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Trimethylsilyl ester radical cations: an ESR study

Christopher J. Rhodes
Department of Chemistry, The University, Leicester. LE1 7RH (Great Britain)

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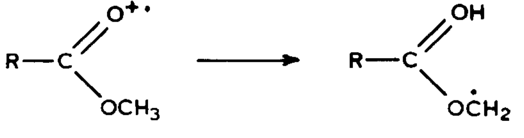
Abstract

The radical cations of the trimethylsilyl esters of acetic and trifluoroacetic acids have been observed by ESR spectroscopy following the γ-irradiation of dilute frozen solutions of the respective esters in $CFCl_3$ at 77 K. The results show that the unpaired electron is largely confined to the Me_3Si group in both cations. On annealing to the matrix softening point, intramolecular proton transfer occurs, to give the rearranged cations $RC(=\overset{+}{O}H)OSiMe_2\dot{C}H_2$.

Results and discussion

The technique of exposing dilute frozen solutions of substrates in Freons to ionising radiation, devised initially for optical studies [1], has been used to produce a wide variety of radical cations for ESR study [2]. Most of the cations so far observed have been organic species, with fewer examples of organometallic radical cations [2].

For the present work we chose to examine the radical cations of the trimethylsilyl esters of acetic and trifluoroacetic acids. Ester cations are of particular interest, since, after much controversy, it is now generally accepted that the primary cations are not observed at 77 K; the ESR spectra obtained are due to radicals resulting from intramolecular hydrogen atom transfer (eq. 1) [3–7]. In higher esters, subsequent fragmentation of the rearranged cations may also occur [4,6], a point which we return to later.



(1)

Our initial interest in these silyl esters derived from our expectation that their cations might be less prone to rearrangement. In as much as the primary cations

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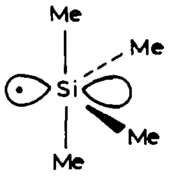
Table 1

Radical	Coupling constants (G) [a]
$CH_3CO_2SiMe_3^{+\cdot}$	14.1 (3H)
	3.0 (6H)
$CF_3CO_2SiMe_3^{+\cdot}$	16.4 (3H)
	3.7 (6H)
$Me_4Si^{+\cdot}$	13.8 (6H) [b]
	4.8 (6H)
$CH_3C(=\overset{+}{O}H)OSiMe_2\dot{C}H_2$	20.5 (2H)
$CF_3C(=\overset{+}{O}H)OSiMe_2\dot{C}H_2$	20.3 (2H)
$Me_3Si\dot{C}H_2$	20.9 (2H) [c]

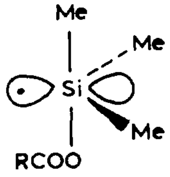
[a] 1 G = 10^{-4} mT. [b] Ref. 8. [c] Ref. 9.

were observed at 77 K, this proved to be the case, but we consider that they should be regarded as substituted alkylsilane cations rather than as carboxylic ester cations, since our ESR data (Table 1) show that the unpaired electron is localised on the Me_3Si unit rather than the RCOO group. It is therefore of interest to compare these results with those for a related cation, that from tetramethylsilane, which was observed recently by Walther and Williams [8].

This cation shows two pairs of equivalent methyl groups, indicating a structure which is distorted from the T_d geometry of the parent molecule. These workers assign a C_{2v} geometry to this cation, in which the unpaired electron occupies an essentially *p*-type orbital on silicon (I). The more strongly coupled pair of methyl groups are assigned to the apical positions, allowing favourable hyperconjugation with the SOMO.



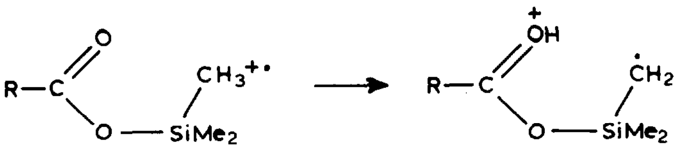
(I)



(II)

The present results show coupling to a single methyl group, and weaker coupling to two equivalent methyl groups. We therefore assign to these cations a geometry similar to that of the $Me_4Si^{+\cdot}$ cation, but with the acyloxy group occupying an apical position (II). The larger coupling to the apical methyl groups in the ester cations may be partly due to less effective electron spin delocalisation by the acyloxy groups than by the second methyl group in the $Me_4Si^{+\cdot}$ cation. However, the 16.4 G coupling in the $CF_3COOSiMe_3^{+\cdot}$ cation is appreciably greater than that in the $Me_4Si^{+\cdot}$ cation, and we feel that other factors must be important. We hope to probe the effect of substituents in silane cations more fully, by studying a wider range of compounds of the type Me_3SiX.

