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BIMOLECULAR NUCLEOPHILIC SUBSTITUTION AT A RESONANCE-STABILIZED CARBENIUM ION: ELEVATED VALUE OF CROSS-INTERACTION CONSTANT, IMBALANCED TRANSITION STATE AND THE NON-INTERACTIVE PHENOMENON

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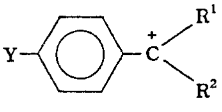
A characteristic feature in the bimolecular nucleophilic substitution reactions at a resonance-stabilized carbenium ion has been shown to be an imbalanced transition state resulting in an elevated value of the cross-interaction constant, which in turn leads to a non-interactive phenomenon. Examples of the reactions of ring-substituted phenylethyl and benzhydryl cations are given.

INTRODUCTION

There has been continuing interest in nucleophilic substitution reactions involving a highly resonance-stabilized carbenium ion centre. Tidwell and coworkers[1] have shown that a strong electron-withdrawing α-substitutuent, e.g. CF_3, on the benzylic carbon induces a strong resonance demand leading to a large negative ρ^+ value in solvolysis. Similarly, the resonance demand parameter, r in equation (1), is found to increase with the electron-withdrawing power, $\Sigma\sigma^*$, of the α-substituents and there exists an approximate linearity between r and $\Sigma\sigma$.[2]

$$\log(k/k_0) = \rho[\sigma^0 + r(\sigma^+ - \sigma^0)] \qquad (1)$$

On the other hand, Amyes *et al.*[3] have shown that replacement of the α-CH_3 group with an α-CF_3 in a 4-methoxybenzyl cation, **I**, with $Y = CH_3O$, $R^1 = H$ and $R^2 = CH_3$ or CF_3, has a large thermodynamic destabilizing polar effect, which is however offset by increased resonance electron donation from the 4-methoxybenzyl ring to the benzylic carbon. The electron-withdrawing polar effect of the α-substituent, R^1 and/or R^2, has been postulated to force the positive charge away from the benzylic carbon on to the oxygen of the 4-methoxy group. Theoretically it has been shown[4] that there is a good linear correlation between the increment of positive charge, $\Delta q = q_{(\text{cation})} - q_{(\text{reactant})}$, on C-$\alpha$ and on the oxygen of the 4-methoxy group with the electron-withdrawing power of the α-substituents, $\Sigma\sigma^*$.



I

In this work, we show that the bimolecular nucleophlic substitution reactions at such a resonance-stabilized carbenium ion centre (S_N2C^+ mechanism) is characterized by a strong interaction between the nucleophile and the carbenium ion with an elevated value of the cross-interaction constant, ρ_{XY}, in the equation

$$\log(k_{XY}/k_{HH}) = \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \qquad (2)$$

where X and Y denote the substituents in the nucleophile and substrate, respectively. This is result of an imbalanced transition state (TS)[5] obtained in such a reaction. A closely related phenomenon to this type of process is a manifestation of the sign reversal of ρ_X (ρ_{NUC}) to $\rho_X > 0$ from the normal $\rho_X < 0$.[6] Since the origin of this sign reversal of ρ_X is the TS imbalance which is related to the resonance structure of the carbenium ion, an increase in the electron demand by a stronger electron-withdrawing α-substituent, R^1 and/or R^2, is expected to strengthen such an effect.

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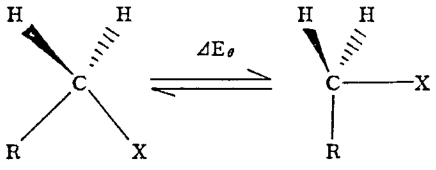
TS IMBALANCE AND ELEVATED ρ_{XY}

Mitchell *et al.*[7] have shown MO theoretically that the energy required to bend an H—C—X (or R—C—X) angle of the sp^3-hybridized carbon centre, **II**, to form an sp^2 carbon centre, **III**, is substantial, 30–70 kcal mol^{-1} (1 kcal = 4·184 kJ) for reactions $X^- + CH_3X \rightarrow XCH_3 + X^-$ with X = H, F, Cl, etc., and forms a part of deformation energy needed to reach the TS in the S_N2 reaction. The deformation energy has been shown to be correlated linearly with the intrinsic barrier, $\Delta E_0^{\neq}$, which is the activation barrier for an identity S_N2 reaction. According to the Marcus equation:[8]



