The Effects of Electronic Excitation on Heterolytic Side-chain Reactions of Substituted Benzenes

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A previously described quantitative theoretical treatment of the reactions mentioned in the title is extended so that it can be used to examine the effects of electronic excitations on the rate constants and equilibrium constants. The electronic excitations considered correspond to the ${}^1A_{1g} \longrightarrow {}^1B_{2u}$ and ${}^1A_{1g} \longrightarrow {}^3B_{1u}$ excitations of benzene. A new explanation emerges of why excitation to the triplet state has little effect on the pK_a value for phenol whereas excitation to the singlet state has a substantial effect. Also, it is concluded that the types of linear free energy relationship which are found among ground state reactions are not, in general, to be expected among excited state reactions. However, the relative effects of *para*- and *meta*-ring substituents are predicted to be simply related to $\sigma_p^0 - \sigma_m^0$. This relationship is shown to be consistent with available experimental data.

We have recently described a new quantitative theoretical treatment of heterolytic side-chain reactions of substituted benzenes in their ground electronic states.[1] The object of the present work is to extend that treatment so that it can be used to predict the effects of electronic excitation within the benzene ring on the rate and equilibrium constants of reactions of that type. A particular aim is to discover if there might be any simple structure–reactivity relationships among photochemical reactions.

Reactions of substituted benzenes in solution are commonly observed only when the reactants are in one of three electronic states, namely, the ground state (S_0), the lowest triplet excited state (T_1), and the lowest singlet excited state (S_1). In benzene itself the ground state is ${}^1A_{1g}$, the lowest triplet excited state is ${}^3B_{1u}$, and the lowest singlet excited state is ${}^1B_{2u}$. In many, although by no means all, substituted benzenes the S_0, T_1, and S_1 states may be regarded respectively as perturbed ${}^1A_{1g}$, ${}^3B_{1u}$, and ${}^1B_{2u}$ benzene states. We shall consider only that class of substituted benzenes in this paper. For convenience we shall use the symbol L_1 to represent 'T_1 or S_1' and the symbol N to represent 'S_0, T_1, or S_1.'

We shall now summarize our treatment of thermal reactions of the type mentioned in the title and indicate how it can be extended to cover corresponding photochemical reactions.

Theory.—Our treatment is based on the field and charge-transfer (FCT) theory of substituent–hydrocarbon interactions.[2] By the FCT theory the direct interactions between a hydrocarbon and a substituent are divided into three types, namely, field, exchange, and charge-transfer. The exchange and the charge-transfer effects depend on the degrees of overlap between orbitals localized on the separate moieties: the field effect is independent of such orbital overlaps. The exchange effect is treated as if it were equivalent to a mutual electrostatic repulsion between the moieties which is not directly felt beyond the atoms involved in the bond between them. It may then be combined with the electrostatic field effect. When the hydrocarbon is benzene the total interaction energy between the moieties can be approximately expressed in terms of six parameters, α_E, α_S, P, A, β_D, and β_A which have values that are characteristic of the nature of the substituent and that are not affected by electronic excitation within the hydrocarbon. The parameters may be evaluated using spectroscopic data. α_E and α_S are measures of the combined field and exchange effects. P and β_D are measures of charge-transfer from the substituent to the hydrocarbon. A and β_A are measures of charge-transfer from the hydrocarbon to the substituent.

The energy of interaction between a substituent and the benzene ring in a ground-state monosubstituted benzene may be expressed in terms of five functions of various combinations of the characteristic substituent parameters [equation (1)]. The analytical forms of

$$E(S_0) = g_1(S_0,\alpha_E) + g_2(S_0,\alpha_S) + g_3(S_0,\alpha_S^2) + g_4(S_0,P,\beta_D^2,\alpha_E,\alpha_S) + g_5(S_0,A,\beta_A^2,\alpha_E,\alpha_S) \quad (1)$$

these functions (labelled g functions) are given at the end of the section. The change in the energy of interaction on exciting benzene to an electronic state L_1 may also be expressed in terms of g functions [equation (2)]. By

$$E(L_1 - S_0) = g_1(L_1) - g_1(S_0) + g_2(L_1) - g_2(S_0) + g_3(L_1) - g_3(S_0) + g_4(L_1 - S_0) + g_5(L_1 - S_0) \quad (2)$$

combining equations (1) and (2) an expression for the energy of interaction in L_1 may be obtained [equation (3)].