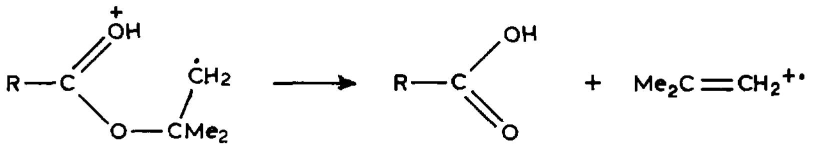
On annealing to the matrix softening point, an irreversible change occurred in the ESR spectrum, a ca. 20.5 G triplet being observed in both cases. This is similar to the 20.9 G α-proton coupling in the $Me_3SiCH_2^{\cdot}$ radical [9], and we attribute this change to the proton transfer reaction (eq. 2). It is of interest to compare this result



(2)

(III)

with the behaviour of t-butyl esters in which the isobutene cation, $Me_2C{=}CH_2^{+\cdot}$, is observed even at 4 K [4]. This implies a facile fragmentation of the initial rearranged cation (eq. 3). Therefore, the cation III appears to be very much more stable than



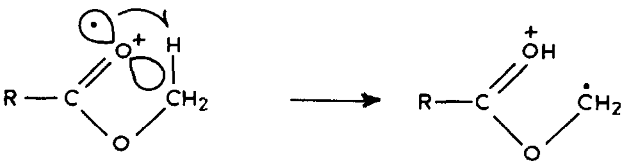
(3)

(IV)

IV, since prolonged annealing of the matrix failed to produce any further change other than the decay of the signal. Likely reasons for the greater stability of the rearranged silyl ester cation III over IV are the greater strength of the Si–O bond than the C–O bond, and the less effective stabilisation of the $Me_2Si{=}CH_2^{+\cdot}$ cation by hyperconjugation involving a silicon centre as compared with a carbon centre in $Me_2C{=}CH_2^{+\cdot}$. This latter may be one reason for the lack of observation of silicenium ions under conditions in which the corresponding carbocations are formed [10].

Mechanism of rearrangement

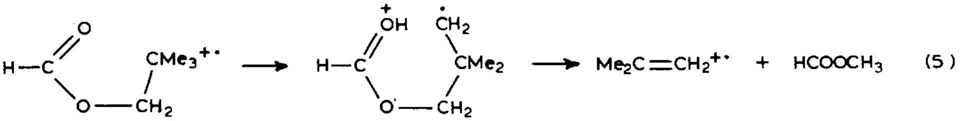
In the case of methyl and ethyl esters of carboxylic acids in $CFCl_3$ it appears that the ionisation takes place from the ester moiety rather than from the alkyl group; this can be rationalised from a consideration of the ionisation potentials (IP's) of methane and ethane (13.0 and 11.65 eV) compared with that of acetic acid (10.7 eV) [11]. In which case, the rearrangement most likely proceeds by the transfer of a hydrogen atom to the carbonyl oxygen atom of the ester group. This is readily seen if the electron loss is from the (*nb*) orbital, as in V (eq. 4).



(4)

(V)

In the case of the neopentyl formate radical cation [6], the ESR spectrum shows that the electron is lost from the neopentyl group. Again, this can be explained by the relative IPs of neopentane (10.3 eV) and formic acid (11.3 eV) [11]; although these values will be modified in the ester, it is clear that electron loss will take place more easily from the alkyl moiety. On annealing, the $HCOOCH_2CMe_3^{+\cdot}$ cation undergoes rearrangement to form the $HC(=\overset{+}{O}H)OCH_2CMe_2\dot{C}H_2$ radical, which, on further heating, fragments (eq. 5), giving the $Me_2C{=}CH_2^{+\cdot}$ cation [6].



(5)

We have demonstrated by our present results that on ionisation of the trimethylsilyl esters the electron loss takes place from the Me_3Si group; which might be expected, since the IP of Me_3SiH is only 9.8 eV [11]. As with the $HCOOCH_2CMe_3^{+\cdot}$ cation, it was necessary to anneal the sample in order to promote the rearrangement (eq. 2), which we feel is an intramolecular acid–base reaction involving proton transfer to the carbonyl oxygen atom, as opposed to hydrogen atom transfer. Since heating of the sample is required in these cases, it would appear that the proton transfer reaction (eq. 2) is less facile than is the intramolecular H-atom abstraction process (eq. 4).

On the basis of IPs, it is more difficult to decide whether the electron loss should be from the alkyl or ester groups in t-butyl acetate, since the IP of isobutane is 10.8 eV, and is very close to that of acetic acid (10.7 eV) [11]. However, since only the $Me_2C{=}CH_2^{+\cdot}$ cation is observed, even at 4 K [4], then the initial step must be loss of an electron from the ester group followed by H-atom transfer; rather than loss from the t-butyl group followed by the apparently more difficult proton transfer reaction.

Experimental

The silyl esters, $CF_3COOSiMe_3$ and $CH_3COOSiMe_3$, were purchased from Aldrich and were used as supplied. Dilute solutions, ca. 0.001 mole fraction, in $CFCl_3$ were prepared, and were reduced to polycrystalline powders by pipetting into liquid nitrogen. The powders were then irradiated to a dose of ca. 0.7 Mrad using a ^{60}Co source. The spectra were recorded with an E109 ESR spectrometer at 77 K, and the samples were annealed, when required, by decanting off the liquid nitrogen from the Dewar flask containing the sample and refreezing when significant spectral changes had occurred.

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