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The thermal decomposition of dibenzylmercury: a suitable model reaction for determination of substituent effects on radical stability? *

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Abstract

The utility of the $\sigma^{\bullet}$ scale based on the thermal decomposition of disubstituted dibenzylmercurials is discussed in the light of other possible scales for radical stabilization by substituents.

Substituents are believed to have an influence (generally stabilizing) on the stability of free radicals, but for many radical reactions, for example, the bromination of substituted toluenes [1] and homolysis of the O–H bond in phenols [2], polar effects appear to dominate. There have been a number of attempts to separate polar and radical stabilization effects [3]; in 1979 we suggested [4] that the thermal decomposition of symmetrically substituted disubstituted dibenzylmercurials in octane is a suitable model reaction, and measured the kinetics of decomposition of twelve such compounds [4–7].

Although solutions of dibenzylmercury in toluene which are more concentrated than 0.1 M show higher than first order kinetic behaviour [8], and Russell's group [9] have obtained evidence for induced decomposition in photolytic reactions at concentrations of about 0.1 M, such reactions should not be important in the much more dilute solutions ($1\text{–}5 \times 10^{-3}$ M) used in our kinetic work. The decompositions at 140.2° followed first order kinetics. A plot of log k against σ^0 gave a reasonably straight line through the points from *meta* substituents, but the points for all *para* substituents, both electron-withdrawing and electron-releasing, lay above the line and these compounds were therefore decomposing faster than predicted from the *meta* regression line. We attributed the faster rate of decomposition of these *para*-substituted compounds to the stabilizing effect of the sub-

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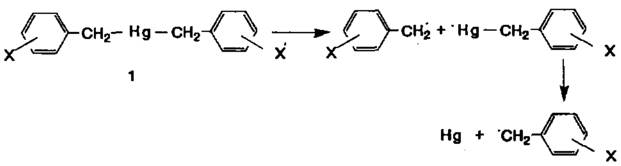
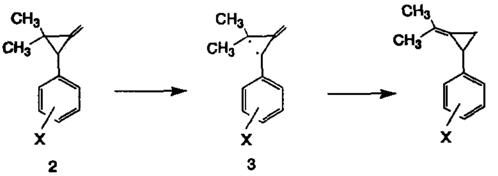
* Dedicated to Professor Alwyn G. Davies in recognition of his outstanding contribution to organometallic and free-radical chemistry.

stituent on the incipient benzyl radical. The kinetics of decomposition of dibenzylmercury itself along with those of the mono- and di-*para*-methoxy substituted compounds indicated that just one of the C–Hg bonds was breaking in the first, rate determining, step of the decomposition (eq. 1); since in a bond homolysis, the transition state is very close to the products, the full stabilizing effect of a substituent should be felt in the transition state.



(1)



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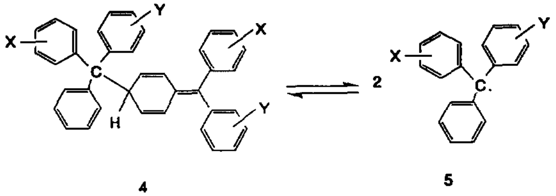


(3)

We expressed our result in the form

$$\log(k_X/k_H) = \rho^0\sigma^0 + \sigma^{\cdot} \qquad (4)$$

The difference between the observed and 'predicted' log k_X for *para* di-substituted compounds was taken as a measure of the stabilization effect of the particular *para* substituent on the benzyl radical. The polar term was taken as being due to stabilization of the molecule which contains $C^{\delta} - Hg^{\delta+}$ bonds. Electron withdrawing substituents on the aromatic ring will stabilize these dipoles, and this stabilization will be lost in the transition state. The ρ^0 value of -0.63 is in line with this. σ^0 was taken as the basis for the polar effect rather than σ on the grounds that a plot of $J(^{13}C-^{199}Hg)$ gave a better plot against σ^0 and also that for substituents such as MeO and CN, through conjugation is unlikely to be important, favouring σ^0 over σ or σ^-.

