Free Radical Reactions in Solution. Part 3.[1] The Decomposition of Dibenzylmercury in Toluene

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Dilute solutions of dibenzylmercury decompose on heating in toluene solution to give mercury and bibenzyl as the main products, along with traces of 1,2,3-triphenylpropane and stilbene. Phenyl-*p*-tolylmethane was absent. The decomposition of dilute solutions of the mercurial initially follows first-order kinetics in the temperature range 130—160°. Arrhenius parameters are $\log_{10} A$ 16.0 ± 0.3; E 38.5 ± 0.5 kcal mol^{-1}. The rate-determining process is probably homolysis of one benzyl–mercury bond. In concentrated solutions, particularly at the higher temperatures, the kinetics of the decomposition are more complex.

DIBENZYLMERCURY has been used extensively as a thermal source of benzyl radicals in solution.[2] The mercurial decomposes in solution at convenient rates at temperatures in the region 125—160°, which makes the compound potentially useful as a radical initiator at temperatures above the limit for t-butyl peroxide. Few kinetic studies of the decomposition have been made: we report here the results of a kinetic study of the thermal decomposition of dibenzylmercury in toluene solution.

EXPERIMENTAL

Dibenzylmercury,[3] 1,2,3-triphenylpropane,[4] and phenyl-*p*-tolylmethane [5] were made by standard methods. Toluene was distilled before use.

Kinetic Studies.—Method A. Determination of the mercury liberated during the reaction. Aliquot portions (5 ml) of a solution of dibenzylmercury in toluene were pipetted into 12 ampoules, which were then degassed and sealed on a vacuum line. The ampoules were placed in a thermostatted oil-bath, withdrawn at intervals, opened, centrifuged, and the toluene solution was removed by a pipette. The mercury remaining was washed with ether, then acetone, and after being blown dry, was dissolved in nitric acid. A known excess of EDTA was added, the solution was neutralized to pH 7, buffer solution was added, and the excess of EDTA was estimated by back titration with standard magnesium sulphate solution, using Solochrome Black T as the indicator.[6]

Method B. Determination of the rate of formation of bibenzyl. A known weight of tridecane was added to the solution of dibenzylmercury, and portions were degassed, sealed in ampoules, and heated in a thermostat as above. The solutions were analysed by g.l.c. (1 ft 5% w/w SE30 on 100—120 mesh silanized Chromosorb G; 80—100° by 2° min^{-1}, flash heater at 90°, flame ionization detector). These conditions did not decompose residual dibenzylmercury. The amount of bibenzyl produced was determined from peak height ratios of bibenzyl : tridecane after calibration.

Investigation of the Formation of 1,2,3-*Triphenylpropane.*—Solutions of dibenzylmercury in toluene, with eicosane as the internal standard, were introduced into ampoules, degassed and sealed, and decomposed in a thermostat until the dibenzylmercury was completely decomposed (20 half-lives). A 5 ft 5% w/w SE30 on 100—120 mesh Chromosorb G column was used at 200° for g.l.c. analysis; areas were compared in this case.

(a) *Variation in amount of triphenylpropane produced at different temperatures.* A solution of dibenzylmercury (990 mg) and eicosane (8.5 mg) in toluene (50 ml) was used. At temperatures of 130.0, 138.5, 150.0, 161.0, and 170.0°, the mole percentages of 1,2,3-triphenylpropane formed after 20 half-lives were 0.55, 0.37, 0.37, 0.41, and 0.38 respectively.

(b) *Variation in amount of* 1,2,3-*triphenylpropane produced as a function of initial concentration of dibenzylmercury.* In experiments carried out at 170° for 20 half-lives, toluene solutions which contained 30.6, 51.6, 61.2, 90.3, 151.5, 261.8, 311.4, and 375.6 mg dibenzylmercury in toluene (10 ml) gave concentrations of 1,2,3-triphenylpropane of 2.8×10^{-5}, 4.0×10^{-5}, 6.5×10^{-5}, 9.7×10^{-5}, 1.7×10^{-4}, 3.0×10^{-4}, 2.8×10^{-4}, and 4.5×10^{-4}M respectively.

During these experiments traces of stilbene were found but phenyl-*p*-tolylmethane could not be detected.

