

GAS PHASE REACTIONS OF SODIUM V. RATES OF REACTION OF SOME (CHLOROALKYL)SILANES

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SUMMARY

The rates of reaction with sodium atoms of some (chloroalkyl)silanes and analogous carbon compounds have been measured. The variations in velocity constants are discussed in terms of bond dissociation energies and negative group effects. It is suggested that the (trimethylsilyl)methyl carbanion is relatively more stable than the corresponding neopentyl carbanion.

INTRODUCTION

In previous papers in this series^{1,2} we have reported measurements of rates of reaction of sodium atoms with Group IV halides $\text{Me}_n\text{MCl}_{4-n}$ ($\text{M}=\text{C}, \text{Si}, n=0-3$; $\text{M}=\text{Ge}, \text{Sn}, n=2,3$). It is of interest to study the analogous reactions of halides containing silyl substituents of the type $\text{Me}_3\text{Si}(\text{CH}_2)_n\text{Cl}$ so that the effect of substitution by the Me_3Si group can be compared with that of the Me_3C group. Evidence of any marked substituent effects would afford an interesting parallel with other studies of substituent effects based upon solution reactions³⁻⁶ and spectroscopic studies⁷. Comparison is also possible with the H atom transfer reaction (1) ($\text{M}=\text{C}, \text{Si}$), for which experimental evidence is available for the cases where $\text{R}=\text{CH}_3$ ⁸⁻¹⁰, CD_3 ⁸, CF_3 ^{8,10}, Cl^{11} , C_2H_5 ⁸ and T^{12} .



EXPERIMENTAL

Materials

Samples of (chloromethyl)trimethylsilane and chlorobis(trimethylsilyl)methane which had not been rigidly purified were kindly donated by Dr. D. R. M. Walton and Professor C. Eaborn. The former of these samples contained one minor less volatile impurity which was removed by trap-to-trap distillation in vacuo whereas the latter which contained seven minor impurities was purified by preparative gas

chromatography. (3-Chloropropyl)trimethylsilane was a commercial product (Pierce Chemical Co.) and was found to be gas chromatographically pure. 1-Chloro-2,2-dimethylpropane (neopentyl chloride) was prepared by Lee and Nolan's method¹³ and purified by distillation followed by preparative gas chromatography. Care was essential to remove all carbon tetrachloride from the product because of the rapidity of reaction of this possible impurity with gaseous sodium. 1-Chloro-3,3-dimethylbutane was a commercial product (Emanuel) which was purified by trap-to-trap distillation *in vacuo* until pure by GLC.

All materials were intensively degassed and stored in the dark at liquid nitrogen temperature when not in use for kinetic purposes. Apparatus and purification of nitrogen followed standard procedures¹.

RESULTS AND DISCUSSION

The procedure for the measurement of the velocity constant is as described in Part I¹ and the values are calculated from the simple diffusion flame equation. The values of the velocity constants given in Table 1 are based upon between five and nine separate runs carried out on different days, a run consisting of a series of velocity constant determinations extending over 2 or more hours. The values are corrected to 520°K as by Warhurst *et al.*¹⁴.

It is interesting to compare the results for two series of carbon compounds and Table 2 illustrates this point. The results of Polanyi¹⁵ were obtained before a critical examination of the sodium flame technique was carried out by Heller¹⁶ and consequently should be regarded primarily as indicating relative rates. The main point to notice is that the trends in both series of compounds are identical, *i.e.* a decrease in rate is observed on going from a tertiary to a primary carbon atom and lengthening of the carbon chain produces an increase in rate. It should be noted that (3-chloro-

TABLE 1
BIMOLECULAR VELOCITY CONSTANTS

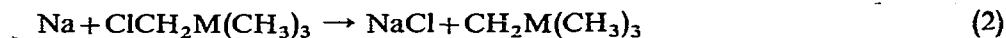
Compound	$10^{-11} k$ (ml·mole ⁻¹ ·sec ⁻¹)	Compound	$10^{-11} k$ (ml·mole ⁻¹ ·sec ⁻¹)
Me ₃ CCH ₂ Cl	1.06	Me ₃ SiCH ₂ Cl	16.2
Me ₃ CCH ₂ CH ₂ Cl	1.39	(Me ₃ Si) ₂ CHCl	230
		Me ₃ SiCH ₂ CH ₂ CH ₂ Cl	3.10

TABLE 2
BIMOLECULAR VELOCITY CONSTANTS

Compound	$10^{-11} k$ (ml·mole ⁻¹ ·sec ⁻¹)	Ref.	Compound	$10^{-11} k$ (ml·mole ⁻¹ ·sec ⁻¹)	Ref.
Me ₃ CCl	2.76	1	Me ₃ CCl	3.33	15
Me ₃ CCH ₂ Cl	1.06	This work	Me ₂ CHCH ₂ Cl	1.42	15
Me ₃ CCH ₂ - CH ₂ Cl	1.39	This work	Me ₂ CHCH ₂ CH ₂ Cl	2.5	15

propyl)trimethylsilane is comparable to these carbon compounds, *i.e.* separation of the silicon and chlorine atoms by three methylene groups produces no unexpectedly marked effect. This is in sharp contrast to the behaviour when one or more silicon atoms are introduced as an α substituent.

