

MO Theoretical Studies on the Benzylic and Resonance Shunt Effects¹

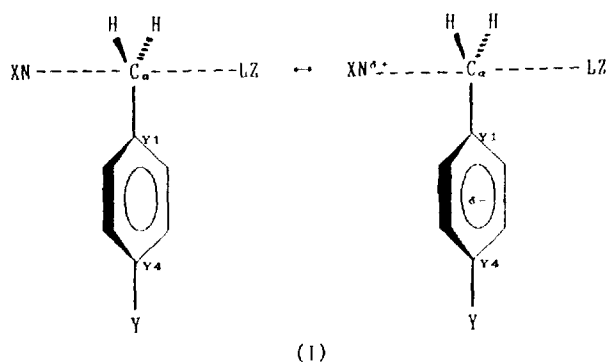
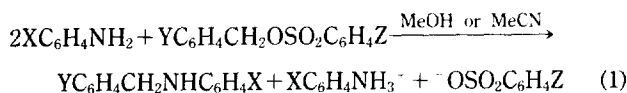
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The reactions of aniline with benzyl and phenacyl compounds are studied by the AM1 method. Two types of modeling were adopted: Cation-neutral, in which a proton is attached to the leaving group F and anion-neutral model, in which aniline was replaced by phenoxide with Cl as the leaving group. The cation-neutral model represented the react very well, reproducing the various solution-phase experimental results. In the benzyl system, the π -electrons of the two rings (X-ring in the nucleophile and Y-ring in the substrate) interact conjugatively in the transition state (TS) resulting in a bond contraction of the C_α - C_{Y1} bond (benzylic effect), whereas in the phenacyl system the π electrons of the X-ring delocalizes more efficiently into the carbonyl group than into the Y-ring (resonance shunt effect) with a bond contraction of the C_α - C_β bond. The bond contraction in the benzylic effect was substantially greater than that in the resonance shunt effect. The TS was rather loose for benzyl while it was tighter for phenacyl system. Various bond length changes with substituents in the TS were, however, found to be irregular.

Introduction

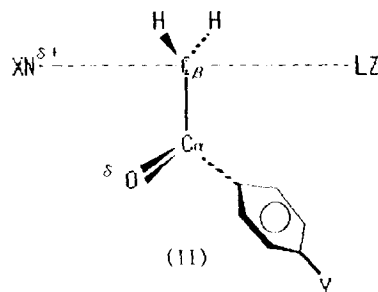
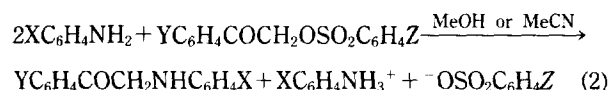
The delocalization of π or lone pair electrons of the nucleophile into the substrate benzene ring stabilizes the TS, (I),² and results in a rate increase as well as an increase in selectivity parameters³ like the Swain-Scott s values.⁴ This "benzylic effect"⁵ should also cause bond contraction of the C_α - C_{Y1} bond so that the cross interaction between the two substituents (Y) in the substrate and (Z) in the leaving group (LZ) will be enhanced as evidenced by the increase in the magnitude of the cross interaction constant ρ_{YZ} ,⁶ especially for the nucleophile with a strong electron-donating substituent (X=*p*-CH₃O) in the reactions of benzyl benzenesulfonates with anilines, Eq (1).⁷



On the other hand, an analogous effect was found to be operative in the reactions of substrate with an α -carbonyl group, which stabilizes the TS (II) and also results in an increased rate as well as in an increased sensitivity to the nucleophile and the LG, due to a similar resonance bond contraction of the C_α - C_β bond; the magnitude of ρ_{YZ} for the reaction of phenacyl benzenesulfonates with anilines, Eq. (2), was indeed found to increase mainly because of the delocalization of the π -electrons of the nucleophile into the carbonyl

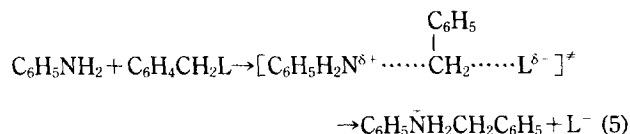
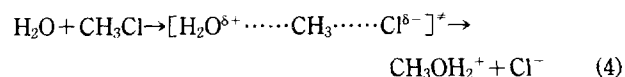
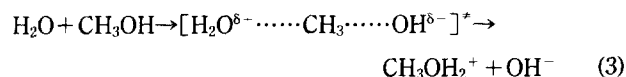
group, (II) (resonance shunt effect).^{6d,8}

The benzylic and resonance shunt effects require thus an efficient delocalization of electrons of the nucleophile into the ring and the carbonyl group respectively, so that the