RESULTS AND DISCUSSION

The kinetics of the decomposition of solutions of dibenzylmercury in toluene were studied initially by estimation of the mercury produced in the decomposition (method A). Reproducible results indicating that first-order kinetics were being followed over at least 2 half-lives were obtained at 129.8°, but at higher temperatures deviations from first-order behaviour were found, indicating that higher order reactions were taking place at least in the more concentrated solutions; reproducible first-order rate constants were only obtained by measuring initial rates of decomposition of dilute solutions (method B: estimation of bibenzyl formed by g.l.c.). The results are shown in the Table. Arrhenius parameters, using the asterisked rate constants, were established as $\log_{10}$ (A/s^{-1}) 16.03 ± 0.27; E 38.48 ± 0.52 kcal † mol^{-1}.

These values may be compared with those obtained for iso-octane solutions [7] ($\log_{10}A$ 16.25, E 38.8 kcal mol^{-1}), for concentrated solutions in phenetole [8] ($\log_{10}A$ 11.7, E 36.0 kcal mol^{-1}) and for the neat liquid [8] ($\log_{10}A$ 14.8, E 39.7 kcal mol^{-1}).

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† 1 cal = 4.184 J.

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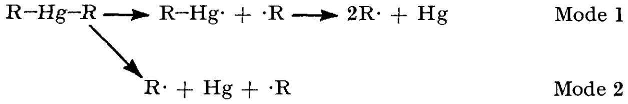


$$R{-}Hg{-}R \longrightarrow R{-}Hg\cdot + \cdot R \longrightarrow 2R\cdot + Hg \qquad \text{Mode 1}$$

$$\searrow R\cdot + Hg + \cdot R \qquad \text{Mode 2}$$

SCHEME 1

Considerable discussion has centred in the past on the question of whether dialkylmercury compounds decompose in one or two stages (Scheme 1). Mode 1 decompositions should be characterized by lower Arrhenius A factors, and by activation energies which should be lower than the energy required to break both carbon–mercury bonds. Both dimethylmercury[9] ($\log_{10}A$ 15.74, E 57.5 kcal mol^{-1}) and diethylmercury[10] ($\log_{10}A$ 15.4, E 45.7 kcal mol^{-1}) appear to decompose in the gas phase by mode 1, though the strength of the remaining R–Hg bond is only a few kcal mol^{-1}. However, Price[11] has warned that present data do not allow an unequivocal distinction between modes 1 and 2 to be made for the decomposition of dialkylmercurials.

Kinetics of decomposition of dibenzylmercury in toluene solution

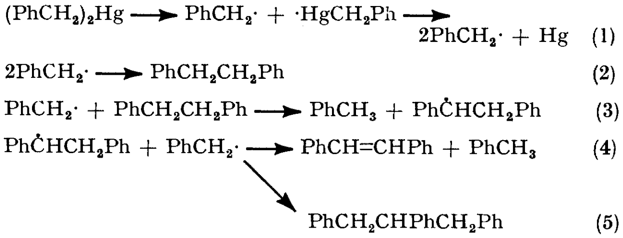
T (°C)	Method	Concentration †	k/s^{-1}
159.5	B	100.7	1.28×10^{-3}
159.5	B	65.9	1.43×10^{-3}
159.5	B	62.0	1.39×10^{-3}
159.5	B	8.7 *	4.10×10^{-4}
159.5	B	3.5 *	3.84×10^{-4}
145.0	B	91.3	1.15×10^{-4}
145.0	B	37.8 *	7.93×10^{-5}
145.0	B	5.8 *	8.17×10^{-5}
129.8	A	20.4 *	1.52×10^{-5}
129.8	A	7.3 *	1.41×10^{-5}

* Value used in Arrhenius plot. † mg mercurial per g toluene. Tridecane added as internal standard to all solutions analysed by method B.

Our data for dibenzylmercury suggest a mode 1 decomposition. The A factor lies in the middle of the range (10^{15}—10^{17}) commonly found for dissociations of molecules into two radicals,[12] though it may be noted that a number of gas-phase decompositions which give benzyl radicals have rather low A factors ($PhCH_2CH_3 \longrightarrow PhCH_2\cdot + \cdot CH_3$, $\log_{10}A$ 14.6;[13] $PhCH_2CH_2CH_3 \longrightarrow PhCH_2\cdot + \cdot CH_2CH_3$, $\log_{10}A$ 14.9;[13] $PhCH_2CH_2Ph \longrightarrow 2PhCH_2\cdot$, $\log_{10}A$ 14.3[14]).