II **III**

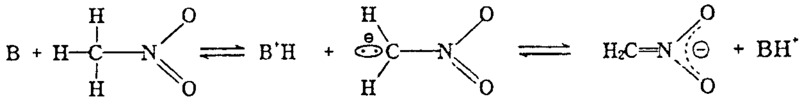
$$\Delta E^{\neq} = \Delta E_0^{\neq} + \tfrac{1}{2}\Delta E^0 + \frac{(\Delta E^0)^2}{16\,\Delta E_0^{\neq}} \qquad (3)$$

the energy barrier, $\Delta E^{\neq}$, for this type of reaction, is the intrinsic barrier, $\Delta E_0^{\neq}$, since an identity S_N2 reaction is thermoneutral, i.e. the thermodynamic barrier, ΔE^0, is zero.

Thus the bending deformation from **II** to **III** is an intrinsically endoergic process. However, this energy is lowered by the stretch of the C—X bond, which proceeds concertedly with the angular deformation in the S_N2 process.[7] If the R group in **II** and **III** is a π-system, the sp^2 form, **III**, will be stabilized by resonance interaction between the C—X bond and the π-orbitals of R; hence form **III** becomes thermodynamically more stable than **II**. In effect, the transformation from **II** to **III** is an intrinsically slow but thermodynamically more favourable process, curves A in Figure 1. The reverse process, **III** → **II**, is in contrast intrinsically fast but thermodynamically unfavourable, curves B in Figure 1. These two cases can be illustrated schematically as in Figure 1.

This kind of situation is indeed encountered in the so-called nitroalkane anomaly[9] and in the S_N1 solvolytic processes of benzyl derivatives.[10] It is well known that resonance development of type **V** in the partially deprotonated TS for the deprotonation of nitromethane is so slow that actually form **IV** may exist as a possible intermediate.[9] Similarly in the S_N1 solvolytic processes of the benzylic derivatives, in which the resonance-stabilized carbenium ion **I** is formed, the resonance development is an intrinsically very slow process so that the intrinsic rate is greatly lowered.[10]

In the reverse direction, **III** → **II** (or **V** → **IV**), the loss of resonance as the TS is reached for the attack of nucleophile on the carbenium ion (or attack of proton on the carbanion) is intrinsically exoergic and hence is fast, but thermodynamically the process is unfavourable. This means that there is an imbalance in



IV **V**

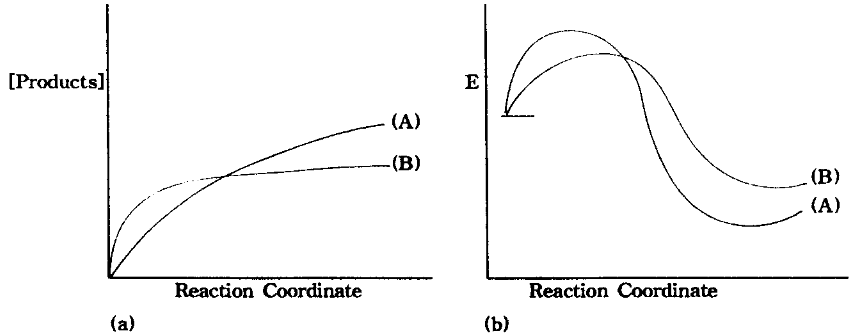


Figure 1. Schematic presentation of intrinsic and thermodynamic barriers involved in **II** ⇌ **III**

the expression of polar and resonance substituent effects; this imbalance will lead to a relatively larger expression of the resonance effect in the initial stages of bond making compared with the expression of the polar effect for the nucleophilic attack on the carbenium ion and a relatively smaller expression in the final stages of the reaction after the TS has been reached. For example, on reacting a triarylmethyl cation with water, 73% of the resonance interaction between the substituent and the charge has disappeared at the TS but only 33% of the polar interaction has disappeared.[11] Similarly in the reaction of the 1-arylethyl cation, 56% of the resonance interaction but 36% of the polar interaction have been shown to have lost in the TS.[10]