$$E(L_1) = g_1(L_1) + g_2(L_1) + g_3(L_1) + g_4(L_1 - S_0) + g_4(S_0) + g_5(L_1 - S_0) + g_5(S_0) \quad (3)$$

When the substituent is a complex of a functional group and a reactant species (hereafter called a functional complex) the values of the characteristic substituent parameters are expected to change during the course of a reaction within the functional complex. As a consequence the substituent–hydrocarbon interaction energy

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[1] M. Godfrey, *J. Chem. Soc.* (*B*), 1971, 1540.

[2] M. Godfrey, *J. Chem. Soc.* (*B*), 1971, 1534.

changes by an amount ΔE. The equilibrium constant for the reaction depends on the value of ΔE. The relative equilibrium constants for corresponding reactions in L_1 and S_0 may be expressed in terms of $\Delta E(L_1)$ and $\Delta E(S_0)$ [equation (4)]. Δg Represents the

$$\begin{aligned}&-\log [K(L_1)/K(S_0)] = \\ &[\Delta E(L_1) - \Delta E(S_0)]/2{\cdot}303RT = \Delta E(L_1 - S_0)/2{\cdot}303RT = \\ &[\Delta g_1(L_1) - \Delta g_1(S_0) + \Delta g_2(L_1) - \Delta g_2(S_0) + \Delta g_3(L_1) - \\ &\Delta g_3(S_0) + \Delta g_4(L_1 - S_0) + \Delta g_5(L_1 - S_0)]/2{\cdot}303RT \qquad (4)\end{aligned}$$

change in the value of g due to the change in the values of the characteristic substituent parameters.

When there are two substituents, Y and Z, in the benzene ring equation (1) is modified as indicated in equation (5). Equations (2) and (3) are correspondingly modified.

$$\begin{aligned}E(S_0) = {} & g_1(S_0,\alpha_{E\mathrm{Y}},\alpha_{E\mathrm{Z}}) + g_2(S_0,\alpha_{S\mathrm{Y}},\alpha_{S\mathrm{Z}}) \\ & + g_3(S_0,\alpha_{S\mathrm{Y}}{}^2,\alpha_{S\mathrm{Z}}{}^2,\alpha_{S\mathrm{Y}},\alpha_{S\mathrm{Z}}) \\ & + g_4(S_0,P_{\mathrm{Y}},\beta_{D\mathrm{Y}}{}^2,\alpha_{E\mathrm{Y}},\alpha_{E\mathrm{Z}},\alpha_{S\mathrm{Y}},\alpha_{S\mathrm{Z}}) \\ & + g_4(S_0,P_{\mathrm{Z}},\beta_{D\mathrm{Z}}{}^2,\alpha_{E\mathrm{Y}},\alpha_{E\mathrm{Z}},\alpha_{S\mathrm{Y}},\alpha_{S\mathrm{Z}}) \\ & + g_5(S_0,A_{\mathrm{Y}},\beta_{A\mathrm{Y}}{}^2,\alpha_{E\mathrm{Y}},\alpha_{E\mathrm{Z}},\alpha_{S\mathrm{Y}},\alpha_{S\mathrm{Z}}) \\ & + g_5(S_0,A_{\mathrm{Z}},\beta_{A\mathrm{Z}}{}^2,\alpha_{E\mathrm{Y}},\alpha_{E\mathrm{Z}},\alpha_{S\mathrm{Y}},\alpha_{S\mathrm{Z}}) \qquad (5)\end{aligned}$$