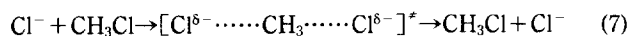
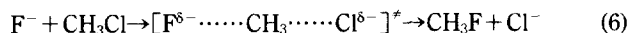
TS geometry should be such that conjugation with the reaction center is permitted. In order to understand more fully the stereoelectronic aspects involved in these effects we have determined theoretically the TS structures involved in model reactions of Eqs. (1) and (2), using the AM1 method.⁹

Computational Strategy. In general, bimolecular substitution reactions can not take place thermally between two neutral molecules in gas-phase; thermal reactions (3)-(5) will not proceed in gas-phase mainly because the ion-pair formation processes are endothermic and require high activation



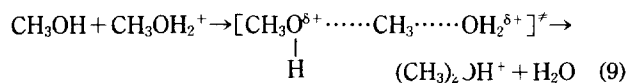
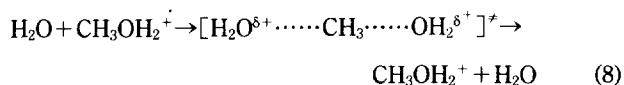
barriers. This means that these processes can not be studied theoretically by molecular orbital calculations. These reactions can, however, occur in solution-phase thermally since the ion-pairs produced are stabilized by recombination or solvation, with cations separating into a protonated solvent molecule and a neutral product, and the processes may become exothermic with relatively lower activation barriers.

In contrast to these neutral-neutral bimolecular substitution, the reactions involving anionic nucleophiles, *e.g.*, reactions (6) and (7), are very fast in gas-phase but slow in solution phase.¹⁰



The main reason why these ion-molecule reactions proceed with much lower barriers in gas-phase than in solution is the formation of charge delocalized TS, which is exoergic in gas-phase but is endoergic in solution due to the desolvation required in the TS.¹¹ The effect of solvation was found to cause a change of the double-well reaction surface of a typical S_N2 reaction in the gas-phase¹² into the unimodal energy surface in solution.^{10,13} Since these processes can occur in gas-phase, MO theoretical calculations on the TS structure are feasible, as have been carried out by many workers using various MO methods.¹⁴

Recently, less usual S_N2 reactions involving a neutral nucleophile and a cation, the protonated substrate, *e.g.*, reactions (8) and (9), have been investigated experimentally¹⁵ in gas-phase and theoretically by MO methods.¹⁶ The investigations of these processes experimental and theoretical, are

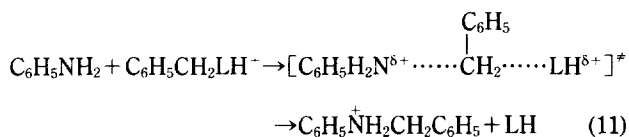
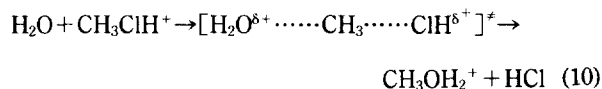


practicable, since the processes are ion-molecule type like reactions (6) and (7). In fact the reaction profiles of these processes obtained by *ab initio* calculations (with relatively high level basis sets) had all the characteristic of the typical gas-phase S_N2 reactions involving anions¹⁶: potential surfaces are in double-well forms, ion-dipole clusters lead to unsymmetrical minima and a more symmetrical TS is formed.

The anion-neutral (Eqs. (6)-(7)), neutral-neutral (Eqs. (3)-(5)) and cation-neutral (Eqs. (8)-(9)) nucleophilic substitution reactions have anionic, neutral and cationic TSs respectively, but all three type of reactions can proceed by a typical S_N2 process in solution with unimodal or nearly unimodal potential energy surface.^{10,11,13} Furthermore the two type of reactions involving an ionic reactant are also similar in gas-phase with a double-well energy surface which is amenable to MO theoretical analysis.^{14,16}

This comparison of the three types of reactions suggests an important technique by which the neutral-neutral substitution reactions, Eqs. (3)-(5), can be examined in the gas-phase and also by the MO theoretical methods: transformation of a neutral-neutral into a cation-neutral reaction by attaching a proton on the leaving group, *i.e.* reactions (3),

(4) and (5) into (8), (10) and (11) respectively.



This technique will enable an MO theoretical analysis of the stereoelectronic characteristics of the TS for reactions (3)-(5), since placement of a proton on the leaving group should not interfere unduly with the TS structure electronically nor sterically; as we have noted above, the charge type (-1, 0 or +1) of the TS does not alter the mechanism of the reactions and a proton is insignificant sterically.

