

NOTE

BOND DISSOCIATION ENERGY RELATIONSHIPS IN SILICON COMPOUNDS

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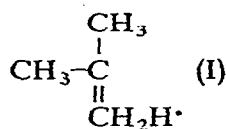
Recent definitive determinations of bond dissociation energy values in trimethylsilyl compounds make it possible to compare these values with those for the silyl compounds and by consideration of the patterns which emerge make a detailed intercomparison of the stabilities of silicon-containing free radicals with the corresponding alkyl radicals. The values are listed in Table 1, where all figures quoted are in kcal·mole⁻¹ rounded off to the nearest whole number. The symbol Δ refers throughout to differences between the two columns.

TABLE 1
INTERCOMPARISON OF BOND DISSOCIATION ENERGIES

M	$D(\text{H}_3\text{M}-\text{MH}_3)$	$D(\text{Me}_3\text{M}-\text{MMe}_3)$	Δ
C	88 ¹	68 ^{1,2}	20
Si	(81 ³) 84 ⁴	67 ⁵	17
	$D(\text{H}_3\text{M}-\text{H})$	$D(\text{Me}_3\text{M}-\text{H})$	
C	104 ¹	91 ¹	13
Si	95 ^{4,6} , 94 ⁷	81 ⁵	13, 14
	$D(\text{H}_3\text{M}-\text{CH}_3)$	$D(\text{Me}_3\text{M}-\text{CH}_3)$	
C	88 ¹	80 ^{1,2}	8
Si	86 ⁷	76 ⁵	10

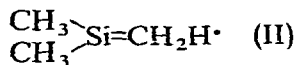
The immediate point of interest is that bonds to trimethylsilyl are weaker than bonds to silyl by approximately the same amount as bonds to tert-butyl are weaker than bonds to methyl and that this is independent of the small ionic contributions to the bond dissociation energy values. It has been suggested that the drop⁸ in $D(\text{R}-\text{H})$ from $\text{R} = \text{Me}$ to $\text{R} = \text{tert-Bu}$ is due to the resonance energy of the tert-butyl radical,

the contributing valence bond structures (I) showing hyperconjugation.



Essentially the same picture is presented by later molecular orbital treatments^{9,10} and the correlation of the molecular orbital picture with ESR data for alkyl free radicals has been discussed by Symons¹¹.

It is suggested that a similar stabilisation by delocalisation occurs for trimethylsilyl radicals as for tert-butyl. In valence bond terms this corresponds to structures (II), where the double bond could be of the $p_\pi-p_\pi$ type.



It has recently been proposed that $p_\pi-p_\pi$ double bonded singlet Si-C intermediates can occur in the pyrolysis of 1,1-dimethylsilacyclobutane¹². Confirmation of our hypothesis would require a detailed ESR study of the trimethylsilyl radical. Should our hypothesis be incorrect, silicon containing molecules require an entirely different theory of bond dissociation energies from carbon compounds. It appears that there is as yet insufficient data to extend these considerations to the analogous germanium compounds and radicals:

ACKNOWLEDGEMENTS

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