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# A UNIMOLECULAR SOLVOLYSIS OF AN ORGANOSILICON PERCHLORATE

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## SUMMARY

Kinetic studies have been carried out on the reaction of the perchlorate $(Me_3Si)_3CSiMe_2OClO_3$ with anhydrous methanol. The effects of added NaOMe, LiCl, $LiNO_3$, and $NaClO_4$ are consistent with rate-determining ionization of the perchlorate.

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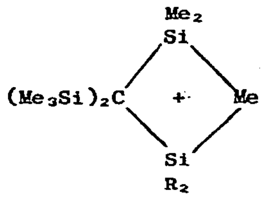
Publications from this laboratory have shown that the very large steric hindrance by the tris(trimethylsilyl)methyl ("trisyl") group, $(Me_3Si)_3C$ (sometimes denoted below by Tsi) inhibits nucleophilic attack at functional silicon centres in compounds of the type $(Me_3Si)_3CSiR_2X$, and so allows observations of unusual types of reactions [1,2]. For example, the iodides $TsiSiR_2I$ undergo reactions with electrophilic species, such as silver or mercury(II) salts in methanol, which appear to proceed through bridged cationic species of the type (I), which can be attacked by nucleophiles to give rearranged products of the form $(Me_3Si)_2C(SiMe_2Y)$-$(SiR_2Me)$ [2]. The iodide $TsiSiEt_2I$ also reacts with $CF_3CO_2H$ to give a mixture of the rearranged and unrearranged trifluoroacetates, $(Me_3Si)_2C(SiMe_2O_2CCF_3)(SiEt_2Me)$ and $(Me_3Si)_3CSiEt_2O_2CCF_3$; the reaction is not accelerated by added $NaO_2CCF_3$, and so it appears to be a unimolecular solvolysis (assisted, of course, by electrophilic attack by the solvent on iodine) [2]. We have now obtained evidence for a unimolecular solvolysis of a trisylsilicon compound under conditions of the type commonly used to observe $S_N1$ reactions of organic halides and related species.



(I)

The compound $TsiSiMe_2OClO_3$ (which was made by treatment of the corresponding iodide with $AgClO_4$ in $CH_2Cl_2$ [3]) was found to react at a

TABLE 1

First order rate constants for solvolysis of $TsiSiMe_2OClO_3$ in MeOH

| At 30°C [a] | | At 35°C [b] | |
|---|---|---|---|
| Salt (Concn, M) | $10^5k(s^{-1})$ | Salt (Concn, M) | $10^5k(s^{-1})$ |
| None | 51 | None | 74 |
| LiCl (0.10) | 61 | NaOMe (0.10) | 90 |
| (0.20) | 64 | (0.45) | 95 |
| (0.31) | 67 | (1.0) | 102 |
| (1.0) | 75 | $LiNO_3$ (0.24)[c] | 71 |
| $NaClO_4$ (0.0085) | 50 | (0.47)[d] | 100 |
| (0.017) | 42 | (0.91)[e] | 117 |
| (0.050) | 50 | | |
| (0.10) | 53 | | |
| (0.68) | 58 | | |

[a] Reaction monitored by UV spectroscopy

[b] Reaction monitored by NMR spectroscopy; 1.5 vol.% $CCl_4$ present

[c] The nitrate constituted 35% of products

[d] The nitrate constituted 50% of products

[e] The nitrate constituted 83% of the products

convenient rate with anhydrous methanol to give the methoxide $TsiSiMe_2OMe$ in a first-order process. As will be seen from Table 1, the rate constant was higher by 22% in the presence of 0.1M NaOMe, but further increase in the base concentration had only a small effect, comparable with that of added LiCl. The latter salt did not affect the product, whereas addition of $LiNO_3$ not only raised the rate somewhat but also produced some nitrate products $TsiSiMe_2ONO_2$, the amount increasing with increasing salt concentration.

We suggest that there is a rate-determining ionization of the $TsiSiMe_2OClO_3$, presumably to give a bridged-ion of the type (I). This ion can be trapped by $NO_3^-$, but not, it seems, by $Cl^-$, though LiCl does have the expected rate-enhancing salt effect. (The formation of nitrate product cannot be attributed to direct attack of $NO_3^-$ on the $TsiSiMe_2OClO_3$, since even with 0.91M $LiNO_3$ only about 40% of the rate constant is attributable to the added salt, yet 83% of the product is nitrate.) There is probably normally some recombination of $ClO_4^-$ ion with (I) to re-form the starting material, and so addition of small amounts of $NaClO_4$ reduces the rate of solvolysis, but at sufficiently high concentrations the usual salt effect balances out this common-ion effect. Addition of a little NaOMe probably leads to effective trapping of the ion (I) by $OMe^-$ and so prevents the return of $ClO_4^-$ and significantly raises the rate (by 22%), but addition of further NaOMe causes only a small further increase in rate, consistent with a salt-effect. Overall the results are very similar to those which are commonly associated with $S_N1$ solvolyses of alkyl halides.

## ACKNOWLEDGEMENTS

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3 For leading references to the preparations and reactions of organosilicon perchlorate see T.J. Barton and C.R. Tully, J. Organometal. Chem., 172 (1979) 11.