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THE STRUCTURE AND STABILITY OF SILYL-SUBSTITUTED CARBONIUM IONS

C. EABORN, F. FEICHTMAYR, M. HORN and J.N. MURRELL*

School of Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ (Great Britain)

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Summary

Ab-initio SCFMO calculations on silyl-substituted alkanes, alkyl-radicals and carbonium ions show that the carbonium ion is destabilized by an α-silyl group but stabilized by a β-silyl group in comparison with the carbon analogues. In contrast, replacement of α or β-methyl by silyl has little effect on the stability of the radicals or alkanes. These results are consistent with observations on the rates of S_N1 solvolysis of trimethylsilylalkyl halides, and indicate that the relative rates are largely determined by the relative stabilities of the carbonium ions.

A non-classical bridged structure for $SiH_3CH_2CH_2^+$ has been found to have an energy approximately 0.5 eV (50 kJ/mole) lower than that of a classical open structure.

Introduction

There has in recent years been considerable interest in the effect of silylalkyl substituents on the spectroscopic properties and reactivities of unsaturated hydrocarbons. In a recent paper [1] we have shown that ab-initio self-consistent-field molecular-orbital calculations provide a basis for interpreting the effects of such substituents on the photoelectron spectrum of ethylene. In this paper we present similar calculations on the energies and structures of the carbonium ions RCH_2^+ where R is SiH_3 and SiH_3CH_2, and compare the results with those for their carbon analogues.

The calculations we present are of particular relevance to the rates of solvolysis of the silyl-substituted alkyl halides, RCH_2X. It is known that the 2-(triorganosilyl) alkylhalides undergo S_N1 solvolysis much more readily than the analogous carbon compound whereas the 1-(triorganosilyl)alkyl halides are

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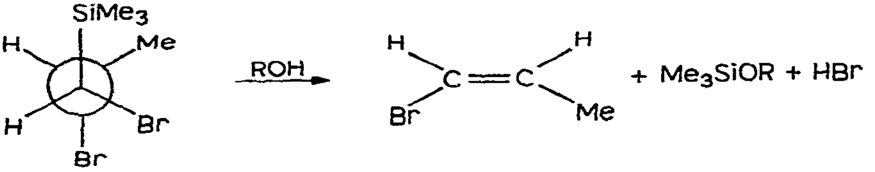
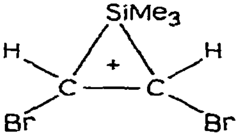
* For communication.

less reactive than their carbon analogues [2—4]. Jarvie, Holt and Thompson [5] showed that the solvolytic elimination reaction represented by eqn. 1 was



(1)

a highly stereospecific *trans* process and attributed this to the formation of the silicon bridged ion (I) in the rate determining step. However, to explain the fact that the proportion of *cis*-elimination increased with increasing ionizing power of the medium, they suggested that this ion was in equilibrium with the open classical carbonium ion.



(I)

Cook, Eaborn and Walton [2] showed that in the incomplete solvolysis of $Me_3SiCH_2CD_2Br$ there was reversible ionization of the C—Br bond and migration of the $SiMe_3$ group between the carbon atoms. They tentatively favoured the formation of the bridged ion in the ionization step, since the rate of solvolysis appeared to be too high to be accounted for only in terms of the effect of the $SiMe_3$ group on the stability of the classical ion.

Pitt [6] has carried out CNDO/2 calculations on the silyl substituted carbonium ions assuming classical structures, and found that migration of electrons to the formally vacant *p* orbital in RCH_2^+ was in the order $R = SiH_3CH_2 > CH_3CH_2 > CH_3 > SiH_3$, and that inclusion of silicon *d* orbitals in the calculation increased the jmigration for the SiH_3CH_2 substituent but decreased it for SiH_3. These results, which he attributed to a hyperconjugative mechanism, allow a qualitative understanding to the relative stabilities of the ions. However, he made no attempt to examine non-classical structures for the ions.

Calculations

The method of calculation was the same as that used in our earlier paper [1]. Self-consistent-field molecular orbitals were calculated using the ATMOL programme with a minimal basis of Slater orbitals supplemented with *d* orbitals for the silicon atom. The basis orbitals had the following exponents:

C(1*s*) = 5.70, C(2*s*) = C(2*p*) = 1.625
Si(1*s*) = 13.57, Si(2*s*) = 4.51, Si(3*s*) = 1.63
Si(2*p*) = 4.97, Si(3*p*) = 1.43, Si(3*d*) = 1.30
H(1*s*) = 1.20 (attached to carbon), = 1.26 (attached to silicon)

The 1*s* orbitals of carbon and silicon were expanded in six gaussian functions and the remaining orbitals in three gaussians.

Geometries for the open classical forms of all molecules, radicals, and ions were based upon tetrahedral silicon fragments [R(Si—H) = 1.48 Å, R(Si—C) = 1.865 Å], tetrahedral carbon fragments [R(C—C) = 1.54 Å, R(C—H) = 1.09 Å] and planar trigonal carbon fragments [R(C—H) = 1.07 Å, $R(Csp^2—Csp^3)$ = 1.49 Å]. Within the accuracy of the calculations we did not consider that the energy difference between staggered and eclipsed configurations (typically 0.1 eV) was significant. The exception was that the Si—C bond in the β-silylethyl radical and cation and the corresponding C—C bond in propyl radical and cation were contained in the plane perpendicular to that of the planar CH_2 group.