When Z is a functional complex, the effect of Y relative to H (the hydrogen atom) on the equilibrium constant for a reaction within Z in any electronic state, is given by equation (6). The corresponding equation

$$\begin{aligned}\log [K(\mathrm{Y})/K(\mathrm{H})] &= [\Delta E(\mathrm{H,Z}) - \Delta E(\mathrm{Y,Z})]/2{\cdot}303RT \\ &= \Delta\Delta E/2{\cdot}303RT \qquad (6)\end{aligned}$$

for the effect of Y on the rate constant is (7), in which

$$\begin{aligned}\log [k(\mathrm{Y})/k(\mathrm{H})] &= [\Delta E^{\dagger}(\mathrm{H,Z}) - \Delta E^{\dagger}(\mathrm{Y,Z})]/2{\cdot}303RT \\ &= \Delta\Delta E^{\dagger}/2{\cdot}303RT \qquad (7)\end{aligned}$$

$\Delta E^{\dagger}$ represents the change in the substituent–hydrocarbon interaction energy in going from the initial state to the transition state of the reaction.

$\Delta\Delta E$ May be calculated from equations of the form of (8), (9), and (10) in which t represents a charge-transfer function and f represents a combined field and exchange function. The symbol $\mathrm{Z} - \mathrm{Z}'$ indicates that the characteristic substituent parameters of Z both before and after the reaction are involved in the function and ζ is a parameter characteristic of the benzene ring.

$$\begin{aligned}\Delta\Delta E(S_0) = {} & [t_1/t_2](S_0,\mathrm{Z} - \mathrm{Z}') \,.\, f_1(S_0,\mathrm{Y}) \\ & + \frac{t_1(S_0,\mathrm{Y}) \,.\, f_1(S_0,\mathrm{Z} - \mathrm{Z}')}{[t_2(S_0,\mathrm{Y}) + f_1(S_0,\mathrm{Z})][t_2(S_0,\mathrm{Y}) + f_1(S_0,\mathrm{Z}')]} \\ & + \zeta(S_0) \,.\, f_2(S_0,\mathrm{Y}) \,.\, f_2(S_0,\mathrm{Z} - \mathrm{Z}') \\ & \equiv \mathrm{A}(S_0) + \mathrm{B}(S_0) + \mathrm{C}(S_0) \qquad (8)\end{aligned}$$

$$\begin{aligned}\Delta\Delta E(L_1 - S_0) = {} & [t_1/t_2](L_1 - S_0,\mathrm{Z} - \mathrm{Z}') \,.\, f_1(L_1,\mathrm{Y}) \\ & + \frac{t_1(L_1 - S_0,\mathrm{Y}) \,.\, f_1(L_1,\mathrm{Z} - \mathrm{Z}')}{[t_2(L_1 - S_0,\mathrm{Y}) + f_1(L_1,\mathrm{Z})][t_2(L_1 - S_0,\mathrm{Y}) + f_1(L_1,\mathrm{Z}')]} \\ & + [\zeta(L_1) - \zeta(S_0)] \,.\, f_2(S_0,\mathrm{Y}) \,.\, f_2(S_0,\mathrm{Z} - \mathrm{Z}') \\ & \equiv \mathrm{A}(L_1 - S_0) + \mathrm{B}(L_1 - S_0) + \mathrm{C}(L_1 - S_0) \qquad (9)\end{aligned}$$