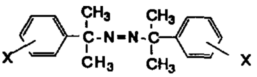
An attractive feature of this scale is that for other reactions involving radicals, where a two parameter Hammett-type relationship can be established

$$\log(k_X/k_H) = \rho^0\sigma^0 + \rho^{\cdot}\sigma^{\cdot} \qquad (5)$$

(where σ^0 can be replaced by σ, σ^+ or σ^- if appropriate for the reaction being considered), $\rho^{\cdot}$ should be a quantitative measure of the proportion of radical character built up in the transition state, ranging from 0.0 for no radical character to 1.0 for full radical build up in the transition state. To establish the suitability of this decomposition as the basis of a suitable scale of substituent constants, hereinafter denoted $\sigma_J^{\cdot}$ to distinguish them from other proposed scales, it is necessary to establish that other reactions fit such an extended Hammett relationship, and desirable to establish a connection between $\sigma_J^{\cdot}$ and an independent estimate of radical stabilization energy.

Shortly after our proposal of a $\sigma_J^{\cdot}$ scale based on mercurials, Creary [10] investigated the thermal rearrangement of 21 *meta* and *para* substituted 2-phenyl-3,3-dimethylmethylenecyclopropanes (**2**), which is thought to proceed through a diradical transition state or intermediate **3** (reaction 2). A plot of log *k* against σ^0 (values from ref. 11) for the *meta* substituted compounds gives a slope of -0.19, and the points for all the *para* substituents except for fluorine lie above this line. A plot of the deviations from the line against $\sigma_J^{\cdot}$ for the 8 substituents in common shows considerable scatter ($r = 0.70$). Since both the $\sigma_J^{\cdot}$ and the $\sigma_C^{\cdot}$ scales are subject to experimental error, a linear regression plot is inappropriate to determine the relationship between the two scales. A regression plot * that minimizes the squares of the perpendicular distances of points from the regression line gave, after correction for the temperature difference between the two sets of measurements, $\sigma_C^{\cdot} = 1.21\ \sigma_J^{\cdot}$. The value of the proportionality constant is not significantly different from 1.0 in view of the scatter of the points, supporting the idea that both reactions 1 and 2 involve production of a radical with effectively full benzylic stabilization in the transition state. The small negative value of ρ^0 for reaction 2 fits the stabilization of the small dipole between the carbon atom and the ring (σ_m for cyclopropyl [11] is -0.07). The deviations from the σ^0 correlation line are denoted $\sigma_{C'}^{\cdot}$ in this paper. (Creary [13] defines $\sigma_C^{\cdot}$ directly in terms of log k_{rel} values and does not apply the (small) polar correction that we use to define $\sigma_{C'}^{\cdot}$.)

Clark and Wayner [14] have recently measured D($XC_6H_4CH_2$–Br) for seven substituted benzyl bromides by the photo-acoustic method. Electron-withdrawing groups weaken the bond; this is attributed as being at least partially due to destabilization of the parent molecule. However, since only *para* substituents were used, and there is much scatter on a plot of D($XC_6H_4CH_2$-Br) against σ^0, a separation into polar and radical stabilization effects is not feasible. The thermal decomposition of azocumenes **6** provides an example of a polar effect in the opposite direction to dibenzylmercurials [15]. From the values of the *meta*-chloro-substituted and the parent compound, $\rho^0 = 0.91$, in accord with nitrogen's greater electronegativity than carbon. Although not enough *para* values have been accumulated to form the basis of a reaction scale, $\rho^{\cdot} = 0.83$, corresponding to substantial breakage of one C–N bond (or partial breakage of both C–N bonds).



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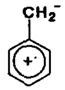

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* Slope = $\dfrac{(S_{xx} - S_{yy}) + \left[(S_{yy} - S_{xx})^2 + 4S_{xy}{}^2\right]^{0.5}}{2S_{xy}}$ (see ref. 12).

