

Theoretical Studies on Phenyl Group Rearrangement of Protonated Ketones

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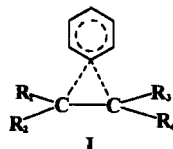
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Gas-phase phenyl group migration within the protonated ketones has been studied MO theoretically using the AM1 method. The initial state structure shows relatively strong resonance delocalization of positive charge into the nonmigrating (Y) ring, while the ring migration (Z-ring) is nearly complete in the transition state. These results are reflected in the large ρ^*_Z (<0) and ρ^*_Y (>0) values and in the predominant contribution of resonance (r) over inductive (field, f) effect, r/f ranging from 1.3 (ρ^*_Y) to 1.5 (ρ^*_Z). The cross-interaction constant ρ_{YZ} is vanishingly small ($\rho_{YZ}=0.03$) which is in contrast to the larger magnitudes for benzylic ($\rho_{YZ}=-0.48$) and azibenzil ($\rho_{YZ}=-0.53$) rearrangement processes. The relationship found between the extent of resonance contribution in the initial state and the magnitude of ρ_{YZ} provides strong support for the proportionality between the magnitude of ρ_{YZ} and the change in the intensity of interaction, ΔI^*_{YZ} , in the activation process.

Introduction

Phenyl group rearrangements have been experimentally observed in carbanionic,¹ radical² and carbocationic³ systems. 1,2-Shifts of phenyl occur readily when the half-mi-



grated structure, I, is stabilized. The structure I can be a transition state (TS) or perhaps an intermediate, in which case the migrating ring has a structure similar to the well-known benzenium ion (or phenonium ion).^{3,4} In previous works, we have studied the cross-interaction between two substituents, Z and Y, in the migrating and non-migrating rings, respectively, in the migrating steps of benzylic⁵ and azibenzil⁶ rearrangements, eqs. (1) and (2), by determining the cross-interaction constant, ρ_{YZ} , eq. (3). This simple second-order expression, eq. (3), is arrived at by a Taylor series expansion of $\log k_{YZ}$ about $\sigma_Y=\sigma_Z=0$ and neglecting the pure second-order (ρ_{YY} and ρ_{ZZ}) and higher-order (ρ_{YYZ} etc.) terms.⁷ The cross-interaction constant, ρ_{YZ} , can be alt-

ernatively given by eq. (4), and the magnitude of ρ_{YZ} represents the change in the intensity of interaction (ΔI^*_{YZ}) between the two substituents, Y and Z, on going from the initial (I^o_{YZ}) to transition state (I^*_{YZ}), eq. (5).⁸

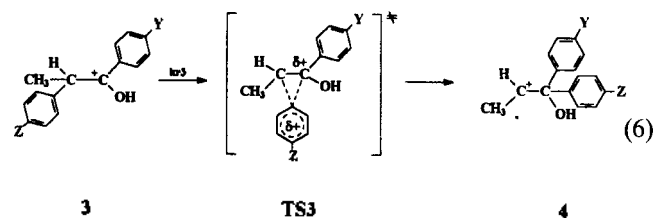
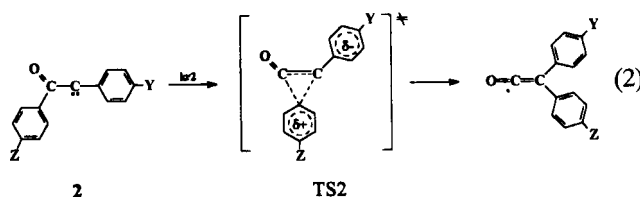
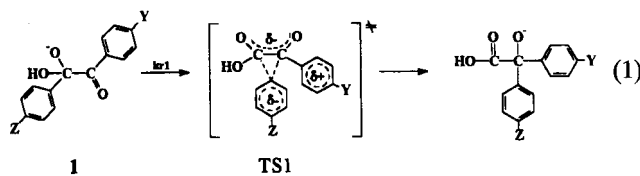
$$\log(k_{YZ}/k_{HH})=\rho_Y\rho_Y+\rho_Z\rho_Z+\rho_{YZ}\sigma_Y\sigma_Z \quad (3)$$

