Variable Temperature Study of Protonation of 1,3-Dialkylbenzenes

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At variance with predictions of *ab initio* calculations, and in apparent contradiction of gas-phase experiments, the 4-protonated isomers of *m*-xylene and 1,3-diethylbenzene predominate heavily in superacid solution over the 2-protonated isomers at all temperatures.

Protonation of 1,3-dialkylbenzenes (1) in superacids was described to give the 4-protonated isomer (2).[1] On the other hand, ion cyclotron resonance (i.c.r.),[2] or high pressure mass spectroscopy (h.p.m.s.)[3] studies on the sequential deuterium exchange of substituted benzenes by protonation with D_2O/D_3O^+, reported that *m*-xylene (1a) exchanged only one hydrogen, while toluene exchanged five, and *p*-xylene exchanged four.[2,3] Since protonation to form (2a) should result in exchange at C-4 and C-6 with equal ease, one might conclude that in those experiments the 2-protonated isomer (3a) was formed preferentially. Subsequently, *ab initio* calcu-

lations indicated that indeed position 2 in (1a) should be protonated preferentially.[4]

Wanting to test whether these divergent results can be explained by the difference in temperature[5] (-60 to -90 °C for the superacid experiments,[1] and room temperature or higher for i.c.r. and h.p.m.s.[2,3]), we studied the variable temperature ^{13}C n.m.r. spectra of (1a) and (1b), protonated in $HF-SbF_5$. The chemical shifts for (2) and (3) and for the averaged signals are as shown in Table 1. The signals for the 2-protonated isomers (3) appear in the positions expected based on the spectra of (2) and of *ortho*-protonated ethyl-

Table 1. Chemical shifts for (2) and (3) [δ, p.p.m. from external (coaxial) Me_4Si].

$T/°C$		C-1	C-2	C-3	C-4	C-5	C-6	C-α	C-β
-60	(2a)	195.6	135.6	200.6	48.2	171.4	133.8	27.1, 25.0	—
	(3a)	—[a]	54.6	—[a]	131.7	—[a]	131.7	—[a]	—
$+95$	(2a), (3a)	199.3	130.2	199.3	*ca.* 93.8 (br)	170.9	*ca.* 93.8	25.7	—
-60	(2b)	199.9	132.4[b]	206.2	47.3	171.5	132.9[b]	34.4, 32.6	11.3, 10.8
	(3b)	205.3	52.3	205.3	130.0	—[a]	130.0	—[a]	—[a]
$+90$	(2b), (3b)	204.5	126.6	204.5	*ca.* 92.5 (br)	170.9	*ca.* 92.5	34.0	10.9

[a] The signal probably coincides with the peak for the major isomer. [b] This assignment might be reversed.

a; R = Me

b; R = Et
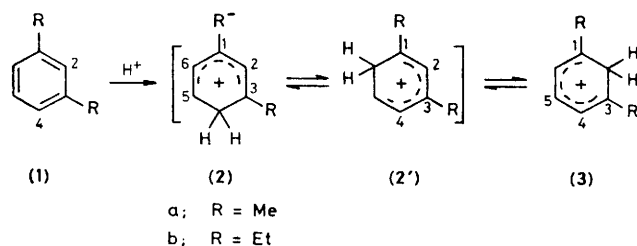
benzene.[6] The relative concentrations of (2) and (3) at low temperature were calculated for each substrate, from the relative intensities of peaks representing the same type of carbon atoms (CH, CH_2, C) in the two isomers.[6,7] At -60 °C, $2.5 \pm 0.5\%$ of (3a) and $2.8 \pm 0.5\%$ of (3b) were found in the mixture with (2a) and (2b), respectively.

The concentration of (3a) and (3b) in the region of fast exchange (above $+80$ °C)† was determined from the chemical shift for C-2: $6.7 \pm 0.3\%$ (3a) at $+95$ °C, and $7.3 \pm 0.3\%$ (3b) at $+90$ °C, respectively. The averaged signals for C-4 and C-6 were still broad at $+95$ °C, but an approximate calculation of the isomer ratios could be made based on their chemical shifts; in each case, the value agreed with that based on C-2. Of all signals, the one for C-5 remained sharp throughout the whole temperature range.

The differences between the isomer compositions for protonated (1a) and (1b) are within the combined range of experimental errors. Moreover, the thermodynamic parameters for the positional isomerization calculated from the equilibrium constants at two temperatures are the same: $\Delta H° = -1.0 \pm 0.4$ kcal/mol, $\Delta S° = 2.4 \pm 1.3$ cal mol^{-1} K^{-1} for (3a) $\rightleftharpoons$ (2a), and $\Delta H° = -1.0 \pm 0.3$ kcal/mol,

$\Delta S° = 2.2 \pm 1.0$ cal mol^{-1} K^{-1} for (3b) $\rightleftharpoons$ (2b).‡ Significantly, the value for $\Delta S°$ is reasonably accounted for by the symmetry difference between (2) and (3), and therefore rules out any difference in solvation between the isomers.[4b,8]

Since differential solvation cannot be involved, it appears probable that in the gas phase protonation also occurs in position 4. However, the high basicity of (1) slows down very much the proton loss from (2), which is necessary in order to observe multiple exchanges. Since an ion suffers a limited number of collisions before it is analysed, the very slow deprotonation is the reason for the single H/D exchange observed.[2,3] On the other hand, the ab initio calculations[4] should be viewed with some caution.

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† The faster, degenerate exchange (automerization) (2) $\rightleftharpoons$ (2′) is observable at much lower temperatures. Thus, the signals for C-4 and C-6 of (2a) are already broadened at -20 °C (as are the signals for C-1, C-3, C-α1, and C-α3) while that for C-2 is unaffected. This behaviour is compatible only with (2a) $\rightleftharpoons$ (2′) being faster than (2a) $\rightleftharpoons$ (3a) and serves to distinguish between the signals of C-2 and C-6 in (2a).

‡ 1 cal $= 4.184$ J.