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RATE CONSTANTS AND SOLVENT ISOTOPE EFFECTS IN THE CLEAVAGE OF PICOLYL- AND (QUINOLYLMETHYL)-TRIMETHYLSILANES BY SODIUM METHOXIDE IN METHANOL *

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Summary

Rate constants have been determined for cleavages of picolyltrimethylsilanes ($PyCH_2SiMe_3$) and (quinolylmethyl)trimethylsilanes ($QnCH_2SiMe_3$) by sodium methoxide in 100% MeOH (at 25°C) and sodium hydroxide in 2/1 v/v $MeOH/H_2O$ (at 50°C), and used to derive σ^- constants for the $PyCH_2$ and $QnCH_2$ systems (2-$PyCH_2$, 0.85, 3-$PyCH_2$, 0.53, 4-$PyCH_2$, 1.07, 2-$QnCH_2$, 1.14, 3-$QnCH_2$, 0.70, 4-$QnCH_2$, 1.20) and approximate pK_a values for the corresponding carbon acids $PyCH_3$ and $QnCH_3$ (2-$PyCH_3$, 29.5; 3-$PyCH_3$, 33.5, 4-$PyCH_3$, 26, 2-$QnCH_3$, 25.5, 3-$QnCH_3$, 31.5, 4-$QnCH_3$, 24.5). Values of the solvent rate isotope effect, the ratio of the rate constant in MeOH to that in MeOD (2-, 3-, and 4-$PyCH_2SiMe_3$, 0.65, 0.49, and 0.54, respectively, 2-, 3-, and 4-$QnCH_2SiMe_3$, 0.56, 0.47, and 0.52, respectively) and of the product isotope effect, the product ratio RH/RD on cleavage of $RSiMe_3$ in 1/1 MeOH-MeOD (2-, 3-, and 4-$PyCH_2SiMe_3$, 5.6, 1.1, and 2.6, respectively, 2-, 3-, and 4-$QnCH_2SiMe_3$, ca. 5, 1.1, and 3.2, respectively) have also been measured. The rate isotope effects for 2-Py- and 2-Qn-CH_2SiMe_3 are significantly higher than is usual for cleavages of this type. Except for 2-$PyCH_2SiMe_3$, the product isotope effects are rather smaller than those given by $XC_6H_4CH_2SiMe_3$ compounds of comparable reactivities.

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* Dedicated to Professor H. Normant on the occasion of the 72nd birthday on June 25th, 1979.

Introduction

A recent joint paper from two of the laboratories named above described a study of the cleavage of some picolyl- and (quinolylmethyl)-trimethylsilanes (denoted below by $PyCH_2SiMe_3$ and $QnCH_2SiMe_3$) by base in an aqueous methanolic medium containing a rather large proportion of the organosilane [1]. (Since the methanol and aqueous-alkali were present in 9/1 v/v ratio, the medium is referred to loosely below as "90%" MeOH.) This unusual medium was employed because the changes in the UV spectrum accompanying cleavage were not in all cases sufficiently large to permit use of the usual spectrophotometric measurement of rates [2,3], and so a GLC method of analysis was adopted, and this required the presence of a substantial amount (ca. 4 vol%) of the organosilane and of an internal standard (ca. 1 vol%). This reduced the accuracy of the rate measurements, and, more important, hindered comparisons with previously studied cleavages of other $RSiMe_3$ compounds, but nevertheless the results were used to derive approximate values of σ or σ^- constants for the $PyCH_2$ and $QnCH_2$ systems and of pK_a values for the related carbon acids $PyCH_3$ and $QnCH_3$ [1]. By employing spectrophotometers which enable even small UV changes to be monitored with accuracy, we have been able to measure the rates for the cleavages of these organosilanes in media previously used for a wide range of $RSiMe_3$ compounds, viz. 100% MeOH [3—5] and 2/1 v/v MeOH (described below as 67% MeOH) [2,6]. The deuterium solvent isotope effects have also been determined for the reaction in 100% methanol.

Results and discussion

The experimental results are shown in Tables 1 and 2. (Data for cleavage of $p\text{-}O_2NC_6H_4CH_2SiMe_3$ are included in Table 1 for comparison.) Listed are the observed second-order specific rate constants, k_s (the observed pseudo-first order constant divided by the concentration of base), the rate isotope effects *RIE* [the ratio, $k_s(MeOH)/k_s(MeOD)$, of the rate constants in MeOH and MeOD, respectively], and the solvent isotope effects, *PIE* (the product ratio RH/RD obtained on cleavage of $RSiMe_3$ in 1/1 MeOH/MeOD containing NaOMe). In systems such as these the *PIE* values are thought to represent the kinetic isotope effects for reactions of the carbanions R^- with methanol [3].