$$\rho_{YZ}=\frac{\partial\rho_Y}{\partial\sigma_Z}=\frac{\partial\rho_Z}{\partial\sigma_Y} \quad (4)$$

$$\rho_{YZ}\propto\Delta I^*_{YZ}=I^*_{YZ}-I^o_{YZ} \quad (5)$$

We found that in the azibenzil case, eq. (2), the initial state, carbene 2, is stabilized by the vicinal n- σ^* overlap and there is a charge reversal in the two benzene rings on going from the initial state to the TS leading to a relatively large structural reorganization and the magnitude of ρ_{YZ} ($=-0.53$) was similar to that involved in the benzylic case ($\rho_{YZ}=-0.48$), eq. (1), for which no such initial state stabilization is possible.⁵

In order to extend this series of work to a system in which there is even stronger interaction between the substituents, Y and Z in the two rings in the initial state, we carried out MO theoretical studies of the gas-phase phenyl group migration within protonated ketones, eq. (6),⁹ using the AM1 method.



Y = Z = OH, CH₃, F, H, Cl or CN

Calculations

The AM1 method¹⁰ was used throughout in this work. Details of the computational procedures are as described in pre-

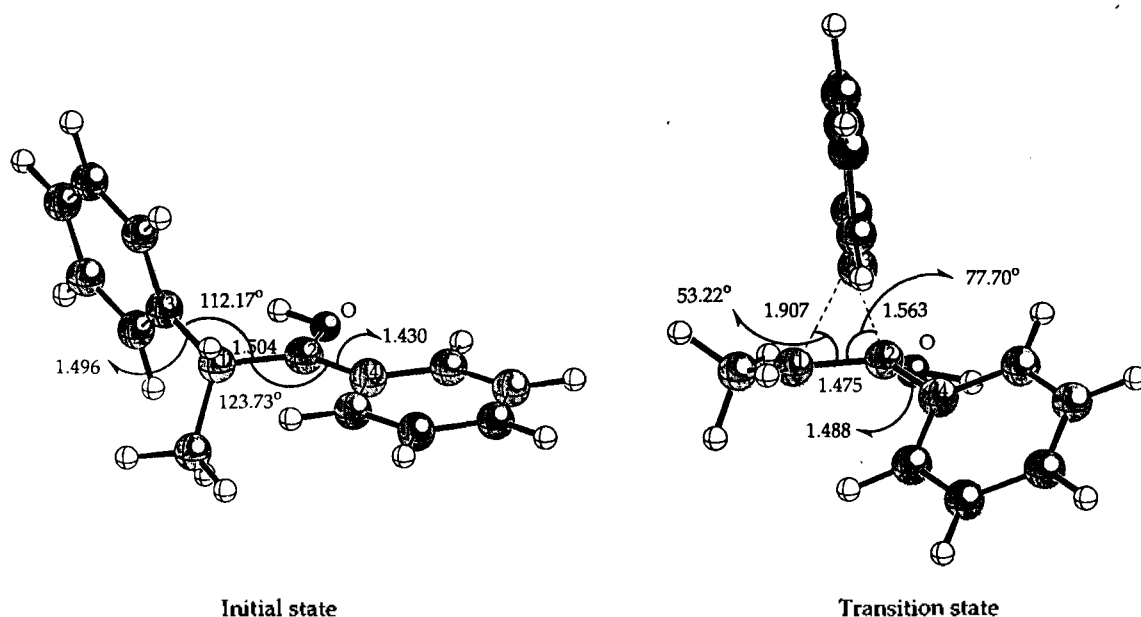


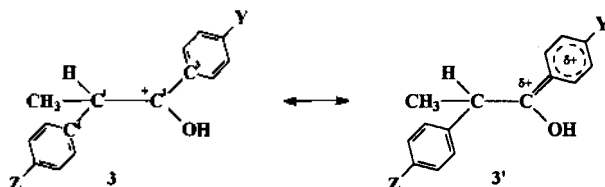
Figure 1. The initial and transition state structures (Y=Z=H). Bond lengths are in Å

