An Improved σ· Scale. The Thermal Decomposition of Substituted Dibenzylmercury Compounds in Alkane Solutions

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Summary From the first order rate constants for the decomposition of ten substituted dibenzylmercury compounds at 140·2 °C, a scale of substituent constants σ· has been derived, which measures the stabilizing effect of substituents at the *para* position of a benzyl free radical.

OVER many years, there has been considerable interest in the extent to which substituent groups can stabilize a free radical. Numerous model reactions have been proposed to investigate such effects (*e.g.*, refs. 1—5): difficulties encountered have included separation of radical stabilization from polar effects, and side reactions, particularly at substituent groups.

We now propose that the decomposition of substituted dibenzylmercury compounds $(XC_6H_4CH_2)_2Hg$ in alkane solutions is a good model reaction for studying substituent effects on free radical reactions. Dibenzylmercury decomposes on heating in solution into mercury and two benzyl radicals [equations (1) and (2)], and the rate determining step appears to be the homolysis of one of the

$$XC_6H_4CH_2\text{–}Hg\text{–}CH_2C_6H_4X \rightarrow XC_6H_4CH_2\cdot + \cdot Hg\text{–}CH_2C_6H_4X \qquad (1)$$

$$\cdot Hg\text{–}CH_2C_6H_4X \rightarrow Hg + XC_6H_4CH_2\cdot \qquad (2)$$

carbon–mercury bonds.[6] We report here our kinetic results for the decomposition of dibenzylmercury itself and nine substituted compounds in dilute alkane solutions at 140·2 °C (*ca.* 5×10^{-3} M solutions in octane except as noted).

TABLE. Rate constants[a] for the decomposition of $(XC_6H_4CH_2)_2Hg$ at 140·2 °C in octane.

X	$10^5 \times k_1$ (s^{-1})	$\sigma\cdot$
H	8·1	0
m-F	5·6	
m-OMe	7·3	
3,5-Me_2[b]	11·3	
p-Cl	7·2	0·06
p-F	9·4	0·07
p-OMe	26·3	0·31
p-Me	26·6	0·38
p-Ph	21·7	0·39
p-NO_2[c]	15·6	0·73

[a] Rate constants are the mean of at least two determinations and are either as measured at 140·2 °C or corrected from values obtained at temperatures within 0·2 °C of this value using the activation energy for the particular compound. [b] Iso-octane solution: this result was obtained here by G. C. March. [c] Dibenzyl ether solution (compound insufficiently soluble in octane). A single check run of dibenzylmercury itself in dibenzyl ether gave $k_1 = 8{\cdot}5 \times 10^{-5}\,s^{-1}$, indicating that the solvent change had little effect.

All the decompositions were kinetically of first order: the Table shows the first order rate constants at 140·2 °C. A plot of log k_1 at 140·2 °C against Hammett's σ is shown in the Figure. The points for *meta* substituted compounds lie on a line with a slope of $-0{\cdot}6$ indicating the presence of a small but significant polar effect on the reaction. Since the rate-determining step in the decomposition of the unsubstituted mercurial involves the homolysis of one of the carbon–mercury bonds, and since the polarity of these bonds is $^{\delta-}C\text{–}Hg^{\delta+}$, the negative ρ value is probably due to stabilization of the reactant molecule by electron withdrawing groups, this stabilization being lost in the transition state which corresponds closely to the product radicals in which these polar influences will have been eliminated [equation (3)].

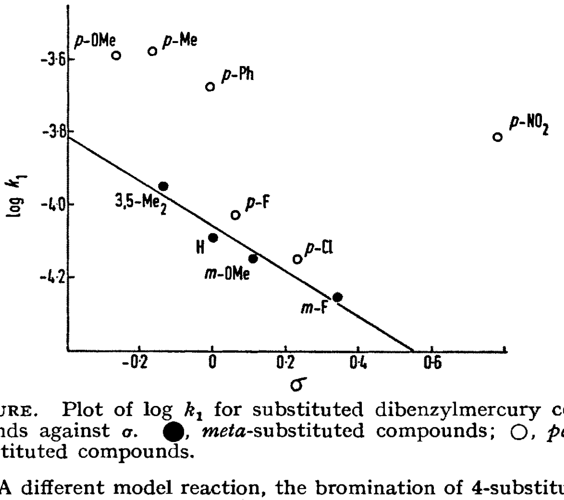

FIGURE. Plot of log k_1 for substituted dibenzylmercury compounds against σ. ●, *meta*-substituted compounds; ○, *para*-substituted compounds.