$$\begin{aligned}\Delta\Delta E(L_1) = {} & [t_1/t_2](L_1 - S_0,\mathrm{Z} - \mathrm{Z}') \,.\, f_1(L_1,\mathrm{Y}) \\ & + [t_1/t_2](S_0,\mathrm{Z} - \mathrm{Z}') \,.\, f_1(S_0,\mathrm{Y}) \\ & + \frac{t_1(L_1 - S_0,\mathrm{Y}) \,.\, f_1(L_1,\mathrm{Z} - \mathrm{Z}')}{[t_2(L_1 - S_0,\mathrm{Y}) + f_1(L_1,\mathrm{Z})][t_2(L_1 - S_0,\mathrm{Y}) + f_1(L_1,\mathrm{Z}')]} \\ & + \frac{t_1(S_0,\mathrm{Y}) \,.\, f_1(S_0,\mathrm{Z} - \mathrm{Z}')}{[t_2(S_0,\mathrm{Y}) + f_1(S_0,\mathrm{Z})][t_2(S_0,\mathrm{Y}) + f_2(S_0,\mathrm{Z}')]} \\ & + \zeta(L_1) \,.\, f_2(S_0,\mathrm{Y}) \,.\, f_2(S_0,\mathrm{Z} - \mathrm{Z}') \\ & \equiv \mathrm{A}(L_1) + \mathrm{B}(L_1) + \mathrm{C}(L_1) \qquad (10)\end{aligned}$$

$\Delta\Delta E^{\dagger}$ Is assumed to be related to $\Delta\Delta E$ for the same reaction in a novel way. The relationship is defined by equation (11) in which γ_1 and γ_2 are constants, with values between zero and unity, for a given reaction within a particular Z. When both γ_1 and γ_2 have values of unity $\Delta\Delta E^{\dagger}$ is equal to $\Delta\Delta E$. The basis of equation (11) is that the charge-transfer effect of the functional complex does not vary with distance along the reaction path in the same way that the corresponding field effect does. In order to explain certain experimental data we have proposed[3] that in the early stages of the rupture of a covalent bond within a functional complex, the charge-transfer effect of the functional complex changes much more rapidly than the combined exchange and field effects. As a consequence if the transition state is reached during the early stages of bond rupture then γ_1 should have a very much greater value than γ_2. But the more advanced the bond rupture is at the transition state, the bigger the $\gamma_2 : \gamma_1$ ratio should be.

$$\Delta\Delta E^{\dagger}(N) = \gamma_1\mathrm{A}(N) + \gamma_2[(\mathrm{B} + \mathrm{C})](N) \qquad (11)$$

Parameters ρ^0 and σ^0 may be defined by equations (12) in which κ is simply a scaling constant ($-0{\cdot}64$/eV) which brings our σ^0 for ground state reactions into direct comparison with the empirical σ^0 defined by Taft.[4]

$$\rho^0(N) = [\gamma_1(N)/2{\cdot}303RT\kappa] \times [t_1/t_2](N,\mathrm{Z} - \mathrm{Z}') \qquad (12a)$$

$$\sigma^0(N) = \kappa f_1(N,\mathrm{Y}) \qquad (12b)$$

We now express the functions g, t, and f in terms of the characteristic substituent parameters. Parameters characteristic of the benzene ring, of which ζ and I are examples, have been evaluated on the assumption that the substituent parameters are in units of the electron volt. The subscript μ labels a ring carbon atom to

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[3] M. Godfrey, *Tetrahedron Letters*, 1972, 753.

[4] R. W. Taft, *J. Phys. Chem.*, 1960, **64**, 1805.

which a substituent is attached. The subscript ν labels any ring carbon atom including μ. q_ν Represents the π-electronic charge on atom ν. Note that the values of g_1 and g_2 are independent of the nature of the electronic state. The subscript 0 labels the π-electronic ground state of unsubstituted benzene and the subscript l labels any corresponding excited state. The subscripts d and a label any one-electron charge-transfer state in which the substituent is respectively an electron donor or an electron acceptor. $\overline{E_0 - E_d}$ and $\overline{E_0 - E_a}$ represent the average values of the energy differences between all appropriate charge-transfer states and the localized ground state. C Represents the electrostatic interaction between a transferred electron and the positive hole it leaves behind. The expressions for $g_4(L_1 - S_0)$ and $g_5(L_1 - S_0)$ reflect the prediction that charge-transfer states involving the simultaneous promotion of one electron within the benzene ring and transfer of another electron between the benzene ring and the substituent, cause a stabilization in L_1 which is equal to the stabilization produced in S_0 by the effects of the one-electron charge-transfer states.[5] The values of the functions f_1, ζ, and I depend on the relative positions of the Y and Z substituents within the benzene ring. The subscripts p and m indicate that Y is respectively *para* and *meta* to Z. Calculated values of ζ and of I are listed in Table 1.