Implications of rate constants

The main features of the data are as follows. (a) The values of log k_s (100% MeOH) determined in 100% MeOH at 25°C show an excellent correlation with the corresponding values of log k_s (67% MeOH) determined in 67% MeOH at 50°C (correlation coefficient, 0.999; slope, 1.20); the correlation is only slightly poorer when the data for $p\text{-}O_2NC_6H_4CH_2SiMe_3$ are included (correlation coefficient, 0.998; slope, 1.17). There is a less satisfactory correlation between log k_s (100% MeOH) and log k_s ("90%" MeOH) (correlation coefficient, 0.996; slope 1.21), but this is attributable to an abnormal value for $2\text{-}QnCH_2SiMe_3$ in the "90%" MeOH. In the latter medium the reported k_s value for this compound was slightly larger than that for its 4-isomer [1], whereas in 100% and 67% MeOH we find that the 4- is more than twice as reactive as

TABLE 1

SPECIFIC SECOND ORDER RATE CONSTANTS k_s FOR CLEAVAGE OF $RSiMe_3$ COMPOUNDS BY NaOMe or NaOH IN 100% MeOH 100% MeOD OR 2/1 v/v $MeOH/H_2O$ (67% MeOH) AND VALUES OF THE RATE ISOTOPE EFFECT

R	λ[a] (nm)	10^3 [NaOMe][b] (M)	Solvent	Temperature (°C)	$10^5 k_s$ ($l\ mol^{-1}\ s^{-1}$)	RIE
$2\text{-}PyCH_2$	275	207	MeOH	25	83	0 65
		205	MeOD		128	
		170	67% MeOH	50	840	
$3\text{-}PyCH_2$	278	520	MeOH	25	1 16	0 49
		520	MeOD		2 35	
		520	67% MeOH	50	23 7	
$4\text{-}PyCH_2$	262	210	MeOH	25	1 420	0 54
		210	MeOD		2 610	
		17 0	67% MeOH	50	12 000	
$2\text{-}QnCH_2$	322	20 0	MeOH	25	4 040	0 56
		20 0	MeOD		7 200	
	323	17 0	67% MeOH	50	21 700	
$3\text{-}QnCH_2$	327	520	MeOH	25	8 1	0 47
		530	MeOD		17 1	
	326	520	67% MeOH	50	167	
$4\text{-}QnCH_2$	295	20 0	MeOH	25	9 500	0 52
		20 0	MeOD		18 100	
	293	5 20	67% MeOH	50	45 000	
$p\ O_2NC_6H_4CH_2$		10 0	MeOH	25	11 500[c]	0 50[c]
		10 0	MeOD		23 000[c]	
		5 20	67% MeOH	50	90 000	

[a] Wavelength used to monitor progress of reaction [b] For convenience the base is referred to as NaOMe throughout although OH^- will also be present in 67% MeOH [c] Data from ref 3

the 2-isomer We believe that the value of k_s reported for the $2\text{-}QnCH_2SiMe_3$ in "90%" MeOH was in error If the point for this compound is omitted there is an almost perfect correlation between the values of log k_s (100% MeOH) and those of log k_s ("90%" MeOH) (correlation coefficient, 1 000, slope, 1 27) Furthermore, the new log k_s values correlate even more satisfactorily than the earlier values with the values of log k for hydrogen exchange in MeOH/MeONa

TABLE 2

PRODUCT ISOTOPE EFFECTS IN CLEAVAGES OF $PyCH_2SiMe_3$ AND $QnCH_2SiMe_3$ COMPOUNDS $RSiMe_3$ BY SODIUM METHOXIDE IN METHANOL AT 25°C

R	MeOH/ MeOD[a]	[NaOMe] (M)	Time (h)	RH/RD		PIE		
				By NMR[b]	By MPD[b]	By NMR	By MPD	Mean
$2\text{-}PyCH_2$	1/4	0 025	48	1 32	1 45	5 3	5 8	5 6
$3\text{-}PyCH_2$	1/2	0 5	48		0 57		1 1	1 1
$4\text{-}PyCH_2$	1/4	0 025	24	0 70	0 57	2 8	2 3	2 6
$2\text{-}QnCH_2$	1/4	0 025	24	1 10	(<2 0)[b]	4 4	(<8)[b]	~5[b]
$3\text{-}QnCH_2$	1/1	0 15	48	1 20	1 00	1 2	1 0	1 1
$4\text{-}QnCH_2$	1/4	0 025	24	0 85	0 73	3 4	2 9	3 2

