Free Radicals in Solution. Part 10.[1] The Thermal Decomposition of Benzylphenylmercury in Solution

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Benzylphenylmercury decomposes in toluene between 140 and 170 °C to give bibenzyl, diphenylmercury, and mercury in a first-order reaction with $\log_{10}(A/s^{-1})$ 16.8, E 41.0 kcal mol^{-1}, and interpreted as involving Hg–CH$_2$Ph bond fission in the rate-determining step. The effects of *m*-chloro and *p*-methyl substitution in the benzyl group on this decomposition have been determined.

Pyrolysis of substituted dibenzylmercurials is a convenient method of assessing the stabilizing effect of substituents on benzyl radicals.[1,2] The evidence supports the one-bond homolysis mechanism (1), and it has been assumed that the predominant influence of the substituent is on the stability of the benzyl radical (**I**), with virtually no effect on the substituted benzylmercury radical (**II**).

$$(XC_6H_4CH_2)_2Hg \longrightarrow \underset{\textbf{(I)}}{XC_6H_4CH_2^{\bullet}} + \underset{\textbf{(II)}}{{}^{\bullet}HgCH_2C_6H_4X} \quad (1)$$

As a possible way of eliminating the (supposedly small) effect of the substituent X on radical (**II**) we have explored the decomposition of a number of benzylphenylmercury compounds $XC_6H_4CH_2HgPh$ (**III**). By analogy with (1) it may be expected that the decomposition will be by equation (2), with

$$\underset{\textbf{(III)}}{XC_6H_4CH_2HgC_6H_5} \longrightarrow XC_6H_4CH_2^{\bullet} + {}^{\bullet}HgC_6H_5 \quad (2)$$

the Hg–CH$_2$C$_6$H$_4$X bond breaking rather than Hg–Ph, because of the extra stabilization of the benzyl radical. In these compounds, the effect of the substituent should be confined to the benzylic radical: the other moiety produced in each case is the $^{\bullet}$HgPh radical.

Results and Discussion

A solution of benzylphenylmercury (70 mg, 1 mol. equiv.) in toluene (3 ml) was decomposed for 16 h at 153 °C. G.l.c. analysis indicated the formation of bibenzyl (0.62 mol. equiv.), diphenylmercury (0.35 mol. equiv.), and benzene (not determined quantitatively) as the major organic products, with smaller quantities of two higher boiling products, and only traces of biphenyl and diphenylmethane. These results suggest that the decomposition most probably follows the Scheme. The formation of diphenylmercury in substantial quantities is in marked contrast to the decomposition of dibenzylmercurials in solution, where all the mercury appears as the element in the products,[3] and accords with the $^{\bullet}$Hg–C$_6$H$_5$ bond being stronger than $^{\bullet}$Hg–CH$_2$C$_6$H$_5$ (which would give the stabilized benzyl radical on homolysis). The diphenylmercury is unlikely to arise significantly from an S_H2 attack of a phenyl radical on a benzylphenylmercury molecule, since phenyl radicals are very reactive and will probably react almost exclusively by abstraction of hydrogen from the solvent. Additionally, in dilute solutions, the reaction is of first order: if the S_H2 reaction on the mercurial were important, the order would rise above unity. In view of the expected greater stability of $^{\bullet}$Hg–C$_6$H$_5$ than $^{\bullet}$Hg–CH$_2$C$_6$H$_5$, reaction (3) may be significantly reversible, which would be a contributing factor in the slower decomposition of benzylphenylmercury compared with dibenzylmercury. Hilpert and Grüttner[4] found that benzylphenylmercury disproportionates slowly to dibenzylmercury and diphenylmercury even at room temperature, presumably by a bimolecular reaction. Our first-order kinetics show that such a reaction (followed by decomposition of the dibenzylmercury) cannot play a significant role in the dilute (~0.01M) solutions used in this work.

$$C_6H_5CH_2\text{–}Hg\text{–}C_6H_5 \xrightarrow{\text{slow}} C_6H_5CH_2^{\bullet} + {}^{\bullet}Hg\text{–}C_6H_5 \quad (3)$$

$${}^{\bullet}Hg\text{–}C_6H_5 \longrightarrow Hg + C_6H_5^{\bullet} \quad (4)$$

$$C_6H_5^{\bullet} + C_6H_5CH_3 \longrightarrow C_6H_6 + C_6H_5CH_2^{\bullet} \quad (5)$$

$$2\ C_6H_5CH_2^{\bullet} \longrightarrow C_6H_5CH_2CH_2C_6H_5 \quad (6)$$

$$2\ {}^{\bullet}Hg\text{–}C_6H_5 \longrightarrow C_6H_5\text{–}Hg\text{–}C_6H_5 + Hg \quad (7)$$

Scheme.

Arrhenius parameters for the decomposition, measured in the temperature range of 140—170 °C are $\log_{10}(A/s^{-1})$ 16.8 ± 0.8, E 41.0 ± 1.6 kcal mol^{-1} (171.7 ± 6.6 kJ mol^{-1}). The A factor is normal for a one-bond homolysis, and the activation energy is very similar to that found[5] for the decomposition of dibenzylmercury in toluene (38.5 kcal mol^{-1}). The rate of decomposition of benzylphenylmercury at 145 °C, calculated from the Arrhenius parameters, is 2.2×10^{-5} s^{-1}, approximately a quarter of the value of the rate of decomposition of dibenzylmercury[5] at this temperature (8.05×10^{-5} s^{-1}). On the basis of the number of Hg–CH$_2$C$_6$H$_5$ bonds present in the molecule, dibenzylmercury would be expected to decompose at twice the rate of benzylphenylmercury: the remaining factor of two probably reflects the electronegativity difference between phenyl and benzyl.