Partial bond formation of the carbenium ion to the nucleophile in the TS, N···C-α^+, leads to a localized (sp^3) fractional positive charge on the central carbon, increasing the ionic character of the TS and attenuating the resonance interaction more than the polar interaction.[12] The resonance-stabilized carbenium ions are less electrophilic owing to a lower, delocalized, positive charge on the reaction centre carbon and a higher π^* LUMO, e.g. the 4-methoxy-1-phenylethyl carbenium ion has a nearly 1 eV higher π^* LUMO than the 4-nitro compound ($-6\cdot2808$ vs $-7\cdot2786$ eV by AM1[13]); this means that they can react only with a σ_n HOMO of the nucleophile which is elevated to a higher level by deprotonation and also by progressing further along the reaction coordinate, i.e. by a very close approach to the σ_n orbital of the nucleophile (extensive bond making).[14] It is well known that in the reactions of stable carbenium ions with water, a second water molecule acts as a general base which deprotonates the nucleophile, water, partially in the TS.[15] The more resonance stabilized is the carbenium ion, the less electrophilic it becomes and requires a greater degree of nucleophile deprotonation.

Extensive bond making and an increased ionic character in the imbalanced TS for the reactions of stable carbenium ions with nucleophiles lead invariably to a stronger interaction between the carbenium ion and the nucleophile. This results in an elevated value of the cross-interaction constants, ρ_{XY}, between substituents Y in the carbenium (substrate) ion and X in the nucleophile [equation (2)]; in the normal S_N2 reactions the magnitude of ρ_{XY} is a measure of the degree of bond making in the TS.[16] On the other hand, proton transfer is a fast process (in most cases diffusion limited),[15] whereas N—C-α bond making is a relatively slow process (activation limited) so that positive charge development can be small or negative charge can develop on the nucleophile; the negative charge left behind on N by a fast proton transfer from N can exceed the amount of electronic charge transferred from N to C-α in the N—C-α bond formation.

As a result, an elevated, i.e. a large, $|\rho_{XY}|$ together with a small ρ_X can lead to an observation of the non-interactive point,[6] $\hat{\sigma}_Y$, at which $\rho_X = 0$ and ρ_X changes sign; ρ_X is positive for $\sigma_Y < \hat{\sigma}_Y$ and ρ_X is negative for $\sigma_Y > \hat{\sigma}_Y$. Equation (2) can be transformed into an isokinetic expression at $\hat{\sigma}_Y$:

$$\log(k_{XY}/k_{HH}) = \rho_Y\sigma_Y + (\rho_X + \rho_{XY}\sigma_Y)\sigma_X$$

$$= \rho_Y\hat{\sigma}_Y = -\frac{\rho_X\rho_Y}{\rho_{XY}} = \text{constant} \qquad (4)$$

where

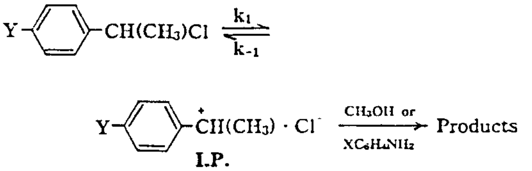
$$\hat{\sigma}_Y = -\frac{\rho_X}{\rho_{XY}} \qquad (5)$$

Equation (5) shows that $\hat{\sigma}_Y$ can be observable or realizable only when $|\rho_{XY}|$ is large and $|\rho_X|$ is relatively small so that the $\hat{\sigma}_Y$ value falls within the observable range of substituent constants σ, i.e. $-1\cdot0$ to $+1\cdot0$, which are normally used in the studies of organic reaction mechanisms.[6,17]

Hence on reacting a resonance-stabilized cation with a nucleophile, the loss of the resonance interaction is more than that of the polar interaction in the TS in which a greater degree of bond making between the cation and nucleophile has progressed with a larger degree of nucleophile deprotonation than those expected from a hypothetical TS where no such imbalance occurs. As a result, an elevated $|\rho_{XY}|$ is obtained and a non-interactive point, $\hat{\sigma}_Y$, becomes observable or realizable.

