Remarkable Brönsted Type Correlation for Base Cleavage of Carbon–Silicon Bonds. Kinetic Isotope Effects for Interaction of Carbanions with Methanol

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Summary The logarithms of the relative rates of cleavage of $RSiMe_3$ compounds [R = 1-indenyl, 9-fluorenyl, 9-(2-bromofluorenyl), 9-(2,7-dibromofluorenyl), PhC⋮C, Ph_3C, Ph_2CH, p-$PhC_6H_4CH_2$, and $PhCH_2$] by aqueous methanolic alkali correlate linearly with the pK's of the corresponding hydrocarbons R–H over a pK_a range of 22 units; the ratio of RH/RD products obtained in 1:1 MeOH–MeOD is thought to be equal to the deuterium isotope effect for interaction of the carbanion R^- with methanol.

BELETSKAYA and her colleagues presented a plot of the logarithms of the specific rate constants for base cleavage of R–$SiMe_3$ bonds against the pK_a's of the hydrocarbon acids, RH, for R = PhC⋮C, 9-fluorenyl, PhCH:$CHCH_2$, Ph_3C, Ph_2CH, and $PhCH_2$.[1] They obtained a curve, which they suggested should be regarded as a rough straight line for all the points except that for $PhCH_2$, which fell well below the line, and concluded that a change in mechanism occurred between R = $PhCH_2$ and R = Ph_2CH. We have amended the plot by (a) adding additional points [*viz.* R = *p*-$PhC_6H_4CH_2$, 1-indenyl, 9-(2-bromofluorenyl), and 9-(2,7-dibromofluorenyl)], some of which extend the pK_a range, (b) using recent, much more reliable pK_a values,[2,3] and (c) omitting the point for R = PhCH:$CHCH_2$ because no reliable pK_a value is available. The plot (in which we use values of k_{rel}, the rate constant relative to that for R = Ph-CH_2[4,5]), based on data in the Table, is shown in the Figure, and is a good straight line within the limits of accuracy of pK_a values for this medium.† The existence of this Brönsted-type correlation (α = 0·35) over such a wide pK_a range is all the more remarkable because the rates of hydrogen-exchange for the RH compounds in methanolic NaOMe do not show a satisfactory correlation over this range;[7] there is a good correlation for substituted fluorenes of pK_a 15·5—24, and another for polyarylmethanes of pK_a 28—33·5, but the values of α, *viz.* 0·37 and 0·58, respectively, are very different, implying, Streitwieser and his colleagues suggest, a change in mechanism.[7] The Brönsted-type correlation for the cleavages suggests that there is probably no change in mechanism for the compounds studied.

TABLE. Relative rates and solvent isotope effects in base cleavage of $RSiMe_3$ compounds.

No.	R	pK_a[a] of RH	logk_{rel}[b]	k_{MeOH}/k_{MeOD}	PIE	(k_{MeOH}/k_{MeOD})/PIE
1	$PhCH_2$	41	0·0		1·2[c]	
	m-$CF_3{\cdot}C_6H_4{\cdot}CH_2$		2·52	0·50	1·2[c]	0·42
2	*p*-$Ph{\cdot}C_6H_4{\cdot}CH_2$	38·7	1·08			
3	Ph_2CH	33·4	3·14	0·48	2·2	0·22
4	Ph_3C	31·45	3·25	0·51	2·3	0·22
5	9-fluorenyl	22·7	6·3	0·59	7·0	0·084
	9-(9-methylfluorenyl)		5·86		9·1	
6	9-(2-bromofluorenyl)	21·2[d]	7·0			
7	1-indenyl	19·9	7·2		8·8	
8	9-(2,7-dibromofluorenyl) . .	19·6	7·8			
9	PhC⋮C	23·2	6·8			
	p-$NO_2{\cdot}C_6H_4{\cdot}CH_2$		6·35	0·52	10·7	0·048

[a] In $C_6H_{11}NH_2$–$C_6H_{11}NHCs$.[2] [b] In 5:1 v/v MeOH–H_2O at 50 °C.[4,5] [c] Ref. 9. [d] Derived from values in H_2O–Me_2SO[3] (*cf.* ref. 5)

