# The Remarkable Thermal Stability of Benzyl[tris(dimethylphenylsilyl)methyl]mercury. How can a Bulky Ligand Stabilize an Organometallic Compound towards Unimolecular Dissociation?

Colin Eaborn,* Karen L. Jones, J. David Smith,* and Kayumars Tavakkoli

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.

Only at 245 °C is the rate of the thermal decomposition of $(Me_2PhSi)_3CHgCH_2Ph$ in diphenyl ether comparable with that of $(PhCH_2)_2Hg$ at 150 °C; it is suggested that this may be because within the collisionally energized molecule there is only slow transmission of energy through the metal atom.

It is generally accepted that dialkylmercurials undergo thermal decomposition by a unimolecular dissociation into radicals, in either a two- (Mode 1) or one-stage (Mode 2) process.[1,2] In a Mode 1 decomposition the activation energy is effectively equal to the bond dissociation energy of the RHg–R bond, and in Mode 2 it is only slightly higher.

Mode 1 R–Hg–R → R–Hg· + R· (slow)
        R–Hg· → R· + Hg (fast)
Mode 2 R–Hg–R → R· + Hg + R·
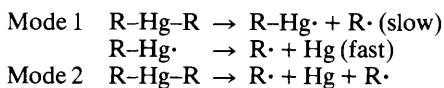
In terms of this picture the high temperature needed for the thermal decomposition of $[(Me_3Si)_3C]_2Hg$ seemed to us anomalous.[3] To throw light on the origin of the stabilization we have compared the ease of thermal decomposition of the diorganomercurial (1), which was more readily available to us than $[(Me_3Si)_3C]HgCH_2Ph$, with that of dibenzylmercury, (2), the thermal decomposition of which in solution has been extensively studied, and shown to involve a Mode 1 process.[2] (The kinetic data were consistent with the possibility of some contribution from a second-order induced decomposition in concentrated solutions, but such a process seems not to be of much importance since the observed first-order rate constants for decomposition of liquid (2) at 117—141 °C are similar to those for solutions in phenetole.[4]) Since the energy of dissociation of the Hg–CH₂Ph bond should be similar in the two compounds, they would, in terms of the accepted mechanism, be expected to show rather similar rates of decomposition.

$$(Me_2PhSi)_3CHgCH_2Ph \quad (PhCH_2)_2Hg$$
$$(1) \qquad\qquad\qquad (2)$$
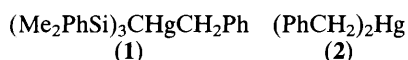
Initially we noted the approximate temperatures at which (1), (2), and some related diorganomercurials began visibly to decompose when the temperature of a molten sample in a sealed melting point tube was raised slowly. The results are shown in Table 1, and the most significant is that (1) decomposed only at a temperature some 85 °C higher than that for (2). The approximate temperatures of onset of

decomposition indicated by differential scanning calorimetry (dsc) were then noted, and the data are again shown in Table 1. There is in most cases reasonable agreement between the two sets of decomposition temperatures, except that the temperature needed to decompose compound (1) appeared to be even higher than that observed by use of a m.p. tube. The fact that the temperature needed for decomposition of $(Me_2PhSi)_3CHgPh$ indicated by dsc was ca. 65 °C higher than that for Ph_2Hg is probably significant in the light of the discussion below.

The large difference between the decomposition temperatures of (1) and (2) as neat liquids must have mechanistic significance, especially since, as noted above, the rate of decomposition of (2) is much the same in the liquid as in solution, but we thought that a more satisfactory comparison might be provided by examining the decompositions of (1) and (2) in diphenyl ether solution, the decomposition of (2) in other solvents having been extensively studied (and the rate found not to vary much with the solvent).[2,5] Each solution was placed in an n.m.r. tube, which was evacuated, sealed, immersed in a sand bath kept at an appropriate temperature, removed after ca. 1 h, and cooled. The ¹H n.m.r. spectrum was then recorded. No significant change in the spectrum was observed until the temperature of the bath was raised to 150 °C in the case of (2) and ca. 245 °C in the case of (1), and at those temperatures it was evident that new species had been formed. The temperature needed in the case of (2) is reasonably consistent with the half-lives of ca. 2.5 and 0.5 h recorded for the decomposition in toluene solution at 145 and 159.5 °C, respectively.[4]

It is evident that the thermal stability of (1) is much greater than that of (2). If it is assumed that the rate of decomposition of (2) at 150 °C is roughly equal to that of (1) at 245 °C, then by use of the value of the activation energy, 161 kJ mol⁻¹, derived for the decomposition of (2) in toluene,[2] it can be calculated that (2) would react roughly 4500 times as rapidly as (1) at 245 °C.

It is tempting to seek to attribute the effect of the $(Me_2PhSi)_3C$ group to its bulk (cf. ref. 3), but there seems no obvious way in which steric hindrance could operate in a Mode 1 or Mode 2 process. In such processes the origin of the low reactivity of (1) must presumably (but see later) be sought in the pre-exponential factor, and as a basis for discussion we very tentatively suggest that the effect may be related to the prediction by Marcus et al. that the rate of energy transfer from one ligand to another on the same metal should be abnormally low when the metal is a heavy one, such as tin.[6]† The magnitude of the effect should increase with increase in the mass of the metal, and so should be especially large for mercury. When the dissolved (1) is in thermal equilibrium

Table 1. Approximate temperatures of apparent onset of decomposition for some diorganomercurials [R = $(Me_2PhSi)_3C$].

Mercurial	Decomposition temperature/°C	
	In m.p. tube	By d.s.c.
RHgBu	280	290
RHgPh	280	280
Ph₂Hg		215
RHgCH₂Ph (1)	240	275
(PhCH₂)₂Hg (2)	155	
RHgC(SiMe₃)₃		330
[(Me₃Si)₃C]₂Hg		300

† We note, however, that experiments by Rabinovitch et al.[7] have cast doubt on the significance of earlier observations by Rowland and his colleagues[8] that appeared to provide support for the Marcus proposals.

with the solvent at a given temperature, a molecule which has acquired an excess of energy at least equal to the energy required for the dissociation of the Hg–CH$_2$Ph bond will usually have most of that excess of energy dispersed within the (Me$_2$PhSi)$_3$C ligand, and this excess may only rarely be transmitted to the Hg–CH$_2$Ph bond before the molecule is deactivated by collision. On this picture it is the molecular complexity of the (Me$_2$PhSi)$_3$C ligand (which contains 63 bonds) that matters in the present case, and not its bulk and overall shape, which are responsible for its undoubted steric inhibition of other types of reaction. If our interpretation is correct, it can be seen that use can be made of the phenomenon in stabilizing other organometallic species towards decompositions that occur by a unimolecular mechanism (and not necessarily only those involving generation of radicals).

We hope to undertake detailed kinetic studies on related systems more amenable to accurate rate measurements in order to determine the activation parameters. On the simple picture above the stabilization would be expected to show up wholly in the pre-exponential factor, but a situation can be envisaged in which the molecule as a whole has to acquire an excess of energy significantly greater than that required for dissociation of the Hg–CH$_2$Ph bond in order that an appropriate fraction of that energy can be transmitted sufficiently rapidly across the metal atom, and this would show up in a higher than expected activation energy.

References

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