Anchimeric Assistance in Methanolysis of Some Organosilicon Halides, Perchlorates, and Trifluoromethanesulphates

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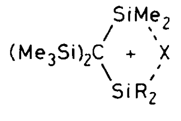
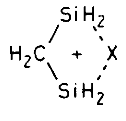
A range of X groups (X = OMe, $OClO_3$, OSO_2CF_3, F, Cl, or I) have been shown to provide anchimeric assistance to the leaving of the Y groups (Y = $OClO_3$, OSO_2CF_3, Cl, or I) in methanolysis of $(Me_3Si)_2C(SiMe_2X)(SiMe_2Y)$ species; the effect is especially large for X = OMe.

The reactions of the iodides $(Me_3Si)_3CSiR_2I$ with silver(I) or mercury(II) salts are thought to proceed *via* bridged ions of type (**1**), (X = Me),[1] and it has been assumed that methanolysis of the compounds $(Me_3Si)_3CSiMe_2Y$ (Y = $OClO_3$ or I) involves rate-determining formation of such an ion (R = X = Me), and thus that the participating Me group provides anchimeric assistance to the leaving of Y.[2–4] If this is the case then much larger effects could be expected from X groups which should bridge more effectively, and we have now obtained evidence for considerable assistance by OZ (Z = Me, SO_2CF_3, or ClO_3) groups and by halogen atoms.†

First-order rate constants, *k*, for solvolysis of $(Me_3Si)_2C(SiMe_2X)(SiMe_2Y)$ compounds in anhydrous methanol are shown in Table 1. The effects of low concentrations of NaOMe were examined in some representative cases and found to be fairly small, and so all the reactions are assumed to proceed *via* rate-determining ionizations (*i.e.* by S_N1 processes). [For example, the ratios of the value of *k* in 0.1 M MeONa–MeOH to that in MeOH alone were: (X, Y =) Me, $OClO_3$, 1.2;[2] Me, I, 1.8;[3] Me, OSO_2CF_3, 1.6; Cl, OSO_2CF_3, 1.3; and I, I, 1.1.]



(**1**)



(**2**)

Table 1. First-order rate constants, *k*, for solvolysis of $(Me_3Si)_2C(SiMe_2X)(SiMe_2Y)$ in MeOH[a]

X	Y	Temp./°C	$10^5k/s^{-1}$
Me	I	50	0.064[b]
Me	Cl	65	<0.006[c]
Me	OSO_2CF_3	35	23
Me	$OClO_3$	35	74[d]
Cl	Cl	65	0.25
F	Cl	60	0.36
OMe	Cl	35	670
Cl	OSO_2CF_3	35	78
Cl	$OClO_3$	35	410
I	I	60	3.1
OSO_2CF_3	OSO_2CF_3	35	>2600[e]
$OClO_3$	$OClO_3$	35	>2600[e]

[a] The rates were measured by monitoring the disappearance of the ^1H n.m.r. peak for the methyl protons of the $SiMe_2Y$ groups. [b] Ref. 3. [c] No detectable ($<5\%$) reaction occurred in 240 h. [d] Ref. 2. [e] Reaction was complete within 2 min.

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† Anchimeric assistance by the OCOMe group was observed previously, but was assumed to be specific to this type of group and to involve bridging by the O–C–O system in a six-membered ring (ref. 5). We now think it likely that this assistance involves simple bridging by oxygen in a four-membered ring system similar to that for the OMe group.

Some large neighbouring group effects are evident. The most striking observation is that whereas no detectable (*i.e.* $<5\%$) reaction of $(Me_3Si)_3CSiMe_2Cl$ occurs in 240 h at 65 °C, methanolysis of $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$ has a half life of only 1.7 min at 35 °C. (After allowance for the temperature difference there is a reactivity ratio of at least 10^6.) Because of the large effect of the OMe group, in the examples in Table 1, except for $X = Me$ or F, the product is $(Me_3Si)_2C(SiMe_2OMe)_2$. [The compound with $X = F$ and $Y = Cl$ gives mainly this product, indicating that even an Si–F bond is rendered active by the γ-OMe group; the minor products were $(Me_2Si)_2C(SiMe_2OMe)(SiMe_2F)$ and, surprisingly, $(Me_3Si)_2C(SiMe_2F)_2$.]

Comparisons of the rate constants for $(Me_3Si)_2C(SiMe_2X)(SiMe_2Y)$ species with $X = Y$ with those for the corresponding $(Me_3Si)_3CSiMe_2Y$ compounds reveal reactivity ratios of ($Y =$) I, 48; Cl, >40; OSO_2CF_3, >110; $OClO_3$, >35. (Where minimum values are given the actual ratios may be much larger.) Comparison of the data for $(Me_3Si)_2C(SiMe_2F)(SiMe_2Cl)$ and $(Me_3Si)_2C(SiMe_2Cl)_2$, indicates that F activates twice as effectively as Cl.

For $(Me_3Si)_2C(SiMe_2Cl)(SiMe_2Y)$ with $Y = Cl$, OSO_2CF_3, or $OClO_3$, if Y is assumed to be the leaving group [which appears to be justified for $Y = OSO_2CF_3$ by the observation that $(Me_3Si)_2C(SiMe_2Cl)(SiMe_2ONO_2)$ was formed in 33% yield in methanolysis in the presence of 0.5 M $LiNO_3$, presumably in trapping by the nitrate ion of the intermediate ion (**1**) with $X = Cl$], then the reactivity increase on changing X from Me to Cl is for $Y = Cl$, >40; OSO_2CF_3, 3.4; and $OClO_3$, 5.5. The fact that the assistance by γ-Cl is markedly larger for leaving Cl^- than for leaving $OSO_2CF_3^-$ or $OClO_3^-$ can be understood in terms of a shift of the transition state towards the intermediate bridged ion (and thus a larger charge development) for a poorer leaving group. (Similar variations are well known in the case of anchimeric assistance by 1,2-bridging in reactions of organic compounds.)

The sequence of ability to provide anchimeric assistance appears to be: OMe $>$ OSO_2CF_3, $OClO_3$ $>$ F $>$Cl, I $>$ Me. It is thus of interest that MNDO calculations by Dr. A. J. Kos[6] give values for the decrease in energy on going from the model acyclic ion $H_2C(SiH_2X)(SiH_2^+)$ to the corresponding bridged ion (**2**) which are consistent with this sequence, *viz.* ($X =$) OH, 63.0; F, 56.6; Cl, 33.2; Me, -0.8 kcal/mol (1 kcal = 4.18 kJ).

In view of the very large effect of an OMe group which is in a position to provide anchimeric assistance, it is noteworthy that the presence of this group in place of an Me group on the silicon atom which bears the leaving group leads to a lower rate of reaction, the value of *k* for $(Me_3Si)_3CSiMe(OMe)OSO_2CF_3$ being $5.0 \times 10^{-5}\ s^{-1}$ at 60 °C. Interestingly there is no rearrangement in this case, the product being $(Me_3Si)_3CSiMe(OMe)_2$.

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