The lowering of the activation energy compared with the decompositions of dimethyl- and diethyl-mercury is a reflection of the development of the stabilization energy of the benzyl radical in the transition state, but the amount of the lowering gives no indication that stabilization energy corresponding to more than one benzyl radical is being produced [$D(CH_3{-}H)$ 105, $D(Et{-}H)$ 98, $D(PhCH_2{-}H)$ 85 kcal mol^{-1}].[15,16]

1,2,3-Triphenylpropane and stilbene have been reported as byproducts[17,18] of benzyl radical combination. Scheme 2 appears likely.



$$(PhCH_2)_2Hg \longrightarrow PhCH_2\cdot + \cdot HgCH_2Ph \longrightarrow 2PhCH_2\cdot + Hg \qquad (1)$$

$$2PhCH_2\cdot \longrightarrow PhCH_2CH_2Ph \qquad (2)$$

$$PhCH_2\cdot + PhCH_2CH_2Ph \longrightarrow PhCH_3 + Ph\dot{C}HCH_2Ph \qquad (3)$$

$$Ph\dot{C}HCH_2Ph + PhCH_2\cdot \longrightarrow PhCH{=}CHPh + PhCH_3 \qquad (4)$$

$$\searrow PhCH_2CHPhCH_2Ph \qquad (5)$$

SCHEME 2

In our experiments, the amount of 1,2,3-triphenylpropane produced (*ca.* 0.4 mol per cent) was not significantly altered by changes in temperature in the range 130—170°. The temperature invariance is to be expected if reaction (3) has an activation energy about half that of reaction (1): there is independent evidence that this is so in analogous hydrogen abstractions from benzylic positions.[1,2c] From Scheme 2, it follows that at a particular temperature the final concentration of 1,2,3-triphenylpropane should be proportional to $[Hg(CH_2Ph)_2]_{initial}^{\frac{3}{2}}$. In accord with this, it was found that a graph of final concentration of 1,2,3-triphenylpropane plotted against $[Hg(CH_2Ph)_2]_{initial}^{\frac{3}{2}}$ showed an approximately linear relationship at low values of initial dibenzylmercury concentration, but the amount of triphenylpropane fell off at higher concentrations of the mercurial. The most likely higher order reactions to take place in more concentrated solutions of dibenzylmercury (see above) are induced decomposition of the mercurial by a benzyl radical to give bibenzyl, mercury, and a benzyl radical, or a bimolecular reaction of two dibenzylmercury molecules to give two mercury atoms, a bibenzyl molecule, and either two benzyl radicals or a further bibenzyl molecule. A contribution from any of these processes would decrease the proportion of benzyl radicals formed in the system and thus would reduce the amount of triphenylpropane in the products.

The absence of homolytic aromatic substitution products such as phenyl-*p*-tolylmethane is not unexpected: the unfavourable thermochemistry makes aromatic substitution by benzyl radicals on benzene compounds unlikely at any temperature,[19] though benzyl radicals will attack aromatic compounds such as anthracene,[20] where formation of the intermediate adduct involves less loss of stabilization energy. Phenyl-*p*-tolylmethane might also be expected if ' head to tail ' dimerization of benzyl radicals took place, followed by re-aromatization

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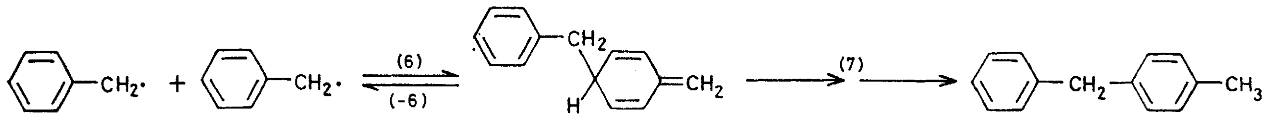
[reactions (6) and (7)]. However, ΔH_f^0 for the head to tail adduct (I) may be calculated by the group value method[12] to be *ca.* +60.5 kcal mol^{-1}, which makes reaction (6) only *ca.* 29 kcal mol^{-1} exothermic. Thus redissociation of (I) into two benzyl radicals [reaction (−6)] should be rapid under our experimental conditions ($t_{\frac{1}{2}} < 1$ s at 140° if $\log_{10}A = 16$ and $E = \Delta H$), and hence it is reasonable that no phenyl-*p*-tolylmethane is formed by this route either.



(I)

Thus dibenzylmercury shows considerable potential as a relatively high-temperature initiator. To avoid reactions other than the simple unimolecular fission, solutions used should be as dilute as possible, particularly at higher temperatures, and should be thoroughly degassed.

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