Another way of examining the neutral-neutral substitution reaction MO theoretically would be to replace the nucleophile by a structurally similar anionic one which can reproduce stereoelectronic characteristics of the neutral nucleophile.

The two reactions we are interested in, Eqs. (1) and (2), are the neutral-neutral type so that the MO theoretical investigation of the TSs is not practicable. We have therefore simplified the calculation by adopting two types of modeling discussed above: We have transformed the reactions into (i) a cation-neutral type by attaching a proton to the LG of F and (ii) an anion-neutral type by replacing aniline nucleophile with phenoxide anion using chloride as a LG.

In this work a semiempirical method was used in the calculations due to the relatively complex reaction system. The AM1 method was adopted throughout since it is known to reproduce the *ab initio* trends rather well.¹⁷ Geometries of all reactants and TSs were fully optimized. TSs were located by the reaction coordinate method¹⁸ and refined by the use of gradient norm minimization method¹⁹ of the program²⁰ on a CRAY-2S computer. All the TSs were characterized by force constant calculation and identifying only one negative eigenvalue in the Hessian matrix.²¹

Results and Discussion

Cation-Neutral Molecule Reaction Model. In this model, a proton is attached to the leaving group; fluoride was adopted as the leaving group which provides suitable leaving ability in the computation of the TS.²² The two gas-phase reactions we are interested in, *i.e.*, Eqs. (1) and (2), have the TS structures depicted as (I) and (II) respectively with $N=C_6H_5NH_2$ and $LZ=FH$. The AM1 optimized TS structures are presented in Figures 1 and 2. The TS for the benzyl system in Figure 1 reveals that the two benzene rings (X-ring in the nucleophile and Y-ring in the substrate) are orthogonal to the plane of the paper mainly to avoid steric crowding between the two rings in the TS. The steric repulsion also causes widening of angles $\angle NC_aC_{Y1}$ and $\angle FC_aC_Y$, which are both 90° in the trigonal bipyramidal 5-coordinate (TBP-5C) TS for the identity methyl transfer reactions,²³ *e.g.*, Eq. (7). This deviation from the TBP-5C type TS structure should lower the degree of overlap of the π -

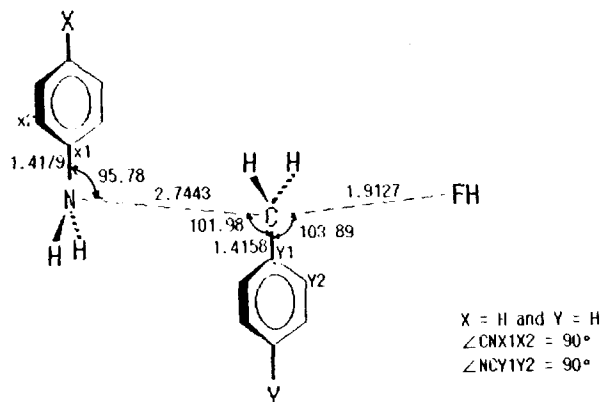


Figure 1. The TS structure for benzyl system with the cation model.

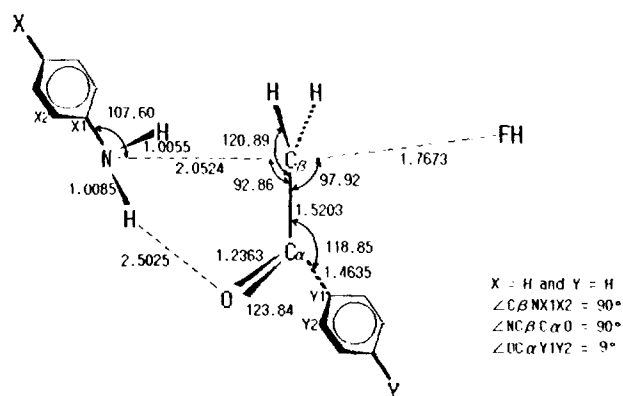


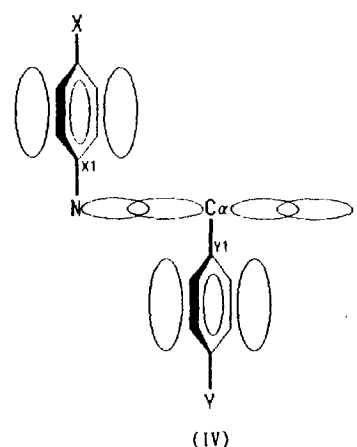
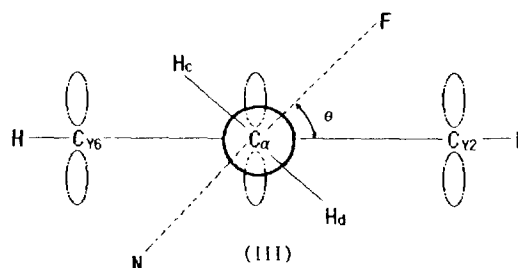
Figure 2. The TS structure for phenacyl system with the cation model.

orbitals of the Y-ring with N-C_α-F, (III), lowering the efficiency of "benzylic" effect. However, the benzylic effect⁵ is maximized by an approach of the X-ring at *ca.* 180° toward the Y-ring as in (IV).