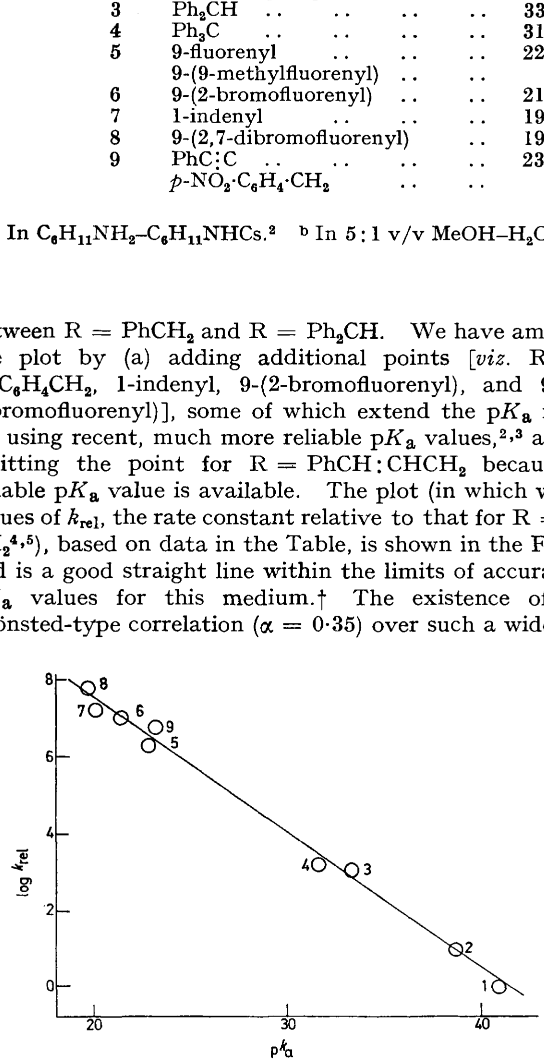

FIGURE. Plot of log k_{rel} for cleavage of $RSiMe_3$ compounds against pK_a for RH (see Table for numbering of points).

We have also measured for some of the compounds and for *p*-nitrobenzyltrimethylsilane the ratio k_{MeOH}/k_{MeOD} of the overall rate constants (at 50 °C) for cleavage by NaOMe in MeOH and MeOD, respectively, and the ratio RH/RD, which we denote PIE (product isotope effect)[8] of products obtained in 1:1 MeOH–MeOD (Table).[8] Whereas for cleavage of some aryl- and benzyl-trimethylstannanes[8,9] and of *m*-trifluoromethylbenzyltrimethylsilane, and for hydrogen evolution from triorganosilanes,[10] the values of the ratio [(k_{MeOH}/k_{MeOD})/PIE] lie in the range 0·41—0·50, the value of this ratio falls for the compounds in the Table to as low as 0·084 for the 9-fluorenyl-compound. This implies, at least for the more reactive compounds and probably for all, that R–H bond formation is not involved in the rate determining step, as we previously tentatively favoured,[8] but that a free carbanion R^- is generated, and thus that the PIE reflects the deuterium isotope effect for interaction of R^- with the methanol. The PIE value for R = $PhCH_2$ agrees with the k_{EtOH}/k_{EtOD} value of 1·2 ± 0·45 reported for the interaction of the benzyl carbanion with ethanol in tetrahydrofuran.[11] The values of 7·0 and 9·1 for the 9-fluorenyl and 9-(9-methylfluorenyl) ions, respectively, correspond roughly, by Schowen's approximate treatment,[12] to k_H/k_D values of 4·8 and 6·1 for reverse reaction involving proton-abstraction from the RH compounds by MeO^-, and within the substantial uncertainties arising from the several necessary approximations these are consistent with values of 5·3 and 6·5 which can be derived from the observed k_D/k_T

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† Little significance can be attached to the point for R = PhC⋮C in view of the variability of the pK_a of phenylacetylene with the medium.[6] The pK_a—log k_{rel} relationship no longer applies when steric effects are too large; *e.g.* 9-phenyl-9-fluorenyltrimethylsilane is much less reactive than expected from its pK_a. The point for the 9-methyl analogue is also omitted from the plot because of a substantial though less marked steric effect.[5]

values of 2·1 and 2·3 at 45 °C.[7] However, our value for the triphenylmethyl compound, *viz.* 2·3, implies a k_H/k_D of 2·0 for triphenylmethane, quite out of keeping with the value of 4·2 at 100 °C derived by Streitwieser and his colleagues;[13] they concluded that the k_H/k_D ratios for the hydrocarbons vary very little over a 13 pK_a range, and comment that this is 'remarkable' and 'does not agree with contemporary thought . . .'.

If our interpretations are correct, determination of PIE values in Me_3SiR cleavages offers a simple way of determining the kinetic isotope effects for interactions of carbanions with methanol and other hydroxylic media.

(*Received, 8th August* 1975; *Com.* 920.)

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