Table 1 shows the energies for the classical structures based upon the above dimensions without and with (asterisk) silicon d orbitals in the basis. It is seen that the energy required to form the carbonium ion by removal of H^- from the hydrocarbon is in the order R = $SiH_3 > C_2H_5 > CH_3 > SiH_3CH_2$. This order is not changed by the inclusion of d orbitals in the basis. The energy for the above process can be separated into the energy for the hydrogen atom extraction and that for ionization, and it is seen that the above order is largely determined by the second process. In other words, the influence of the substituent on the carbonium ion is the most important factor. This supports the conclusions of Pitt [6] already referred to, and indeed our order of occupation of the formally vacant $p(\pi)$ orbital on the carbonium centre is the same as found by him. There are only small differences in the calculated energies of hydrogen atom abstraction from the alkane and silane, and these may not be significant given the small basis chosen for the calculation and the fact the molecular geometries have not been optimized.

We find that the replacement of CH_3 by SiH_3 in the propyl radical increases the electron occupation of the $p(\pi)$ orbital by only 0.015 without Si d orbitals or 0.007 with d orbitals, but the same replacement in the cation increases the occupation by 0.06 (without d) or 0.07 (with d). This again confirms that it is the effect of SiH_3 on the cation that is the dominant stabilizing factor. In other words, there is evidence for a substantial increase in the hyperconjugation for the cation when CH_3 is replaced by SiH_3, and this is not the case for the radical.

The replacement of CH_3 by SiH_3 in the α series leads to an increase in the ionization potential of the radical, and this can be attributed to a destabilization of the cation by SiH_3 (relative to CH_3) rather than to any substantial effect of

TABLE 1

ENERGIES OF CLASSICAL STRUCTURES

The asterisk indicates values calculated with silidon d orbitals in the basis

R	$E(RCH_2)$ (a.u.)	$E(RCH_2)$ $-E(RCH_3)$ (eV)	$E(R\overset{+}{C}H_2)$ $-E(RCH_2)$ (eV)	$E(R\overset{+}{C}H_2)$ $-E(RCH_3)$ (eV)
H	— 40.0683	17.39	9.06	26.45
CH_3	— 78.9867	17.22	7.90	25.12
SiH_3	—329.2878	17.26	8.13	25.39
SiH_3*	—329.3769	17.10	8.71	25.81
CH_3CH_2	—117.8802	17.43	7.76	25.19
SiH_3CH_2	—367.8358	17.34	7.10	24.44
SiH_3CH_2*	—367.9254	17.32	7.30	24.62

SiH_3 on the radical. The donation of electrons to the $p(\pi)$ orbital on the carbonium centre from SiH_3 is less than from CH_3, so that a smaller hyperconjugative effect for SiH_3 can explain the results. However, there is a large redistribution of charge in the σ system of the radical on ionization (a migration from SiH_3 to CH_2), as was found in our calculations on the silylethylenes [1], hence the relative importance of the inductive effect of the SiH_3 and CH_3 group is impossible to measure.

The energies for hydrogen abstraction from methane and for ionization of the methyl radical are both larger than for the α-CH_3 or -SiH_3 derivative (Table 1 This result is not necessarily in conflict with the observation that replacement of even an α-H atom by a Me_3 Si group may lower the rate of S_N1 solvolysis of an alkyl halide [4a], since (a) there may be small differences between the energies of the halides themselves (e.g. there may be interaction between halogen and silicon orbitals), and (b), there may be a small difference between the effects of H_3Si and Me_3Si groups.

The effect of *d* orbitals on the relative energies of the β-silylethyl series is considerably smaller than their effect in the α-silylmethyl series. This can be attributed to the stabilization of electrons in $p(\pi)$ type orbitals of the molecular radical by delocalization to the Si *d* orbitals. This delocalization is absent for the cation as the $p(\pi)$ orbital is not occupied.

Radom and co-workers [7] have made extensive calculations on the propyl cation and optimum geometries have been deduced for both open classical and bridged non-classical structures. In view of the larger numbers of electrons in the molecules we are considering such calculations would be very expensive of computing time, and we have not attempted to obtain optimum geometries for the classical structures. For the bridged form of the β-silylethyl cation, however, we did carry out a three point minimization with respect to the C—Si bond length and obtained 2.30 Å, which is considerably longer than the normal C—Si single bond length of approximately 1.9 Å. The other dimensions assumed for this ion were chosen by comparison with the optimum geometry for the corresponding structure of the propyl cation found by Radom et al. [7], with some allowance for the greater height of the triangle. Our geometry is shown in Fig. 1.

The result of our calculations was to obtain an energy for the bridged structure lower than that for the open classical structure 0.6 eV without *d* orbitals and 0.4 eV

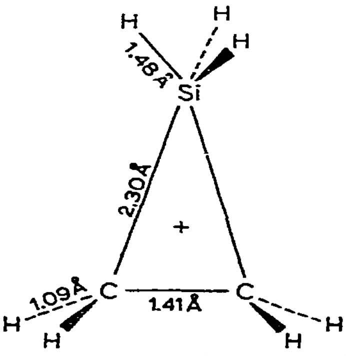


Fig. 1. Geometry of the bridged β-silylethyl cation with optimized R(C—Si). The following angles were adopted: HSiH = 109°; HCH = 117°; the CH_2 planes were displaced 15° from the basal plane.

with *d* orbitals. For comparison, Radom found the difference in energy between the optimum open and methyl bridged structures of the propyl cation to be 0.1 eV with the open form being the more stable. It is possible that our finding that the bridged form of the β-silylethyl cation is more stable than the open classical form would be reversed in calculations that allow for electron correlation but the present calculations support the view of Cook and co-workers [3] that the bridged structure is the dominant species in any equilibrium between bridged and open forms.

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