Bond lengths of the two bonds that are breaking (C_α-F) and forming (N-C_α) indicate that the TS is rather loose and relatively early along the reaction coordinate, which are consistent with a dissociative S_N2 mechanism (*vide infra*). The rotation of angle θ in (III) clearly shows the benzylic effect resulting in a resonance bond contraction in the TS; the TS is formed (the benzylic effect is "on") at $\theta=90^\circ$ when

Table 1. Bond length(d) vs Rotation Angle (θ) of the Y-ring in the Benzyl System

θ/degree	$d(\text{C}_\alpha\text{-C}_{\text{Y1}})/\text{\AA}$	$\Delta H_f/\text{kcal mol}^{-1}$
90 ("on")	1.4158	164.31 (TS)
60	1.4195	167.18
30	1.4320	174.21
0 ("off")	1.4471	180.44



the bond length of the C_α-C_{Y1} bond is a minimum, which is reduced by 0.0561 Å from the original bond in the reactant. When the benzylic effect is "off" at $\theta=0^\circ$ the C_α-C_{Y1} bond stretches by 0.0313 Å as compared with that for the "on" structure at $\theta=90^\circ$ as shown in Table 1.

The effects of substituents X and Y on the TS structure are summarized in Table 2. All substituents, X=*p*-OCH₃ or *p*-NO₂, and Y=*p*-NO₂, lead to a closer approach of the nu-

Table 2. Bond length(d) and Atomic Charge(q) and Enthalpies of Activation for the Reactions of Benzyl System with Anilines

X	Y	Bond length (Δd) ^a				Charge (Δq) ^b		ΔH^{ac}
		N-C _α	C _{X1} -N	C _α -C _{Y1}	C _α -F	C	F	
H	H	2.7442	1.4179 (+0.0168)	1.4158 (-0.0561)	1.9127 (+0.4368)	+0.2532 (+0.1676)	-0.2065 (-0.2425)	6.61
OCH ₃	H	2.5120	1.4223 (+0.0182)	1.4246 (-0.0474)	1.8944 (+0.4185)	+0.2604 (+0.1748)	-0.2039 (-0.2399)	6.57
NO ₂	H	2.6121	1.4142 (+0.0349)	1.4183 (-0.0537)	1.9051 (+0.4292)	+0.2536 (+0.1680)	-0.2049 (-0.2409)	14.51
H	NO ₂	2.6239	1.4207 (+0.0196)	1.4256 (-0.0534)	1.9299 (+0.4621)	+0.2761 (+0.1962)	-0.2133 (-0.2564)	8.06

^a $\Delta d = d(\text{TS}) - d(\text{Reactants})$ in Å, ^b $\Delta q = q(\text{TS}) - q(\text{Reactants})$ in electronic charge unit, ^c $\Delta H^* = \Delta H_f(\text{TS}) - \Delta H_f(\text{Reactants})$ in kcal/mol.

Table 3. Bond length(*d*) vs Rotation Angle(θ) of the Y-ring in the Phenacyl System

θ /degree	0.0 ("on")	8.51 (TS)	90.0 ("off")	
ΔH_f /kcal mol ⁻¹	152.79	152.79	156.40	
<i>d</i> /Å	C $_{\alpha}$ -C $_{Y1}$	1.4635	1.4635	1.4732
	C $_{\alpha}$ =O	1.2365	1.2363	1.2308
	C $_{\alpha}$ -C $_{\beta}$	1.5190	1.5203	1.5208