[a] For determinations of RH/RD ratios by NMR CD_3OH/CD_3OD mixtures were used [b] See Experimental section

at 135°C [7] and EtOH/EtOK at 25°C [8], for the log k_s (100% MeOH) and log k (EtOH/EtOK) values the correlation coefficient is 0.999 Moreover, the sequence of reactivities in corresponding structures now agrees fully with that in the deuteration in EtOH/EtOK the previously reported log k_s ("90%" MeOH) values indicated that 2-$QnCH_2SiMe_3$ was more reactive than 4-$QnCH_2SiMe_3$ in the cleavage, whereas 4-$QnCH_3$ is more reactive than 2-$QnCH_3$ in hydrogen-exchange [8]

(b) The new data can be used in conjunction with those for p-$O_2NC_6H_4CH_2SiMe_3$ to derive σ^- constants for the $PyCH_2$ and $QnCH_2$ systems with more confidence than previously Based solely on the value of k_s for p-$O_2NC_6H_4CH_2SiMe_3$ and $PhCH_2SiMe_3$ in 67% MeOH at 50°C *, the value of ρ is 5.06, a value of 1.24 being used for the σ^- constant for the p-NO_2 group **. Use of this ρ value gives the σ^- constants for the $PyCH_2$ and $QnCH_2$ systems shown in Table 3. (For 3-$PyCH_2$ and 3-$QnCH_2$ these constants are presumably identical with the σ constants.) A similar procedure, involving use of a ρ value of 5.73, gives values of the σ constants derived from the rates in 100% MeOH at 25°C, and these are also shown in Table 3, in this case the experimental value (0.885×10^{-8} l $mol^{-1} s^{-1}$) obtained by extrapolation from data at higher temperatures [3]) of k_s for cleavage of $PhCH_2SiMe_3$ with 2.0 M NaOMe has to be halved to make an approximate correction for the dependence of k_s on the base concentration in this medium [13]. The mean values of the σ^- constants listed in Table 3 are thought to be fairly reliable, except for the 2-$QnCH_2$ system they differ only slightly from those previously derived, by making several approximations, from the data in "90%" MeOH [1] It should be appreciated that these σ^- values are all related to the value of 1.24 used for the p-NO_2 group, and if in a future correlation a different value is used for the latter, the values for the $PyCH_2$ and $QnCH_2$ systems should be appropriately amended.

The previous discussion [1] of the comparison of the derived σ^- constants with those suggested by other workers [10] need not be significantly modified in the light of the new results

(c) Using the k_s values for 67% MeOH, values rather more accurate than those previously derived [1], but necessarily still rough, can be deduced for the pK_a's of the carbon acids $PyCH_3$ and $QnCH_3$ by use of the relationship $pK_a = -2.86 \log k_{rel} + 41$ which applies in this medium [11], where k_{rel} is the rate of cleavage of the $RSiMe_3$ compound relative to that of $PhCH_2SiMe_3$ and the pK_a refers to the equilibrium ion-pair acidity of the corresponding carbon acid RH in $CsNHC_6H_{11}NH_2C_6H_{11}$, based on a pK_a of 18.6 for 9-phenylfluorene [12] ***. For references to other derivations of pK_a values for the $PyCH_3$ and $QnCH_3$ compounds see ref. 1.

Solvent isotope effects

For cleavage of a wide variety of $RSiMe_3$ compounds (R = Ar or $ArCH_2$), the

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* Actually the rate constant for the latter compound refers to cleavage in 39 wt% H_2O in MeOH [2] which is closer to 66 than 67 vol% MeOH but such a change in medium has a negligible effect on the rate

** For a larger range of compounds in this medium and using a value of 1.27 for the p-NO_2 group a slope of 4.88 was derived [2].

*** The relationship may possibly give systematically low values in the pK_a region 27—32 [13]

TABLE 3

DERIVED VALUES OF σ^- CONSTANTS FOR PyCH$_2$ AND QnCH$_2$ SYSTEMS R AND pK_a OF THE CARBON ACIDS RH

R	σ^- (100% MeOH) [a]	σ^- (67% MeOH) [a]	Mean σ^-	pK_a
2-PyCH$_2$	0.87	0.84	0.85	29.5
3-PyCH$_2$	0.54	0.53	0.53	33.5
4-PyCH$_2$	1.08	1.07	1.07	26
2-QnCH$_2$	1.16	1.12	1.14	25.5
3-QnCH$_2$	0.69	0.70	0.70	31.5
4-QnCH$_2$	1.23	1.18	1.20	24.5

[a] All values are related to the value of 1.24 for the p-NO$_2$ group. For 3-PyCH$_2$ and 3-QnCH$_2$ the σ^- constants are probably identical with the σ constants.