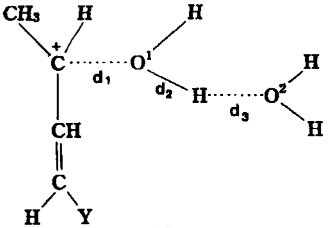
REACTIONS OF 1-PHENYLETHYL CHLORIDES IN METHANOL

This reaction has been shown to proceed by an ion-pair (S_N2C^+) mechanism:[17]



(6)

In the reaction with methanol, the carbenium ion of the tight ion pair, I.P., reacts with MeOH in the rate-limiting step. The solvent isotope effects, k_{CH_3OH}/k_{CH_3OD},[17a] are greater than unity for the electron-donating Y substituents but they are less than unity for the electron-withdrawing Y substituents. This is in line with the fact that the resonance-stabilized carbenium ion requires general base catalysis, i.e. partial deprotonation of the nucleophile, CH_3OH, by a second molecule of CH_3OH. This general base catalysis is, however, not needed for the localized cation formed with an electron-withdrawing Y substituent; in this case only the desolvation of the nucleophile, CH_3OH, is required. The deprotonation of CH_3OH leads to a



VI

Scheme 1

primary kinetic isotope effect, $k_{CH_3OH}/k_{CH_3OD} > 1·0$, whereas the desolvation process results in an inverse secondary kinetic isotope effect, $k_{CH_3OH}/k_{CH_3OD} < 1·0$. We have shown these two types of solvent effects by MO calculations using an allyl system, **VI**, as a model for the 1-phenylethyl system. Gas phase studies on such a process as in Scheme 1 fail since such a system merely leads to a simple addition of water to **VI**. We therefore simulated the solution-phase process by applying the self-consistent reaction field (SCRF) method[18] with a dielectric constant of 78·54 for water.

The SCRF method has been shown to be very useful in simulating a solution-phase process by applying a constant dielectric continuum around the gas-phase TS.[19] The results of our RHF/3–21G[20] calculations are given in Table 1. In this computation, all geometries were fully optimized and the TSs were characterized by confirming only one negative eigenvalue in the Hessian matrix.[21] We note that a strong electron-donating substituent, Y = NH_2, requires general base catalysis, i.e. partial deprotonation ($\Delta d_2 > 0$ and $\Delta d_3 < 0$) of the water nucleophile, whereas when there is no substituent, Y = H, only the desolvation ($\Delta d_3 > 0$) of the water nucleophile is required. In the former a later TS with a greater degree of C—O bond making is obtained; the C—O distance is *ca* 0·6 Å shorter in the TS with the resonance-stabilized cation (Y = NH_2). The deprotonation with an advanced degree of bond making in the resonance-stabilized carbenium ion reaction supports the interpretation of the results of the solvent isotope effect studies above.

The reaction of 1-phenylethyl cation with the aniline nucleophile exhibits a similar behaviour.[17b] In this case, the kinetic isotope effects, k_H/k_D, with deuterated anilines are all greater than unity, indicating that general base catalysis, i.e. partial deprotonation of aniline, also takes place. According to our AM1 computations, the deprotonation energies are 360·04, 333·45 and 313·78 kcal mol^{-1} for H_2O, CH_3OH and $C_6H_4NH_2$, respectively, so that the deprotonation should be a feasible process for the aniline molecule as for methanol.

In this reaction of 1-phenylethyl chlorides with anilines [equation (6)], the ρ_{XY} values observed are $-2·05$ and $-1·34$ for the electron-donating and -withdrawing Y substituents, respectively.[17b] The difference in the magnitude of the two ρ_{XY} values should certainly reflect the elevated nature of the resonance-stabilized carbenium ion reaction (for Y = electron-donating substituents). Thus the difference, $-2·05-(-1·34)=-0·71$, represents the fractional loss of resonance interaction in excess of the fractional loss of polar interaction in the TS, which is given by $(\rho_{XY})_{EWS} = -1·34$. Therefore, the exalted fractional loss of resonance interaction is approximately half of the fractional loss of polar interaction ($0·71/1·34 \approx 0·53$), in almost fortuitous agreement with the amount proposed by Kresge.[9a] Owing to this large magnitude of ρ_{XY} observed for the electron-donating Y substituents, at $\hat{\sigma}_Y = -(-0·47/-2·05) = -0·23$ [equation (5)] the Hammett reaction constant for the aniline nucleophile, ρ_X, becomes zero, and for substituents with σ_Y below this value of $-0·23$ ρ_X is now positive whereas for substituents with σ_Y higher than this value ($-0·23$) ρ_X is negative.[17b] Since in an S_N2 TS the nucleophile transfers electronic charge towards the substrate reaction centre, C-α^+, normally a negative ρ_X is expected as observed for $\sigma_Y > \hat{\sigma}_Y$, and hence it is highly unusual to obtain the positive ρ_X for $\sigma_Y < \hat{\sigma}_Y$. At the non-interactive point of $\hat{\sigma}_Y = -0·23$, cross-interaction between the nucleophile and the substrate cation disappears, i.e. non-interactive, and the reactivity becomes constant i.e. isokinetic [equation (4)], with $\rho_X = 0$.