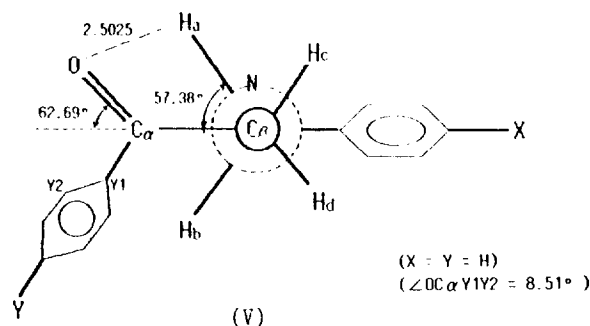
cleophile with a lesser amount of bond contraction for the C $_{\alpha}$ -C $_{Y1}$ bond. This is not entirely consistent with our experimental results of substituent effects for reaction (1) in methanol-acetonitrile mixture^{3a,7}; our secondary inverse kinetic isotope effects (KIE) involving deuterated aniline nucleophiles have shown that a more electron donating substituent (EDS) (X=*p*-OCH $_3$) in the nucleophile and a more electron withdrawing substituent (EWS) (Y=*p*-NO $_2$) in the substrate resulted in a greater degree of bond formation but a more EWS (X=*p*-NO $_2$) in the nucleophile led to a lesser degree of bond formation.²⁴ On the other hand the magnitude of cross interaction constant between substituents Y in the substrate and Z in the LG indicated that the C $_{\alpha}$ -C $_{Y1}$ bond contraction was greater with a more EDS in the nucleophile.^{3b,6} These discrepancies must result from our modeling of the reaction, (1), in solution by a cation gas-phase reaction.

The enthalpies of activation, ΔH^\ddagger , calculated show, however, quite reasonable trend; a stronger nucleophile (X=*p*-OCH $_3$) and a more EDS in the substrate (Y=*p*-OCH $_3$) lower the activation barrier in agreement with a faster rate of the reactions in solution.^{3a,7}

The TS structure for phenacyl system is shown in Figure 2. In this case the X-ring and the carbonyl group (C=O) are perpendicular to the paper plane but the Y-ring is distorted somewhat ($\theta=8.51^\circ$) from the C $_{\beta}$ -C $_{\alpha}$ =O plane which is orthogonal to the plane of the paper. The coplanar ("on") structure with $\theta=0^\circ$ seems to have better conjugation of the Y-ring with the π -electrons of the X-ring through the C-N bond as evidenced by a greater bond contraction of the C $_{\alpha}$ -C $_{\beta}$ bond in Table 3. The TS structure with $\theta=8.51^\circ$ is, however, a compromise between a lower steric repulsion (against the carbonyl group) and a better conjugation of the Y-ring. If we rotate the Y-ring by 90.0° ("off") the bond con-

traction of C $_{\alpha}$ -C $_{\beta}$ becomes less.

Widening of angles \angle NC $_{\beta}$ C $_{\alpha}$ and \angle FC $_{\beta}$ C $_{\alpha}$ from orthogonality is not so serious as in the benzyl system (Figure 1), since an extra intervening group, C=O, renders considerable release of the steric crowding for the Y-ring in the TS. The carbonyl oxygen attracts the neighboring amino hydrogen, H $_a$ in (V), so that the N-H $_a$ bond stretches by 0.0126 Å from that in the reactant aniline; as a result N-H $_a$ is longer by 0.0031 Å than N-H $_b$ in the TS, and suggests a possibility of hydrogen bond formation between N and O, (V). This is indeed reflected in the very small primary KIE for the phenacyl system in our solution phase studies with deuterated aniline nucleophiles.²⁵ The distance between O and H $_a$ increases with X=*p*-OCH $_3$ ($d=2.5100$ Å) and decreases with X=*p*-NO $_2$ ($d=2.4985$ Å) compared to that for the unsubstituted nucleophile, X=H, ($d=2.5025$ Å) so that the hydrogen bond will be stronger with X=*p*-NO $_2$ but weaker with X=*p*-OCH $_3$; this is in agreement with a greater primary KIE with X=*p*-NO $_2$ and a smaller KIE with X=*p*-OCH $_3$ observed in



our solution-phase experiment.²⁵

The bond lengths of the breaking (C-F) and forming (N-C $_{\beta}$) bonds are in general substantially shorter (by *ca.* 0.15 Å and 0.69 Å respectively) than those in the benzyl system, suggesting that the phenacyl system reacts by an associative S $_N$ 2 mechanism with a relatively tight TS, as experimentally observed.^{6d,8} The effects of substituents on the relative bond lengths N-C $_{\beta}$, C $_{\alpha}$ -C $_{\beta}$ and C-F are again irregular (Table 4). We note, however, that resonance bond contraction of C $_{\alpha}$ -C $_{\beta}$ ($\Delta d = -0.0176$ Å) is smaller than that of C $_{\alpha}$ -C $_{Y1}$ ($\Delta d = -0.0561$ Å) in the benzyl system, which is in agreement with a greater change in the magnitude of the cross interaction constant ρ_{YZ} for the benzyl system compared to that for the phenacyl system.^{3a,6d,7} The bond contraction of the C $_{\alpha}$ -C $_{\beta}$ bond

