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Appearance potentials of trialkylsilyl ions

Recent attempts to evaluate bond dissociation energies in trimethylsilyl compounds have relied on appearance potential measurements to establish dissociation energy differences, and on a value for D(Me_3Si–$SiMe_3$), obtained either by calculation[1] or from gas kinetic experiments[2,3], to put the series on an absolute basis. In this situation, the appearance potential of the trimethylsilyl ion from hexamethyldisilane is particularly important, but two conflicting values of 10.7 eV and 10.0 eV have been reported[1,2]. We have recently[3] confirmed that the appearance potential of m/e 73 from hexamethyldisilane is 10.0 eV, but the ion observed might be the doubly-charged molecular ion, $Me_3SiSiMe_3^{++}$, and we do not think that the shape of the ionization efficiency curve precludes this possibility.

We have therefore attempted to eliminate this possible ambiguity by measuring the appearance potentials of m/e 73 and m/e 87 from ethylpentamethyldisilane, $Me_3SiSiMe_2Et$. This compound would have the same silicon–silicon bond dissociation energy as hexamethyldisilane[3], but m/e 73 and 87 could only be the trimethylsilyl and ethyldimethylsilyl ions respectively.

We used the MS9 mass spectrometer, with argon and benzene as standards, and analyzed the ionization efficiency curves by two methods[4,5]. We obtained 10.1 ± 0.1 eV for the appearance potential of m/e 73, and 9.7 ± 0.1 eV for m/e 87; these results indicate that Haszeldine and his co-workers[2] correctly ascribed the appearance potential of 10.0 eV for m/e 73 from hexamethyldisilane to the trimethylsilyl ion. In agreement with this conclusion, no peak at m/e 80 due to the doubly-charged molecular ion was observed in the mass spectrum of ethylpentamethyldisilane.

The ionization potentials of the trialkylsilyl radicals, calculated from our appearance potential results and our value[3] for D(Me_3Si–$SiMe_2Et$), are given in Table 1, with those of their carbon analogues.

TABLE 1

RADICAL IONIZATION POTENTIALS

Radical	*I.P. ev*	*Ref.*
Me_3Si	7.0	this work
$EtMe_2Si$	6.6	this work
Me_3C	7.42	6
$EtMe_2C$	7.12	7

The lower values for the silicon radicals are of interest in relation to the possible rôle of ionic or partly ionic intermediates in organosilicon reaction mechanisms[8].

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