TABLE 1

Calculated values of $\zeta/10^{-3}$ eV and of I*$/10^{-3}$ eV^2

State	ζ_m	ζ_p	$\zeta_p - \zeta_m$	I
S_0	3	−24	−27	63
T_1	−12	−24	−12	12
S_1	−52	64	116	88

* For a single substituent.

$$g_1(N) = \sum_\nu q_\nu(N)\alpha_E = 6\alpha_E \quad (13)$$

$$g_2(N) = q_\mu(N)\alpha_S = \alpha_S \quad (14)$$

$$g_3(N) = I(N)\alpha_S{}^2 \quad (15)$$

$$g_4(S_0) = \tfrac{2}{3}\beta_D{}^2/(\overline{E_0 - E_d}) \qquad g_4(L_1 - S_0) = \tfrac{1}{6}\beta_D{}^2/(E_l - E_d) \quad (16)$$

$$E_0 - E_d = (P - A_d + C_d) + \sum_\nu (q_{\nu d} - q_{\nu 0})\alpha_E + (q_{\mu d} - q_{\mu 0})\alpha_S \quad (17)$$

$$g_5(S_0) = \tfrac{2}{3}\beta_A{}^2/(\overline{E_0 - E_a}) \qquad g_5(L_1 - S_0) = \tfrac{1}{6}\beta_A{}^2/(E_l - E_a) \quad (18)$$

$$E_0 - E_a = (P_a - A + C_a) + \sum_\nu (q_{\nu a} - q_{\nu 0})\alpha_E + (q_{\mu a} - q_{\mu 0})\alpha_S \quad (19)$$

$$t_1(S_0) = \tfrac{2}{3}\beta_D{}^2 \qquad t_2(S_0) = \overline{(E_0 - E_d)}^2 \quad (20)$$

$$f_{1\mathrm{p}}(S_0) = \tfrac{5}{12}\alpha_S + \tfrac{2}{3}\alpha_E \qquad f_{1\mathrm{m}}(S_0) = \tfrac{1}{6}\alpha_S + \tfrac{3}{2}\alpha_E \quad (21)$$

$$t_1(L_1 - S_0) = \tfrac{1}{6}\beta_D{}^2 \qquad t_2(L_1 - S_0) = (E_l - E_d)^2 \quad (22)$$

$$f_{1\mathrm{p}}(T_1) = \tfrac{1}{3}\alpha_S + \alpha_E \qquad f_{1\mathrm{m}}(T_1) = \tfrac{1}{12}\alpha_S + \alpha_E \quad (23)$$

$$f_{1\mathrm{p}}(S_1) = \alpha_E \qquad f_{1\mathrm{m}}(S_1) = \tfrac{1}{4}\alpha_S + \alpha_E \quad (24)$$

$$f_2(N) = \alpha_S \quad (25)$$

Applications of Theory.—We now report five applications of our theory each of which leads to a novel explanation or prediction of chemical behaviour.

(*a*) We have calculated the effects of excitations from S_0 to S_1 and from S_0 to T_1, on the equilibrium constant for the dissociation of phenol. We used equation (4) and the values of substituent parameters listed in Table 2. The results of our calculations indicate that log K should be quite similar in value in S_0 and T_1 but very different in S_0 and S_1. This prediction, which matches experiment,[6] reflects the fact that the values of $[\Delta g_4 + \Delta g_5](L_1 - S_0)$ and $\Delta g_3(L_1) - \Delta g_3(S_0)$ have the same sign for the S_0 to S_1 excitation but opposite signs for the S_0 to T_1 excitation. Since the values of g_1 and of g_2 are independent of the nature of the electronic state, both $\Delta g_1(L_1) - \Delta g_1(S_0)$ and $\Delta g_2(L_1) - \Delta g_2(S_0)$ must be equal to zero.