Table 4. Bond Length(*d*) and Atomic Charge(*q*) and Enthalpies of Activation for the Reactions of Phenacyl System with Anilines

X	Y	Bond length (Δd) ^a					Charge (Δq) ^b			ΔH^\ddagger ^c
		N-C $_{\alpha}$	C $_{\alpha}$ -C $_{\beta}$	C $_{\alpha}$ -C $_{Y1}$	C $_{\alpha}$ =O	C $_{\beta}$ -F	C $_{\beta}$	O		
H	H	2.0524	1.5203 (-0.0176)	1.4635 (+0.0007)	1.2363 (+0.0110)	1.7673 (+0.3256)	+0.1285 (+0.1964)	-0.2290 (-0.0644)	13.05	
OCH $_3$	H	2.0647	1.5188 (-0.0192)	1.4637 (+0.0010)	1.2364 (+0.0111)	1.7681 (+0.3264)	+0.1271 (+0.1950)	-0.2292 (-0.0646)	11.53	
NO $_2$	H	2.0547	1.5199 (-0.0181)	1.4620 (-0.0007)	1.2365 (+0.0113)	1.7977 (+0.3560)	+0.1378 (+0.2057)	-0.2278 (-0.0632)	23.75	
H	NO $_2$	2.0710	1.5166 (-0.0187)	1.4698 (+0.0031)	1.2352 (+0.0103)	1.7758 (+0.3320)	+0.1304 (+0.1937)	-0.2092 (-0.0611)	11.47	

^a $\Delta d = d(\text{TS}) - d(\text{Reactants})$ in Å ^b $\Delta q = q(\text{TS}) - q(\text{Reactants})$ in electronic charge unit. ^c $\Delta H^\ddagger = \Delta H_f(\text{TS}) - \Delta H_f(\text{Reactants})$ in kcal/mol.

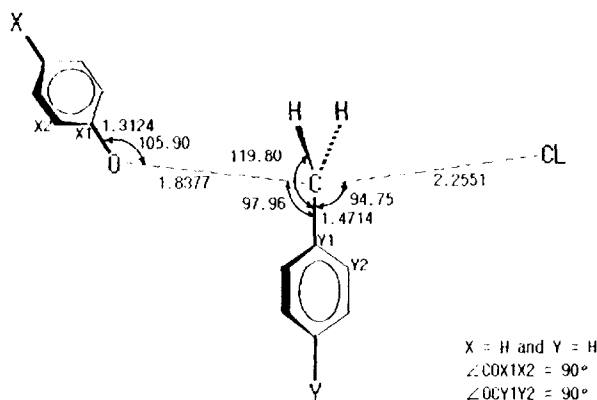


Figure 3. The TS structure for benzyl system with the anion model.

is accompanied by stretching of the $C_{\alpha}=O$ bond ($\Delta d = +0.0110$ Å) with very small changes in the $C_{\alpha}-C_{Y1}$ bond ($\Delta d = +0.0007$ Å). This indicates that the π -electrons of the X-ring mainly delocalize into the carbonyl group with very little flow into the Y-ring, partly because the Y-ring is not coplanar with the $C_{\beta}-C_{\alpha}=O$ plane and partly an electron attracting ability of the carbonyl oxygen is greater compared to that of the non-coplanar Y-ring. This efficient electron conjugation of the X-ring with the carbonyl group, but little with the Y-ring, has been termed as "resonance shunt effect".^{6d,8} This electron leak or shunt had significant consequences on the experimental results: (i) The magnitude of the cross interaction constants between substituents X in the nucleophile and Y in the substrate, $|\rho_{XY}| (=0.11$ for $Z=H$), were unduly small,^{6d} compared to those for the reactions of benzyl system ($|\rho_{XY}| = 0.62$ for $Z=H$)^{3a,7} even though in fact the bond distance, d_{XY} , between N and the reaction center carbon in the TS is substantially shorter for the phenacyl system, *i.e.*, the degree of bond formation is greater, as we have noted above. (ii) The electron flow into the carbonyl oxygen causes an increase in the electron density (q) on O ($\Delta q = -0.0644$) and a decrease in the $H_{\alpha}-O$ distance (as noted above) so that weak hydrogen bond formation is made possible between O and N as evidenced by the small primary KIE in solution phase experiment.²⁵ Here again the enthalpies of