A most interesting development has been the recent publication [16] of a series of equilibrium constants for the dissociation of dimers of mono- and di-substituted triarylmethyl radicals (5) (reaction 3, X = H or X = Y). A $\log {}'K/\log K$ plot for the disubstituted compounds against the monosubstituted compounds has a slope of 1.87 ($r = 0.84$), using the "perpendicular" method described above, indicating that two substituents have nearly twice the stabilizing effect of one. All the K values for substituted triphenylmethyl radicals in the series are higher (after statistical correction of the unsubstituted value) than for the parent triphenylmethyl, implying that all the groups studied are stabilizing in the *para* position. *Meta* substituents were not studied, but on the assumption that $\rho^0 = 0$ (reaction 2, which should be similar, has $\rho^0 = -0.19$), the value of $\rho^{\cdot}$, from the "normal" regression line, is 0.99, or 0.72 after correction to 140.2°. The "perpendicular" regression line gives a slope of 1.17, or 0.84 after correction to 140.2°. The effect of a substituent on a triphenylmethyl radical is likely to be somewhat less than on a benzyl radical.

A disadvantage of kinetic scales such as those defined for reactions 1 and 2 is that values have not been obtained for all substituents of interest. Two non-kinetic scales have been suggested. In the first, $\sigma^{\cdot}_{\mathrm{H}}$ for *para* substituents is defined as $|\sigma^{\pm} - \sigma|/n$; $\sigma^{\pm}$ is the value of σ^{+} or σ^{-}, depending on whether the substituent is electron-releasing or electron-withdrawing [6]. The absolute value of this difference is divided by n; n is normally 1, but is taken as 2 for conjugatively releasing first period substituents such as OCH_3 and F to take account of the fact that the extra electron in a radical system (compared with a cation system) is going into an antibonding orbital. This scale has the advantage that Hammett polar substituent constant values are available for a very wide variety of substituents, and therefore substituent constants are available for a much larger number of substituents than any other scale. Correlations of this scale with other scales are quite acceptable (see Table 1).

The last scale to be considered is the scale suggested by Dust and Arnold [17], based on the ESR coupling constants for the α-CH_2 protons in substituted benzyl radicals. In general, substituents which stabilize radicals will lower the coupling constant. Dust and Arnold suggest that the relationship between $a(CH_2)$ and stabilization energy will be linear, though we have argued that this may not necessarily be so [5]. An interesting point made by Wayner and Arnold [18] is that

Table 1

Correlations between $\sigma^{\cdot}$ type scales

	$\sigma^{\cdot}_{\mathrm{J}}$	$\sigma^{\cdot}_{\mathrm{C'}}$ [a]	$a_{\mathrm{H'}} - a_{\mathrm{X}}$ [b]	$\log(K_{\mathrm{X}}/K_{\mathrm{H}})$ [c]	$\sigma^{\cdot}_{\mathrm{H}}$	$\sigma^{\cdot}_{\mathrm{av}}$
$\sigma^{\cdot}_{\mathrm{J}}$	1.00	0.70	0.71	0.87	0.82	0.90
$\sigma^{\cdot}_{\mathrm{C'}}$	*8*	1.00	0.84	0.90	0.74	0.96
$a_{\mathrm{H}} - a_{\mathrm{X}}$	*6*	*8*	1.00	0.93	0.84	0.97
$\log(K_{\mathrm{X}}/K_{\mathrm{H}})$	*6*	*6*	*7*	1.00	0.72	0.97
$\sigma^{\cdot}_{\mathrm{H}}$	*10*	*12*	*11*	*10*	1.00	0.83
$\sigma^{\cdot}_{\mathrm{av}}$	*10*	*11*	*11*	*10*	*15*	1.00

Figures in the top right triangle are correlation coefficients between scales. Italic figures in the bottom left triangle are the numbers of data points in common. [a] Data from ref. 10. Data from ref. 13 at other temperatures have not been used. [b] $a_{\mathrm{H}} - a_{\mathrm{X}}$ used instead of $1 - a_{\mathrm{X}}/a_{\mathrm{H}}$ to avoid rounding errors. [c] Equilibrium constants for reaction 3.

meta substituents (which should not, to a first approximation, affect radical stabilization) do affect $a(CH_2)$, and that the effect appears to be polar with electron withdrawing substituents raising $a(CH_2)$. We have carried out an investigation on a series of 3,5-disubstituted benzyl radicals [19] and find that there is indeed a good correlation with σ_m ($r = 0.96$), but that this correlation is improved ($r = 0.99$) if a $\sigma^{\cdot}$ component is included and the plot is made against ($1.20\,\sigma_m - \sigma^{\cdot}_H$). We interpret this as supporting the contribution of structures such as **7** to the structure (and stabilization) of the radical.