This is clearly not a result of the desolvation effect of the aniline nucleophile. According to Abraham,[22] the solute hydrogen bond basicity of the aniline nucleophiles (most of them used in the study) is smaller than that of the solvent methanol, so that any desolvation that takes place in the reaction should be an

Table 1. SCRF RHF/3–21G calculations with $\varepsilon = 78·54$ for the system shown in Scheme 1

	Y = NH_2			Y = H		
	d_1	d_2	d_3	d_1	d_2	d_3
Reactant cation	3·2414	0·9788	1·7860	2·8764	0·9846	1·6889
TS	2·0698	0·9906	1·6506	2·6983	0·9842	1·6936
$\Delta d^{\neq}$ (Å)	−1·1716	+0·0118	−0·1354	−0·1782	−0·0004	+0·0047
$\Delta E^{\neq}$ (kcal mol^{-1})	8·34			2·24		

exoergic process, i.e. the desolvation of the nucleophile will be a barrierless process and hence it will have no effect on the rate of reaction.

The appearance of the non-interactive point, $\hat{\sigma}_Y = -0{\cdot}23$, at which ρ_X changes sign, is a true reflection of charge reversal at the N atom of the aniline. This can be interpreted as follows. Since in the nucleophilic substitution reaction of a resonance-stabilized carbenium ion an imbalanced TS is obtained with an elevated degree of nucleophile deprotonation and of bond making, negative charge accumulates on the N atom leading to a positive ρ_X. This type of phenomenon will not be manifested unless the carbenium ion is resonance stabilized and the TS is imbalanced, in which the diffusion-controlled proton transfer in the deprotonation of the nucleophile precedes or exceeds the electronic charge transferred from the nucleophile to C-α in the N—C-α bond formation.

The non-interactive phenomenon ($\rho_X = 0$) may therefore be ascribed to the TS imbalance which arises in the process of bond making at the resonance-stabilized cation centre. The TS imbalance provides a necessary condition for the appearance of the non-interactive phenomenon, even though it may not be a sufficient condition. The high resonance demand of the carbenium ion, which requires base catalysis involving deprotonation of the nucleophile, is therefore an essential factor conducive to the manifestation of the sign reversal of ρ_X.

REACTIONS OF BENZHYDRYL CHLORIDES IN ACETONITRILE

If resonance delocalization of positive charge on C-α decreases owing to a weaker electron-withdrawing power of the α-substituent, R^1 and/or R^2 in **I**, then C-α becomes more positively charged because electron demand of C-α from the Y-ring is weaker. On the other hand, even if resonance demand of C-α with strong electron-withdrawing α-substituents is strong, C-α will be more positive when there is no Y substituent which is strongly electron donating so that positive charge can be driven away from C-α effectively. Hence a strong resonance demand can only be accommodated effectively by reducing the positive charge of C-α by a strong electron donor Y. This interplay between the two (α and Y) substituents can be understood more clearly by changing Y to a weaker electron donor (Y = H) and measuring changes in the positive charge increment from that for a strong Y donor ($Y = OCH_3$), $\delta\,\Delta q_{C\text{-}\alpha^+} = \Delta q_{C(Y=H)} - \Delta q_{C(Y=OCH_3)}$. This change in the positive charge increment, $\delta\,\Delta q_{C\text{-}\alpha}$, for Y = H should reflect the role of Y as an electron donor in accommodating the resonance demand acquired by a strong electron-withdrawing α-substituent.