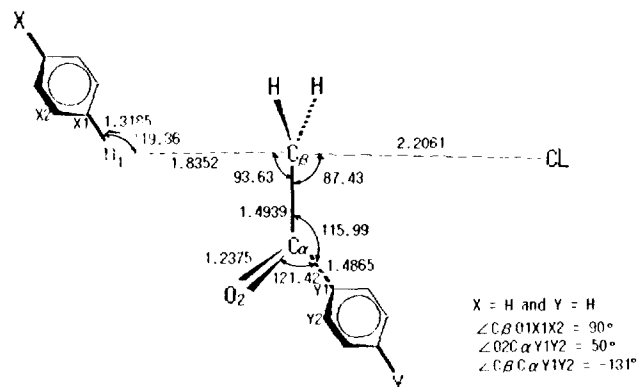


Figure 4. The TS structure for phenacyl system with the anion model.

activation (Table 4) seem to reflect correctly the slow rate of the phenacyl system^{6d} in general ($\Delta H^{\ddagger} = 13.05$ for phenacyl *vs* 6.51 kcal/mol for benzyl system) and the rate variation with substituents, *i.e.*, faster with $X=p-OCH_3$ and slower with $X=p-NO_2$.

In summary, the cation-neutral model seems to represent the solution phase reactions of benzyl and phenacyl compounds with anilines fairly well correctly reproducing various experimental results: (i) Benzyl system has a relatively loose TS^{3a,7} whereas phenacyl system has a tighter TS.^{6d}; (ii) The π -electrons in the two rings, X- and Y-ring, interact conjugatively in the TS resulting in a substantial bond contraction of the $C_{\alpha}-C_{Y1}$ bond in benzyl system (benzylic effect).⁵; (iii) The π -electrons of the X-ring delocalize more effectively into the carbonyl group than into the Y-ring (resonance shunt effect)^{6d,8} in the TS for the phenacyl system; (iv) Hydrogen bond formation is possible by an amino hydrogen (H_{α}) toward the carbonyl oxygen in the TS for phenacyl system albeit the hydrogen bond may be very weak²⁵; (v) The ΔH^{\ddagger} value is higher with a weak nucleophile ($X=p-NO_2$), while it is lower with a stronger nucleophile ($X=p-OCH_3$) in both system.^{3a,6d,8}

As far as the bond length variations with substituents are concerned, some irregularities are found.

The Anion-Neutral Molecule Model. In this model,

Table 5. Bond Length(d) and Atomic Charge(q) and Enthalpies of Activation for the Reactions of Benzyl System with Phenoxide Anions

X	Y	Bond length (Δd) ^a				Charge (Δq) ^b		$\Delta H^{\ddagger c}$
		O-C	$C_{\alpha}-O$	$C-C_{Y1}$	C-Cl	C	Cl	
H	H	1.8377	1.3124 (+0.0435)	1.4714 (-0.0108)	2.2551 (+0.4953)	+0.2106 (+0.2857)	-0.7466 (-0.6271)	21.86
NO ₂	H	1.7650	1.3048 (+0.0476)	1.4731 (-0.0091)	2.3141 (+0.5543)	+0.2013 (+0.2764)	-0.7808 (-0.6613)	34.06
OCH ₃	H	1.8254	1.3117 (+0.0450)	1.4719 (-0.0103)	2.2634 (+0.5036)	+0.2103 (+0.2854)	-0.7518 (-0.6323)	23.99
NH ₂	H	1.8406	1.3135 (+0.0442)	1.4713 (-0.0109)	2.2538 (+0.4940)	+0.2096 (+0.2847)	-0.7459 (-0.6264)	22.13
O(-)	H	2.1216	1.3198 (+0.0216)	1.4655 (-0.0167)	2.0658 (+0.3060)	+0.1308 (+0.2059)	-0.6089 (-0.4894)	-9.02

^a $\Delta d = d(\text{TS}) - d(\text{Reactants})$ in Å. ^b $\Delta q = q(\text{TS}) - q(\text{Reactants})$ in electronic charge unit. ^c $\Delta H^{\ddagger} = \Delta H_f(\text{TS}) - \Delta H_f(\text{Reactants})$ in kcal/mol.