A feature of the $\sigma^{\cdot}_{\alpha}$ scale is that it predicts that *meta* and *para* F and CF_3 substituents destabilize a radical. Though there is little direct evidence on stabilization energies, the fact that both mono and di-*para*-CF_3 substitutions increase the value of the equilibrium constant of reaction (3) suggests that $a(CH_2)$ and stabilization energy may not always be linearly related for every substituent, but the broad applicability of this relationship is shown by using the energy relationship

$$\Delta\text{stabilization energy/kJ mol}^{-1} = -(5.75 \pm 0.2)\ \Delta a/\text{Gauss} \qquad (6)$$

(where Δa is the change in the α-CH_2 coupling constant) derived by Nicholas and Arnold [20] and the approximately linear relationship between $\sigma^{\cdot}_J$ and $\sigma^{\cdot}_{\alpha}$ to estimate the stabilization energy corresponding to a difference in $\sigma^{\cdot}_J$ values of 1. This comes to 9.7 kJ mol^{-1}, compared with 7.9 kJ mol^{-1} derived from the kinetic data in reaction 1 on the assumption that the differences in rates are due to enthalpy rather than entropy differences. This agreement also provides support for the contention that the transition state for reaction 1 does in fact correspond to almost complete breaking of one (not two) C–Hg bonds.

Conclusion

The reasonable agreement between the various measures of radical stabilization by substituents as shown in Table 1 provides strong support for the contention that radical stabilization by substituents is real and can be separated from polar effects. However, radical stabilizing effects are relatively small and can easily be swamped by polar effects. Our $\sigma^{\cdot}_J$ scale has the advantage of relating directly to the production of a benzyl radical, giving a definite meaning to $\rho^{\cdot}$ values when applied to other systems. The Creary scale has been applied to more substituents, but does not relate directly to the production of benzyl radicals. The Neumann scale will be suitable for reactions involving triarylmethyl radicals. The non-kinetic $\sigma^{\cdot}_{\alpha}$ scale derived from $\alpha(CH_2)$ coupling constants for benzyl radicals correlates well with the other scales (Table 1). However, a value is not available for the key NO_2 substituent, and the apparent destabilizing effect of F and CF_3 (not found for CF_3 in triphenylmethyl radicals [16]) requires further clarification. The $\sigma^{\cdot}_H$ scale, though empirical, has the advantage of being defined for many more substituents than the other scales.

By scaling the four experimental scales used in Table 1, using the $\sigma^{\cdot}_H$ scale as a reference, and averaging values for substituents which have been measured on two or more scales, renormalizing to the $\sigma^{\cdot}_J$ scale and correcting to 25°C, the $\sigma^{\cdot}_{av}$ scale shown in Table 2 is derived. This (naturally) correlates with all the other scales on the whole better than they do with each other, and since it relates to radical

Table 2

Values of $\sigma^{\cdot}_{av}$

Substituent	H	F	CF_3	^{t}Bu	Cl	Br	CH_3	OMe	CO_2Me	SMe	$COCH_3$	Ph	CN	COPh	NO_2
$\sigma^{\cdot}_{av}$	0.0	−0.03	0.09	0.13	0.18	0.23	0.23	0.35	0.54	0.55	0.58	0.59	0.63	0.65	0.76
s.d. [a]	–	0.14	0.16	0.05	0.06	0.02	0.17	0.14	0.13	0.08	0.05	0.11	0.22	0.12	0.11

[a] Standard deviation.

stabilization at room temperature, $\rho^{\cdot}$ values for other reactions based on this scale will provide a quantitative measurement of radical build up or destruction in the transition state. Since it is an average scale, updating will be necessary at intervals as new results become available, but this scale may prove convenient for use at the present time.

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