It is instructive to compare the changes in the velocity constants for the related reactions (1) and (2)



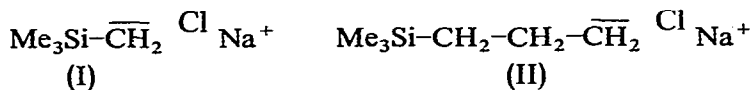
when M is C and Si respectively. It is apparent that the ratio for $(k_2)_{\text{Si}}/(k_2)_{\text{C}}$ of 15 is much greater than for $(k_1)_{\text{Si}}/(k_1)_{\text{C}}$ which varies between 1 and 4 according to the character of the attacking radical R. The simplest explanation for an increase in rate for reactions of this type is a decrease in the bond dissociation energy of the bond broken in the molecule subject to attack. The difference in the bond dissociation energies $D[(\text{CH}_3)_3\text{CCH}_2\text{-H}] - D[(\text{CH}_3)_3\text{SiCH}_2\text{-H}]$ has been estimated⁸ on this basis as $2 \text{ kcal}\cdot\text{mole}^{-1}$. Using the relationship^{1,2}

$$\Delta E = \alpha \cdot (\Delta D)$$

with $\alpha = 0.3$ would imply that $D[(\text{CH}_3)_3\text{CCH}_2\text{-Cl}] - D[(\text{CH}_3)_3\text{SiCH}_2\text{-Cl}] = 9 \text{ kcal}\cdot\text{mole}^{-1}$. This is contrary to expectation. All surveys of bond dissociation energies (*e.g.* ref. 17) indicate that changes in $D(\text{C-Cl})$ on substitution at the carbon atom are always much less than the corresponding changes in $D(\text{C-H})$. We therefore do not ascribe this enhancement of reactivity to a bond dissociation energy effect in (chloromethyl)trimethylsilane. It follows that any attempt to explain our results in terms of an enhanced stability of the (trimethylsilyl)methyl radical^{6,18} suffers from the same drawback because this effect will contribute at least as significantly to reaction (1) as to reaction (2).

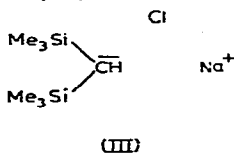
We therefore suggest that some extra effect is present in reaction (2) which results in an enhancement in rate for the silicon compound. Release of electrons by Me_3SiCH_2 groups to an attached carbon atom has been revealed by both spectroscopic⁷ and kinetic⁴ studies. If the same release occurs to chlorine then this would be stronger in $\text{Me}_3\text{SiCH}_2\text{Cl}$ than in $\text{Me}_3\text{CCH}_2\text{Cl}$, *i.e.* the chlorine atom would acquire a larger negative charge in the silicon compound than in the carbon compound. Smith and Eyring¹⁹ imply that this effect would reduce the rate of the silicon compound in reaction (2) compared with the carbon analogue, *i.e.* they correlate increasing rate with decreasing negative charge on the halogen.

The negative group effect has been invoked to account for the enhanced rate of a number of sodium flame reactions²⁰. If this is to apply in this case it is required that structure (I) can contribute to the transition state of reaction (2) for (chloromethyl)trimethylsilane but that there is no marked contribution of structure (II) for (3-chloro-



propyl)trimethylsilane. A further contribution to structure (I) may involve $(p \rightarrow d)\pi$ delocalisation of the negative charge into the d -orbitals of the Si atom, *i.e.* $\text{Me}_3\overline{\text{Si}}=\text{CH}_2$ which would not be possible with β or γ substituted compounds.

These tentative considerations are supported by the results for the chlorobis-(trimethylsilyl)methane. The rate is enhanced relative to the corresponding primary compound by a factor of 14. For carbon compounds the corresponding factor¹⁵ is approximately 2. A similar explanation to that advanced above is evident invoking structure (III) which makes a correspondingly greater contribution than (I).



It has recently been shown²¹ that the (trimethylsilyl)methyl carbanion can act as a ligand in the formation of a new class of σ -alkyl-transition metal complexes of high thermal and chemical stability. We consider that our results add some further support to this in that they imply the trimethylsilyl radical to be only slightly more stable than the neopentyl radical whereas the corresponding anion is markedly more stable than the neopentyl anion. It would obviously be of interest to have direct confirmation by measurement of the appropriate electron affinities. Such evidence as is available²² for the silyl radical indicates that the electron affinity ($41.5 \text{ kcal} \cdot \text{mole}^{-1}$) is greater than for the analogous methyl radical.

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