TABLE 2

FCT parameter values for OH and for O$^-$

Substituent	α_E/kK	α_S/kK	$\beta_D{}^2$/eV^2	P/eV
OH	0·5	10	4	12
O$^-$	−2	13	4	10

The idea that the charge-transfer effects of the functional group contribute significantly to the overall effects of excitations on the equilibrium constant for a reaction is not new.[5] The present work shows that the combined field and exchange effects of the functional group contribute to a comparable degree.

(*b*) Equation (26) is the appropriate expression for $\log[k(L_1,\mathrm{Y})/k(L_1,\mathrm{H})]$ in reactions for which $\gamma_2(L_1)[\mathrm{B} + \mathrm{C}](L_1)$ is very much smaller than $\gamma_1(L_1)\mathrm{A}(L_1)$. The condition is met not only when γ_2 is very much smaller than γ_1 or when B and C tend to cancel out, but also when B and C are small because the changes in the combined exchange and field effects of the functional complex are small. The changes in field effect must be small when during the reaction there is no net flow of charge within that region of the functional complex which is close to the benzene ring. When comparing equation (26) with equations (12) we noticed that the relationship (27) is *not* valid. The types of linear free energy relationship which are found among reactions in S_0 are not therefore expected to be found among reactions in L_1.

$$\log[k(L_1,\mathrm{Y})/k(L_1,\mathrm{H})] = \{\gamma_1(L_1)\cdot[t_1/t_2](L_1 - S_0,\mathrm{Z} - \mathrm{Z}')\cdot f_1(L_1,\mathrm{Y})\}/2{\cdot}303RT + \{\gamma_1(L_1)\cdot[t_1/t_2](S_0,\mathrm{Z} - \mathrm{Z}')\cdot f_1(S_0,\mathrm{Y}\}/2{\cdot}303RT \quad (26)$$

$$\log[k(L_1,\mathrm{Y})/k(L_1,\mathrm{H})] = \rho^0(L_1)\sigma^0(L_1) \quad (27)$$

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[5] M. Godfrey and J. N. Murrell, *Proc. Roy. Soc.*, 1964, *A*, **278**, 71.

[6] E. L. Wehry and L. B. Rogers, *J. Amer. Chem. Soc.*, 1965, **87**, 4234.

(*c*) We noticed that by expanding equation (12b) in terms of the characteristic substituent parameters we could obtain equations (28) and hence equations (29).

$$
\begin{aligned}
[\sigma_p{}^0 - \sigma_m{}^0](S_0) &= \tfrac{1}{4}\kappa\alpha_S \\
[\sigma_p{}^0 - \sigma_m{}^0](T_1 - S_0) &= \tfrac{1}{4}\kappa\alpha_S \\
[\sigma_p{}^0 - \sigma_m{}^0](S_1 - S_0) &= -\tfrac{1}{4}\kappa\alpha_S \qquad (28)
\end{aligned}
$$

$$
\begin{aligned}
[\sigma_p{}^0 - \sigma_m{}^0](T_1 - S_0) &= [\sigma_p{}^0 - \sigma_m{}^0](S_0) \\
[\sigma_p{}^0 - \sigma_m{}^0](S_1 - S_0) &= -[\sigma_p{}^0 - \sigma_m{}^0](S_0) \qquad (29)
\end{aligned}
$$

From equations (12) and (26) we obtained equation (30)

$$
\begin{aligned}
\log\,[k(L_1,p\text{-Y})/k(L_1,m\text{-Y})] \\
= \rho^0(L_1 - S_0)[\sigma_p{}^0 - \sigma_m{}^0](L_1 - S_0) + \\
\rho^0(S_0)[\sigma_p{}^0 - \sigma_m{}^0](S_0) \qquad (30)
\end{aligned}
$$