The thermal decomposition of diphenylmercury in the gas phase is believed to take place in two steps:[6] the activation energy for the decomposition is assumed to be close to the ΔH for (8a), and by using known heats of formation for the other species,[7,8] the $^{\bullet}$Hg–C$_6$H$_5$ bond strength can be deduced to be 9 kcal mol^{-1} and ΔH_f ($^{\bullet}$Hg–C$_6$H$_5$) as 84 kcal mol^{-1} (in this discussion it is assumed that activation energies and thermodynamic quantities derived for the gas phase are valid in solution and *vice versa*).

$$(C_6H_5)_2Hg \xrightarrow{a} C_6H_5^{\bullet} + {}^{\bullet}Hg\text{–}C_6H_5 \xrightarrow{b} Hg + C_6H_5^{\bullet} \quad (8)$$

Use of this value for ΔH_f ($^{\bullet}$Hg–C$_6$H$_5$), thermodynamic parameters,[8] and the experimental activation energy for (3) allows us to estimate $\Delta H_f(C_6H_5CH_2HgC_6H_5)$ as 88 kcal mol^{-1}. The difference between this value and that of $(C_6H_5)_2$Hg is −6 kcal mol^{-1}, close to the 'normal' −5 kcal mol^{-1} increment for CH$_2$ insertion into an alkane [*n.b.*[7] $\Delta H_f(C_6H_6)$ −

$\Delta H_f(C_6H_5CH_3) = 8$ kcal mol^{-1}]. If we apply a similar increment for the change $C_6H_5CH_2HgC_6H_5 \longrightarrow (C_6H_5CH_2)_2Hg$, we obtain $\Delta H_f[(C_6H_5CH_2)_2Hg]$ 82 kcal mol^{-1}. By using the known activation energy[5] of reaction (9), $\Delta H_f({}^{\bullet}HgCH_2C_6H_5)$ 76 and ΔH(9b) -16 kcal mol^{-1}.

$$(C_6H_5CH_2)_2Hg \xrightarrow{a} C_6H_5CH_2^{\bullet} + {}^{\bullet}Hg\text{–}CH_2C_6H_5 \xrightarrow{b} Hg + {}^{\bullet}CH_2C_6H_5 \qquad (9)$$

This implies that in contrast to $C_6H_5\text{–}Hg^{\bullet}$, $CH_3\text{–}Hg^{\bullet}$, and $C_2H_5\text{–}Hg^{\bullet}$ (bond dissociation energies of 9, 3, and 3 kcal mol^{-1} respectively, as estimated above with additional kinetic data from ref. 9), $C_6H_5CH_2\text{–}Hg^{\bullet}$ has a negative bond dissociation energy. There is considerable uncertainty in these figures, but it is very unlikely that the true value of $D(C_6H_5CH_2\text{–}Hg^{\bullet})$ is positive, although there could still be a barrier to its decomposition.

We have also been able to compare the rate of decomposition at 155.4 °C of unsubstituted benzylphenylmercury with those of the *m*-chloro and *p*-methyl derivatives, substituted in the benzyl ring. Rates are: 8.3×10^{-5} (unsubstituted), 2.0×10^{-5} (*m*-Cl), and 24×10^{-5} s^{-1} (*p*-CH$_3$). The decrease caused by the substitution of a chlorine atom in the *meta* position is in line with the polar effects found for the decompositions of substituted dibenzylmercurials,[2] and would correspond to ρ -1.7 compared with ρ -0.6 for $(C_6H_5CH_2)_2Hg$. Using the unsubstituted and *m*-chloro substituted benzylphenylmercury rate figures to predict the rate for the *para*-methyl compound shows that the methyl compound is decomposing 1.7 times faster than expected on the basis of the polar effect, providing evidence for stabilization of the incipient benzyl radical by the *para* methyl group; with only three points an extended Hammett-type treatment of the results is not justified.

Experimental

The mixed benzylphenylmercury compounds were prepared from phenylmagnesium bromide and the appropriate benzylmercury(II) chloride in ether.[10] Benzylphenylmercury had $\delta(CDCl_3)$ 2.63 [s, J(Hg–H) 139 Hz, CH$_2$].

p-*Methylbenzylphenylmercury* was recrystallized twice from ether as crystals, m.p. 38—40 °C, $\delta(CDCl_3)$ 2.64 [s, J(Hg–H) 137 Hz, CH$_2$] and 2.33 (s, CH$_3$) (Found: C, 43.7; H, 3.7. $C_{14}H_{14}Hg$ requires C, 43.9; H, 3.7%).

m-*Chlorobenzylphenylmercury* was prepared as a yellow liquid, purified by t.l.c. (silica gel), $\delta(CDCl_3)$ 2.57 [s, J(Hg–H) 139 Hz, CH$_2$] (Found: C,39.2; H, 3.1. $C_{13}H_{11}ClHg$ requires C, 38.7; H, 2.8%).

Kinetic experiments were carried out on degassed ampoules containing solutions of the mercurial in toluene (7—10 × 10^{-3}M) with pentadecane, octadecane, or eicosane as internal standards. The mercurial remaining after a particular time was monitored by g.l.c. Results from first order plots over 1—3 half-lives (substituent: temp; 10^5k_1/s^{-1} values) were: unsubstituted: 140.4 °C; 1.25, 1.38, 1.02; 155.4 °C; 8.34, 8.30; 170.4 °C; 34.0, 34.8, *p*-methyl: 155.4 °C; 24.5, 23.0; *m*-chloro: 155.4 °C; 2.04, 1.93.

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