Table 6. Bond Length(d) and Atomic Charge(q) and Enthalpies of Activation for the Reactions of Phenacyl System with Phenoxide Anions

X	Y	Bond length(Δd) ^a				Charge(Δq) ^b			ΔH^\ddagger ^c
		O-C _{β}	C _{α} -C _{β}	C _{α} -C _{γ_1}	C _{α} =O	C _{β} -Cl	C _{β}	O ^d	
H	H	1.8352	1.4939	1.4864	1.2375	2.2061	+0.1294	-0.3112	17.02
			(-0.0145)	(+0.0116)	(+0.0001)	(+0.4581)	(+0.3055)	(-0.0328)	
NO ₂	H	1.7691	1.4975	1.4848	1.2377	2.2485	+0.1276	-0.3056	30.68
			(-0.0109)	(+0.0100)	(+0.0003)	(+0.5005)	(+0.3037)	(-0.0281)	
OCH ₃	H	1.8297	1.4932	1.4857	1.2387	2.1969	+0.1314	-0.3184	17.94
			(-0.0152)	(+0.0109)	(+0.0013)	(+0.4489)	(+0.3075)	(-0.0400)	
NH ₃	H	1.8428	1.4928	1.4959	1.2385	2.1892	+0.1301	-0.3117	15.96
			(-0.0156)	(+0.0111)	(+0.0011)	(+0.4412)	(+0.3062)	(-0.0394)	
O(-)	H	2.0791	2.0791	1.4910	1.2410	2.0569	+0.0720	-0.3475	19.49
			(-0.0256)	(+0.0162)	(+0.0036)	(+0.3089)	(+0.2481)	(-0.0691)	

^a $\Delta d = d(\text{TS}) - d(\text{Reactants})$ in Å. ^b $\Delta q = q(\text{TS}) - q(\text{Reactants})$ in electronic charge unit. ^c $\Delta H^\ddagger = \Delta H_f(\text{TS}) - \Delta H_f(\text{Reactants})$ in kcal/mol. ^d Carbonyl Oxygen.

the neutral nucleophile, aniline, was replaced by an anion nucleophile, phenoxide. The two TS structures in Figures 3 and 4 for reactions with benzyl and phenacyl systems are again similar to those in Figure 1 and 2, respectively.

In Figure 3 the two rings, X- and Y-ring, are both orthogonal to the plane of the paper as those in Figure 1 for the cation-neutral model, but the lack of two amino hydrogens in the phenoxide-benzyl system seem to lower somewhat the steric crowding of the two rings in the TS, with an angle between them of *ca* 170°. Rotation of the Y-ring to the "off" ($\theta = 0^\circ$) from the "on" (TS) structure ($\theta = 90^\circ$) leads to a lesser amount of bond contraction by $\Delta d = -0.0076$ Å of the C _{α} -C _{γ_1} bond, which is much less compared to that ($\Delta d = -0.0313$ Å) involved in the corresponding change for the cation-neutral model. The TS with this model shows a relatively tight structure compared to that with the cation-neutral model. The bond length changes with substituents in Table 5 are again somewhat irregular and the activation enthalpies are considerably higher than those for the corresponding reactions in the cationic model. This means that the anion-neutral reactions will be slower in gas-phase than the cation-neutral reactions.

The reaction of phenacyl system in this model shows nearly the similar degree of bond-formation and -breaking (Figure 4) as that for the reaction of benzyl system, Figure 3. The distortion of the Y-ring from the "on" structure ($\theta = 90.0^\circ$) is considerably larger ($\theta = 40^\circ$) than in the cation model ($\theta = 9^\circ$). Now the approach of the nucleophile is nearly orthogonal to the C _{β} -C _{α} =O plane, with which the X-ring forms *ca* 150°. Rotation of Y-ring further by $\sim 40^\circ$ to the "off" structure was found to result in stretching of the C _{α} -C _{β} bond ($\Delta d = +0.0021$ Å). On the other hand, in this reaction C _{α} -C _{β} contracts ($\Delta d = -0.0145$ Å) while C _{α} -C _{γ_1} stretches ($\Delta d = +0.0116$ Å) with little change in the C=O bond length in the TS (Table 6). Here again, the bond length changes with substituents are irregular. ΔH^\ddagger values in Table 6 are somewhat lower than those of the corresponding reactions of benzyl compounds (Table 5).

This model also predicts resonance bond contractions of the C _{α} -C _{γ_1} and C _{α} -C _{β} bonds in the TS for the reactions of benzyl and phenacyl systems respectively, but the extent of the contraction is relatively smaller than in the cation model. The relative barrier heights (ΔH^\ddagger) for the substituted phe-

noxide nucleophiles are, however, not correctly predicted in this model; for both benzyl and phenacyl systems, for example, the ΔH^\ddagger values are higher for X=*p*-OCH₃ than for the unsubstituted phenoxide contradicting a trend of faster rate for this nucleophile in the solution-phase reactions, Eqs. (1) and (2).

We conclude that for the MO theoretical study of a neutral-neutral type reaction in solution, the cation model, in which a proton is attached to the LG, is better than the anion model, in which the neutral nucleophile is replaced by a structurally similar anionic nucleophile. The benzylic and resonance shunt effects are, however, correctly predicted in both models by the resonance bond contraction in the substrate molecules.

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