which like equation (26) is valid only for reactions for which $\gamma_2(L_1)[\mathrm{B} + \mathrm{C}](L_1)$ is very much smaller than $\gamma_1(L_1)\mathrm{A}(L_1)$. Substituting for $[\sigma_p{}^0 - \sigma_m{}^0](L_1 - S_0)$ in equation (30) we obtained equation (31). This can be used to obtain the expression (32) for comparing the relative effects of *para*- and *meta*-Y substituents in two reactions, one in L_1 and one in S_0, each with the same value of γ_1. In both equation (31) and equation (32)

$$
\begin{aligned}
\log\,[k(L_1,p\text{-Y})/k(L_1,m\text{-Y})] \\
= \{\rho^0(S_0) \pm \rho^0(L_1 - S_0)\}[\sigma_p{}^0 - \sigma_m{}^0](S_0) \qquad (31)
\end{aligned}
$$

$$
\begin{aligned}
\log\,[k(L_1,\mathrm{Z}_1,p\text{-Y})/k(L_1,\mathrm{Z}_1,m\text{-Y})]/ \\
\log\,[k(S_0,\mathrm{Z}_2,p\text{-Y})/k(S_0,\mathrm{Z}_2,m\text{-Y})] \\
= [\rho^0(\mathrm{Z}_1,S_0) \pm \rho^0(\mathrm{Z}_1,L_1 - S_0)]/\rho^0(\mathrm{Z}_2,S_0) \qquad (32)
\end{aligned}
$$

$\rho^0(S_0)$ and $\rho^0(L_1 - S_0)$ should be added when L_1 is T_1 and subtracted when L_1 is S_1.

Suppose that $\rho^0(\mathrm{Z}_1,S_0)$, $\rho^0(\mathrm{Z}_2,S_0)$, and $\rho^0(\mathrm{Z}_1,L_1 - S_0)$ all have the same sign. Then when L_1 is T_1 the sign of $\log\,[k(p\text{-Y})/k(m\text{-Y})]$ for any Y should be the same in the two reactions. But when L_1 is S_1 the sign of $\log\,[k(p\text{-Y})/k(m\text{-Y})]$ should be different in the two reactions when $\rho^0(\mathrm{Z}_1,S_1 - S_0)$ has a greater absolute value than $\rho^0(\mathrm{Z}_1,S_0)$.

(*d*) We noticed that $[\mathrm{C}_p - \mathrm{C}_m](L_1)$, like $[\mathrm{A}_p - \mathrm{A}_m](L_1)$, is directly proportional to $[\sigma_p{}^0 - \sigma_m{}^0](S_0)$. When $\gamma_2\mathrm{C}(L_1)$ is very much greater than $[\gamma_1\mathrm{A} + \gamma_2\mathrm{B}](L_1)$ equation (33) should hold approximately. Since the

$$
\begin{aligned}
\log\,[k(L_1,p\text{-Y})/k(L_1,m\text{-Y})] \\
= \gamma_2(L_1)\,.\,[\mathrm{C}_p - \mathrm{C}_m](S_1) \\
= 4\gamma_2(L_1)\,.\,[\zeta_p - \zeta_m](L_1)\,.\,\alpha_S(\mathrm{Z} - \mathrm{Z}')\,. \\
[\sigma_p{}^0 - \sigma_m{}^0](S_0)/2{\cdot}303RT \qquad (33)
\end{aligned}
$$

absolute value of $[\zeta_p - \zeta_m]$ is very much greater in S_1 than in S_0, the condition is likely to be met in real situations when L_1 is S_1 and the $\gamma_2 : \gamma_1$ ratio is not very small.

Applying the equation to the dissociation of phenols ($\gamma_2 = \gamma_1 = 1$) we predict that $\log\,[K(S_1,p\text{-Y})/K(S_1,m\text{-Y})]$ should be approximately equal to about four times the value of $[\sigma_p{}^0 - \sigma_m{}^0](S_0)$ for most Y groups. The experimental data[6] listed in Table 3 are in reasonable agreement with this prediction.