The decrease in resonance delocalization as expressed by an increase in $\delta\,\Delta q_{(C^+)}$ (>0) when substituent Y is varied to a less electron-donating or a more electron-withdrawing ($\delta\sigma_Y > 0$) type is dependent on the electron-withdrawing power, $\Sigma\sigma^*$, of the α-substituents, R^1 and/or R^2 (Table 2). Examination of Figure 2 indicates that the slope of the plot of $\delta\,\Delta q_{(C^+)}$ vs σ^* is positive, i.e. $\delta[\Delta q_{(C^+)}]/\partial\sigma^* > 0$, so that for a more electron-withdrawing α-substituent (e.g. CF_3) the loss or decrease in the resonance delocalization is greater ($\delta\,\Delta q_{(C^+)} \approx 0{\cdot}06$–$0{\cdot}08$) when the Y-substituent in the ring is changed to a less electron-donating type (e.g. Y = H). However, when a phenyl group is α-substituted, e.g. for benzhydryl with $R^1 = H$ and $R^2 = C_6H_5$, the loss of resonance delocalization is abnormally small ($\delta\,\Delta q_{C\text{-}\alpha} = 0{\cdot}03$); for the benzhydryl compound, a weak electron-donating or a weak electron-withdrawing Y substituent does not lose much of the strong resonance electron delocalization that was observed for a strong electron-donating Y substituent ($Y = CH_3O$). This means that when benzhydryl carbenium ion is involved in the S_N2 attack, the TS imbalance phenomenon can still be observed with a much less electron-donating or even with a somewhat electron-withdrawing Y substituent. This is due to a variable resonance electron delocalization of the phenyl

Table 2. AMI positive charge increments, $\Delta q = \Delta q_{\text{cation}} - \Delta q_{\text{reactant}}$, for $YC_6H_5CHR^1Cl \rightarrow YC_6H_5C^+HR^1 + Cl^-$ with $Y = CH_3O$ and Y = H

	Δq^a			
R^1	$Y = CH_3O$	Y = H	$\delta\,\Delta q = \Delta q_H - \Delta q_{MeO}{}^a$	$\sigma^*\,(R^1)^b$
t-Bu	0·152	0·216	0·064	−0·30
CH_3	0·146	0·210	0·064	0·0
H	0·129	0·200	0·071	0·49
C_6H_5	0·152	0·186	0·034	0·60
CF_3	0·046	0·123	0·077	2·61

[a] Electronic charge unit.

[b] Taft's polar substituent constant.

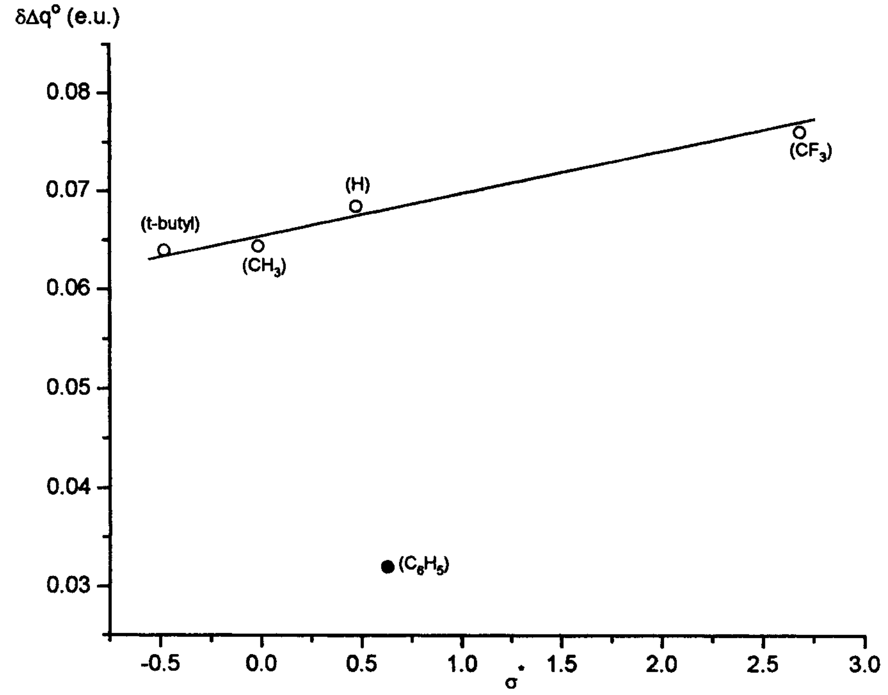


Figure 2. Plot of $\delta\,\Delta q^0 = \Delta q(Y = H) - \Delta q(Y = CH_3)$ vs σ^*

group depending on the electron-withdrawing power of C-α; for a strong electron-withdrawing C-α (i.e. with an electron-withdrawing Y), the phenyl group donates electron by resonance delocalization, whereas for a weak electron-withdrawing (or an electron-donating) C-α, (i.e. with an electron-donating Y), it accepts electrons by a polar effect. However, the phenyl group is a weak resonance electron donor when it is attached to a cation centre, C-α.

