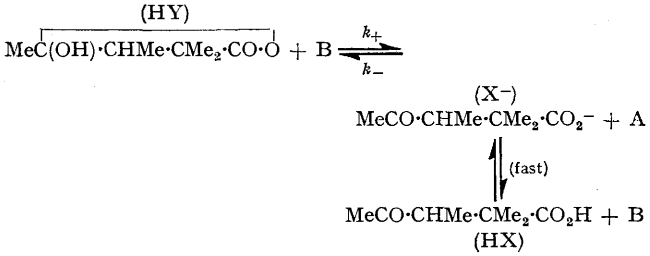
[1] R. P. Bell, B. G. Cox, and B. A. Timimi, *J. Chem. Soc.* (*B*), 1971, 2247. In this paper the relaxation velocity constants shown in Tables 4 and 5 are all too high by a factor of 10^4. However, the velocity constants in the remainder of the paper are given correctly, and the conclusions still stand.

[2] C. Pascual, D. Wegmann, U. Graf, R. Scheffold, P. F. Sommer, and W. Simon, *Helv. Chim. Acta*, 1964, **47**, 213.

[3] R. P. Bell and A. D. Covington, preceding paper.

[4] R. P. Bell, B. G. Cox, and J. B. Henshall, *J.C.S. Perkin II*, 1972, 1232.

component, together with component due to catalysis by the anion of the oxo-acid: they also show that at constant anion concentration the rate is independent of pH. This is the same behaviour as was found with 2-formylbenzoic acid, and the same mechanistic arguments apply, leading to the illustrated Scheme, where



SCHEME

A–B is any acid–base pair. In our experiments the only such pairs are H_3O^+–H_2O and HX–X^-, and since $[H^+] \ll [X^-]$ throughout, the usual relaxation treatment gives equation (i) for the observed first-order velocity

$$k = (k_+[H_2O] + k_+'[X^-])\{1 + K[X^-]/(K_{HX}^* + [X^-])\} \quad \text{(i)}$$

constant. In equation (i) $[H_2O] = 55.5$, K is the equilibrium constant [HY]/[HX], and K_{HX}^* is the value at the appropriate ionic strength of the 'true' dissociation constant of the open-chain acid, $[H^+][X^-]/[HX]$, as distinct from the dissociation constant measured by conventional means, which also includes [HY]. Measurements on the catalytic effect of X^- in the decomposition of nitramide[3] gave the thermodynamic values $K = 6.9$, $K_{HX} = 1.42 \times 10^{-5}$, and the assumption $f_\pm = 0.69$ in 0.14M-potassium nitrate yields $K_{HX}^* = 3.0 \times 10^{-5}$. The values of k(calc.) in the last three columns of Table 1 have been calculated from equation (i) by using these equilibrium constants, together with the values of k_+ and k_+' in Table 2. Agreement with experiment is usually within experimental error, and the small systematic deviations at low concentrations could be removed by choosing $f_\pm = 0.60$. Table 2 also contains values of k_- and k_-', derived from $k_-/k_+ = 55.5\ K/K_{HX}^*$ and $k_-'/k_+' = K$, together with the corresponding velocity constants for 2-formyl- and 2-acetylbenzoic acids.

TABLE 2

Collected velocity constants ($dm^3\ mol^{-1}\ s^{-1}$)

Acid	k_+	k_-	k_+'	k_-'
2,2,3-Trimethyllevulinic	9.0	1.15×10^8	9.3×10^4	6.5×10^5
2-Formylbenzoic	23	2.5×10^7	2.2×10^5	3.2×10^6
2-Acetylbenzoic	$>7 \times 10^3$	$>3 \times 10^9$		

For each of the first two acids in Table 2 the quantity k_+'/k_+ is *ca.* 10^4, to be compared with ratios of $4 \times 10^6 : 1$ and $2 \times 10^5 : 1$ between the basic strengths of X^- and H_2O, corresponding to a base-catalysed process (see Scheme) with Brönsted exponents of 0.6 and 0.75. It is difficult at present to rationalize the relative values of the velocity constants for the different acids, since several steric and electronic effects must be involved.

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