TABLE 3

A comparison of measured values of $\Delta\mathrm{p}K_\mathrm{a}$ for phenols with $\sigma_p{}^0 - \sigma_m{}^0$

	$\mathrm{p}K_\mathrm{a}(p\text{-Y}) - \mathrm{p}K_\mathrm{a}(m\text{-Y})$		
Substituent	S_1	S_1/S_0	$\sigma_p{}^0 - \sigma_m{}^0$
OMe	1·0	1·7	−0·25
F	0·6	0·9	−0·18
Br	0·3	1·0	−0·10
Me	0·3	1·5	−0·08

The slope of $\log\,[K(S_1,p\text{-Y})/K(S_1,m\text{-Y})]$ against $[\sigma_p{}^0 - \sigma_m{}^0](S_0)$ is positive. For the ground state dissociation of phenols $\log\,[K(p\text{-Y})/K(m\text{-Y})]$ *versus* $\sigma_p{}^- - \sigma_m{}^-$ also has a positive slope. Since $\sigma_p{}^- - \sigma_m{}^-$ usually has the same sign as $[\sigma_p{}^0 - \sigma_m{}^0](S_0)$, for most substituents the ratio of $\log\,[K(S_1,p\text{-Y})/K(S_1,m\text{-Y})]$ to $\log\,[K(S_0,p\text{-Y})/K(S_0,m\text{-Y})]$ should be positive. This prediction is supported by the data in Table 3.

Since $[\zeta_p - \zeta_m](T_1)$ is small, equation (33) cannot be applied legitimately to the calculation of $\log\,[K(T_1,p\text{-Y})/K(T_1,m\text{-Y})]$.

(*e*) By combining equations (31) and (33) we obtained an expression [(34)] for $\log\,[k(L_1,p\text{-Y})/k(L_1,m\text{-Y})]$ when $\gamma_1\mathrm{A} + \gamma_2\mathrm{C}$ is very much greater than $\gamma_2\mathrm{B}$. We expect this condition to be met commonly when L_1 is S_1, and therefore equation (34) should be useful for predicting values of $\log\,[k(S_1,p\text{-Y})/k(S_1,m\text{-Y})]$.

$$
\begin{aligned}
\log\,[k(L_1,p\text{-Y})/k(L_1,m\text{-Y})] \\
= \{\rho^0(S_0) \pm \rho^0(L_1 - S_0) + \\
4\gamma_2[\zeta_p - \zeta_m](L_1)\,.\,\alpha_S(\mathrm{Z} - \mathrm{Z}')\}[\sigma_p{}^0 - \sigma_m{}^0](S_0) \\
= \rho(L_1)[\sigma_p{}^0 - \sigma_m{}^0](S_0) \qquad (34)
\end{aligned}
$$

The sign of $\log\,[k(p\text{-OMe})/k(m\text{-OMe})]$ for solvolysis reactions of some benzyl derivatives in the S_1 state has been found to be the opposite of that found in ground state solvolysis reactions of similar compounds.[7] For these reactions Z is a weak electron donor with a small value of α_S whereas Z′ is a strong electron acceptor with a large negative value of α_S. Therefore each of $\rho^0(S_0)$, $\rho^0(S_1 - S_0)$, and $[\zeta_p - \zeta_m](S_1)\alpha_S(\mathrm{Z} - \mathrm{Z}')$ should have a negative value. The empirical $\rho(S_0)$ is negative and therefore $\rho(S_1)$ must be positive. In order that $\rho(S_1)$ might be positive $\{\rho^0(S_1 - S_0) - 4\gamma_2[\zeta_p - \zeta_m](S_1)\,.\,\alpha_S(\mathrm{Z} - \mathrm{Z}')\}$ must have a greater absolute value

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[7] H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, 1963, **85**, 915.

than $\rho^0(S_0)$. Because $\zeta_p - \zeta_m$ is so large this condition can be met only if γ_2 is small.

For the dissociation of phenols in the T_1 state γ_2B is *not* very much smaller than γ_1A + γ_2C for all Y, and therefore equation (**34**) cannot be applied to the prediction of values of log $[K(T_1,p\text{-Y})/K(T_1,m\text{-Y})]$.

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