$$XC_6H_4\overset{\delta-}{C}H_2\text{–}\overset{\delta+}{Hg}\text{–}\overset{\delta-}{C}H_2C_6H_4X \rightarrow XC_6H_4CH_2\cdot + \cdot Hg\text{–}CH_2C_6H_4X \qquad (3)$$

The points for all the *para*-substituted compounds lie above the line, corresponding to faster rates of decomposition. The deviations from the line are insignificant for *p*-Cl and *p*-F, but are substantial for the other four substituents: we attribute these deviations to the stabilizing effect of the *para* substituent on the benzyl free radical. (Substituent effects on the $\cdot Hg\text{–}CH_2C_6H_4X$ radical are likely to be insignificant because of the insulating effect of the CH_2 group). Delocalization of the free electron onto a *para* chlorine or fluorine substituent would involve charge separation, expansion of the octet, or use of antibonding orbitals, which would be unfavourable. In contrast, isovalent contributing structures can be written for *para* nitro and phenyl substituents and these are also possible for methyl and methoxy substituents if hyperconjugation is taken into account. The fact that both electron-withdrawing and electron-releasing conjugating groups enhance the rate is evidence that the effect is indeed one of radical stabilization and not a polar effect.

We therefore propose that this reaction forms a suitable basis for evaluating the effects of *para* substituents on the stability of benzyl radicals. We define $\sigma\cdot$ as the difference between log k_1 for any *para* substituent and the appropriate point on the regression line shown in the Figure;† values of $\sigma\cdot$ for six *para* substituents are shown in the Table. In effect, this involves the use of an extended Hammett equation (4) where $\rho\cdot = 1$ for reactions (1 and 2) in which a

$$\log k/k_0 = \rho\sigma + \rho\cdot\sigma\cdot \qquad (4)$$

free benzyl radical has been formed during the reaction. For other reactions in which less radical character is created or destroyed, smaller values of $\rho\cdot$ will be involved. (The $\rho\sigma$ term could be replaced by a $\rho^+\sigma^+$ or $\rho^-\sigma^-$ term if appropriate.) Advantages of our model reaction include the greater degree of radical development involved in a thermolysis compared with many other radical reactions, and the fact that we are following the first and rate-determining step in a reaction rather than **a** later step in a complex system.

Comparison of our scale with other proposed scales is made difficult by the differing substituents used by different workers, but correlation coefficients between our $\sigma\cdot$ and four other scales[1–4] lie between 0·83 and 0·92. A fifth scale[5] gave a worse correlation (0·63) but this scale is unusual in proposing negative stabilization for some groups, which appears unlikely. An advantage of the $\rho\cdot$ values derived

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† A different model reaction, the bromination of 4-substituted 3-cyanotoluenes has been suggested as a basis for a $\sigma\cdot$ scale (ref. 5). For the reasons given in the following paragraph, we believe that our model reaction forms a better basis for a $\sigma\cdot$ scale.

from the use of our scale is that they should relate directly to the amount of radical character developed or destroyed in the reaction (1·0 for complete development of a benzylic radical). In a radical transfer reaction of a benzylic radical with a substituted toluene for example, a $\rho\cdot$ value of *ca.* 0·5 will be expected: we deduce a value of 0·47 from the results of Yamamoto and Otsu[3] on the reactions of polystyryl radicals with substituted cumenes. On the other hand, homolytic aromatic substitution reactions are thought to have a transition state close to the intermediate cyclohexadienyl radical in which the full stabilizing effect of a *para* substituent will be felt: a value for $\rho\cdot$ of 1·07 is deduced from the results of Simamura and his co-workers[2] on the arylation of *para* substituted benzenes. Further discussion of the considerable volume of literature on the effects of substituents on radical reactions is deferred to the full paper, but it is worth stressing here that by using our $\sigma\cdot$ scale, $\rho\cdot$ can be used as a probe of the amount of radical character developed in the transition state.

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