This type of variable resonance delocalization is not possible for other α-substituents, however strong its electron-withdrawing power may be (e.g. $R^1 = CF_3$); the resonance delocalization becomes depressed rapidly as the electron-donating power of the Y substituent decreases when the α-substituent is strongly electron withdrawing.

In the benzhydryl system, the two benzene rings, α- and Y-rings, can interchange the role they play in accommodating resonance demand. Thus, if the α-ring has a strong electron-withdrawing substituent the Y-ring supplies electrons, whereas if the Y-ring has a strong electron-withdrawing substituent now the α-ring can supply electrons to C-α. Hence when only one of the two rings is substituted, the unsubstituted ring can play the role of an α-ring when Y is a strong electron donor, whereas it plays the role of a Y-ring when the substituent is a strong electron-withdrawer, which in turn forms an α-ring. This means that for the monosubstituted benzhydryl carbenium ion, the unsubstituted phenyl ring ($\sigma^* = +0{\cdot}60$) forms a lower limit to both the electron-donating (Y-ring) (when the substituent is an electron withdrawer) and electron-withdrawing (α-ring) power (when the substituent is an electron donor).

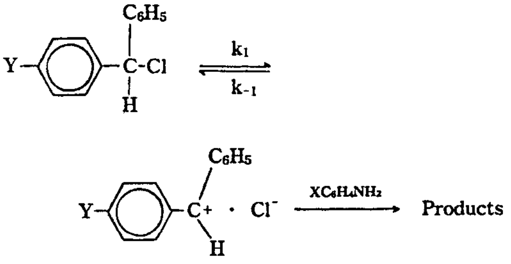
Amyes *et al.*[3] have shown that there is a greater fractional loss of resonance than of polar interactions when capture of $4\text{-}MeOC_6H_4C^+R^1R^2$ by a nucleophile progresses from the ground state to the TS. Such 'imbalance' or 'non-perfect synchronization' between the loss of resonance and polar interactions becomes greater with a stronger electron-withdrawing α-substituent.

In the benzhydryl carbenium ion, the resonance demand remains high even with a weak electron-donating Y substituent. Since a high resonance demand causes a greater imbalance between the loss of resonance and polar interactions, the benzhydryl carbenium ion will exhibit substantial imbalance with a relatively weak electron-donating Y substituent. Moreover, when Y is an electron-withdrawing substituent the unsubstituted (α) ring plays the role of an electron donor so that there is a possibility that for the benzhydryl system the TS imbalance can be high even with an electron-withdrawing Y substituent.

Since the non-interactive phenomenon ($\rho_X = 0$)

becomes observable when there is imbalance between the loss of resonance and polar interactions in the TS, leading to a strong cross-interaction, i.e. a large magnitude of ρ_{XY}, the non-interactive point, $\hat{\sigma}_Y$, at which ρ_X changes sign can be observed at a positive σ_Y value in the capture of the benzhydryl carbenium ion by the nucleophile.

In the reactions of monosubstituted benzhydryl chlorides with anilines in acetonitrile



(7)

I. P.

a non-interactive point ($\rho_X = 0$) has been observed at the much more electron-withdrawing side of the Y substituent, $\hat{\sigma}_Y \approx 0{\cdot}17$,[23] with a large cross-interaction between substituents in the nucleophile (X) and substrate (Y), $\rho_{XY} = -1{\cdot}96$.

At the non-interactive point observed, $\hat{\sigma}_Y \approx 0{\cdot}17$, ρ_X becomes zero and the reactivity becomes isokinetic. For $\hat{\sigma}_Y < 0{\cdot}17$, ρ_X is positive and the N atom becomes more negatively charged in the TS. The non-interactive point of $\hat{\sigma}_Y = 0{\cdot}17$ is a shift of $+0{\cdot}40$ σ unit compared with $\hat{\sigma}_Y = -0{\cdot}23$ for the 1-phenylethyl carbenium ion reaction. This large shift must result from an exchange of the role played by the two rings, i.e. the ring with an electron-withdrawing Y substituent plays the role of an α-substituent (acceptor) and the unsubstituted ring plays the role of a resonance electron donor.

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