RIE values fall in the range 0.42—0.50 [3—5], and such values are consistent with the proposed mechanism in which R$^-$ separates in the rate-determining step, and the anion MeO$^-$ is fully or almost fully attached to silicon in the transition state, with complete or almost complete liberation of the methanol initially solvating the anion [2,5]. *RIE* values significantly larger than 0.50 were noted in three cases, however, viz. 0.57 for cleavage of 9-fluorenylSiMe$_3$ [5], 0.70 for 9-fluorenylSi-i-Pr$_3$, and 0.71 for p-O$_2$NC$_6$H$_4$CH$_2$SiPh$_3$ [14]. The *RIE* values for the least reactive PyCH$_2$SiMe$_3$ and QnCH$_2$SiMe$_3$ compounds, the 3-isomers, are below 0.50, while those for 4-isomers, 0.54 and 0.52, may not be significantly above this value, but the value for 2-QnCH$_2$SiMe$_3$, viz. 0.56, is definitely high, while that for 2-PyCH$_2$SiMe$_3$, viz. 0.65, is markedly so. It is probably significant that *RIE* values significantly above 0.50 observed up to now are associated with highly reactive compounds, although high reactivity does not usually imply high *RIE* values [3]. There is not yet sufficient information to justify a lengthy discussion of the implications of high *RIE* values, but we note that the simplest explanation would be that the methoxide ion is significantly less than fully attached to the silicon atom in the transition state of the rate-determining step; if this were the correct explanation it would imply that a 5-coordinate silicon intermediate of the type [MeOSiRMe$_3$]$^-$ is not formed before the rate-determining step, and thus that the mechanism must be of the B$_s$ rather than the B type [3]. It would then be plausible that this effect might show up only in the more reactive systems, since in a concerted formation of the MeO—Si and breaking of the Si—R bond, the degree of separation of the anion R$^-$, and thus the degree of attachment of the MeO$^-$, should be smaller the better the leaving group ability of R (i.e. the greater the stability of the anion R$^-$). But if high *RIE* values are indeed associated with high reactivities in this way, we cannot at present suggest any reason why they appear in only some of the reactive systems, and why with the PyCH$_2$SiMe$_3$ and QnCH$_2$SiMe$_3$ compounds the very high *RIE* values are associated with the 2-isomers, which are less reactive than the corresponding 4-isomers.*

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* Because in the few cases for which data are available *RIE* values seem to increase on increasing the size of the R′ groups in RSiR′$_3$ compounds, we suspect that higher *RIE* values may in some cases at least be associated with increased steric hindrance.

We could look to special secondary solvent isotope effects for explanation of the high *RIE* values for the $PyCH_2SiMe_3$ and $QnCH_2SiMe_3$ compounds. Thus hydrogen-bonding to the nitrogen atom of these compounds must have a substantial influence on electronic effects in these systems, and more effective hydrogen-bonding in MeOH than in MeOD could lead to greater stabilization of the separating carbanion, but even if this effect were large enough to influence the *RIE* values it would be difficult to explain why it should be especially marked for the 2-derivatives.

Turning to the *PIE* values, we first note that the value for 2-$QnCH_2SiMe_3$ is only approximate, for reasons which are explained in the Experimental section. There is little doubt, however, that the *PIE* for this compound is higher than that for the 4-Py- and 4-Qn-CH_2SiMe_3 compounds, and it is probably comparable to that for 2-$PyCH_2SiMe_3$. The pattern of variation in *PIE* values with k_s values for $XC_6H_4CH_2SiMe_3$ and 9-X-fluoren-9-ylSiMe$_3$ compounds [3,5] had led us to expect that the *PIE* values for the range of $PyCH_2SiMe_3$ and $QnCH_2$-$SiMe_3$ compounds, might, in view of the relevant k_s values, span the range 1—10, (cf. Table 4), but this is not the case. As expected, the least reactive compounds, 3-$PyCH_2SiMe_3$ and 3-$QnCH_2SiMe_3$, give *PIE* values close to unity, while their more reactive isomers give substantially higher values, however, the only really high values, 5.8 and ca. 5 are given by the 2-isomers, each of which is less reactive than its 4-isomer. Except for 2-$PyCH_2SiMe_3$ the *PIE* values are markedly smaller than those for $XC_6H_4CH_2SiMe_3$ compounds of comparable reactivities. It is clear that the parallel between *PIE* values and reactivity is far from exact, and that any relationship between *PIE* and k_s values cannot be carried over quantitatively from one type of $RSiMe_3$ compound to another.

Since the *RIE* and *PIE* values for 2-Py- and 2-Qn-CH_2SiMe_3 both seem abnormally high compared with those of the other isomers, it is conceivable that a different mechanism, associated with the proximity of the N atom and the $SiMe_3$ group, operates in the case of the 2-derivatives. The fact that the points for the 2-$PyCH_2$ and 2-$QnCH_2$ systems fall exactly on the excellent linear plot of log k_s for the cleavages against log k_s for the cleavages against log k for deuteration in EtOD/EtOK argues against this possibility.

TABLE 4

VALUES OF THE SPECIFIC RATE CONSTANTS k_s AND PRODUCT ISOTOPE EFFECTS, *PIE*, FOR CLEAVAGE OF $RSiMe_3$ COMPOUNDS BY SODIUM METHOXIDE IN 100% METHANOL AT 25°C

R	$10^5\ k_s$ ($l\ mol^{-1}\ s^{-1}$)	*PIE*	R	$10^5\ k_s$ ($l\ mol^{-1}\ s^{-1}$)	*PIE*
m-$NCC_6H_4CH_2$	1.7	1.2	3-$PyCH_2$	1.2	1.1
m-$O_2NC_6H_4CH_2$	3.2	1.3	3-$QnCH_2$	8.1	1.1
p-$NCC_6H_4CH_2$	315	2.0	2-$PyCH_2$	83	5.6
p-$PhO_2SC_6H_4CH_2$	470	2.9	4-$PyCH_2$	1420	2.6
p-$PhCOC_6H_4CH_2$	640	7	2-$QnCH_2$	4040	ca. 5
o-$O_2NC_6H_4CH_2$	2 340	10	4-$QnCH_2$	9500	3.2
p-$O_2NC_6H_4CH_2$	11 500	10			

Experimental

Preparation of PyCH$_2$SiMe$_3$ and QnCH$_2$SiMe$_3$ compounds

These compounds were prepared as described previously [1], and purified by distillation through a Perkin—Elmer Model 151 spinning band fractionating column The 3-QnCH$_2$SiMe$_3$ was further purified by column chromatography (silica gel, 10% ether/pentane) [1]

Rate measurements

Rates were measured spectrophotometrically [2,3—6], usually with a Hitachi—Perkin—Elmer Model 323 UV Spectrometer The wave length used in each case is shown in Table 1

The 67% MeOH was prepared by mixing 2 vol of MeOH with 1 vol of aqueous alkali at ca 22°C

PIE measurements

Product RH/RD ratios were determined in two ways The first involved the use of the Applied Chromatography Systems Organic Analyzer MPD 850 linked to a Pye Model 64 Gas Chromatograph [3—6] a 5 m × 6 mm column of 5% Carbowax 20M (for picolines) or 5% OV 17 (for quinolines) on Chromosorb G at 180°C was used; the RH/RD ratios obtained from cleavage in 100% MeOH containing MeONa were satisfactorily close to the theoretical values (2-PyCH$_2$SiMe$_3$, 6 09 (calcd 6 0), 3-PyCH$_2$SiMe$_3$, 5 98, 4-PyCH$_2$SiMe$_3$, 6 01, 3-QnCH$_2$SiMe$_3$, 7 91 (calc. 8 0), 4-QnCH$_2$SiMe$_3$, 7 96), except for 2-QnCH$_2$SiMe$_3$ For this compound a ratio of 8 4 was obtained, compared with the calculated 8 0, and thus the apparent RH/RD ratio of 2 0 obtained on cleavage in 1/4 MeOH/MeOD (corresponding to a *PIE* value of 8 0) is likely to be substantially too high However, it seems unlikely that the true *PIE* is quite as low as the 4 4 indicated by the NMR method, and so we have used an estimated *PIE* value of 5 for this compound

The second method of determining *PIE* values involved cleavages in CD$_3$OH/CD$_3$OD mixtures and integration on the Varian XL100 spectrometer of the ^{1}H NMR resonance from the methyl protons of the ArCH$_3$/ArCH$_2$D product solutions, with use of the integrated signals from the aromatic protons for calibration Several determinations were made with each compound and the mean value is reported in Table 2 It will be seen from Table 2 that, except for the special case of 2-QnCH$_2$SiMe$_3$, the RH/RD ratios obtained in this way agreed within 20% with those from the first method

These analytical methods were also used to confirm that no deuteriation of the parent PyCH$_3$ and QnCH$_3$ compounds occurred in MeOD under the cleavage conditions used for determinations of *PIE* values

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