vious papers.^{5,6}

Results and Discussion

Structures

Initial states. The structure of the initial, 3, and tran-



sition state, TS3, are shown in Figure 1. In the initial state, **3**, the positive charge on C² is delocalized into the Y-ring, **3**→**3'** (on-form). Reference to Table 1 reveals that bond length of the bond C²-C³ is considerably shorter than those of C¹-C² and C¹-C⁴ (e.g. 1.416 vs 1.505 and 1.497 Å, respectively with Y=OH:Z=CN). This bond becomes stretched by *ca.* 0.05 to 1.462 Å when the Y-ring is rotated 90° (off-form) around C²-C³ to break the conjugation. The resonance structure **3'** is stabilized by a stronger electron donor Y, and destabilized by a stronger electron acceptor Y. These effects of substituent Y on the on-form, **3'**, are reflected in the bond lengths of C²-C³ (Table 1). The positive charge delocalization in **3'** is also reflected in the relatively large positive charge (+0.30~+0.38 electronic

Table 1. AM1 optimized bond lengths in reactant (d_R) and changes, Δd^+ ($=d_{TS}^+ - d_R$) and Δd^- ($=d_T - d_R$) in Å

Z	Y	d_R				Δd^+				Δd^-			
		d_1^a	d_2^b	d_3^c	d_4^d	Δd_1^+	Δd_2^+	Δd_3^+	Δd_4^+	Δd_1^-	Δd_2^-	Δd_3^-	Δd_4^-
OH	OH	1.494	1.506	1.418	2.487	0.496	-0.025	0.071	-0.941	0.787	-0.010	0.082	-0.964
	CH ₃	1.494	1.505	1.425	2.486	0.492	-0.024	0.065	-0.940	0.988	-0.009	0.099	-0.985
	F	1.494	1.505	1.426	2.485	0.493	-0.023	0.064	-0.941	0.778	-0.009	0.098	-0.984
	H	1.494	1.505	1.430	2.485	0.491	-0.024	0.061	-0.939	0.783	-0.010	0.072	-0.961
	Cl	1.494	1.505	1.428	2.484	0.493	-0.023	0.063	-0.939	0.778	-0.010	0.074	-0.960
	CN	1.494	1.504	1.434	2.483	0.494	-0.022	0.059	-0.940	0.776	-0.009	0.069	-0.960
CH ₃	OH	1.496	1.505	1.418	2.488	0.445	-0.028	0.069	-0.933	0.814	-0.009	0.083	-0.964
	CH ₃	1.495	1.505	1.425	2.489	0.442	-0.028	0.063	-0.933	0.819	-0.008	0.078	-0.966
	F	1.495	1.504	1.427	2.487	0.443	-0.026	0.062	-0.933	0.816	-0.007	0.076	-0.964
	H	1.495	1.504	1.430	2.487	0.442	-0.027	0.059	-0.932	0.818	-0.007	0.074	-0.964
	Cl	1.495	1.504	1.428	2.486	0.443	-0.026	0.061	-0.932	0.815	-0.007	0.076	-0.963
	CN	1.495	1.504	1.435	2.485	0.441	-0.026	0.056	-0.933	0.812	-0.007	0.070	-0.962
F	OH	1.496	1.506	1.417	2.489	0.434	-0.029	0.069	-0.931	1.002	-0.010	0.084	-0.965
	CH ₃	1.495	1.505	1.424	2.492	0.430	-0.028	0.063	-0.934	0.99	-0.008	0.099	-0.989
	F	1.495	1.505	1.425	2.491	0.432	-0.027	0.063	-0.935	0.83	-0.006	0.079	-0.969
	H	1.495	1.504	1.429	2.491	0.431	-0.027	0.060	-0.934	0.838	-0.005	0.076	-0.970
	Cl	1.495	1.504	1.427	2.490	0.430	-0.026	0.061	-0.934	0.829	-0.006	0.077	-0.968
	CN	1.495	1.504	1.433	2.488	0.430	-0.026	0.057	-0.933	0.828	-0.005	0.073	-0.967

Table 2. Continued

Z	Y	d_R		Δq^{\ddagger}					Δq°				
		c_1	c_2	Z-Ph	Y-Ph	$\Delta q(C^1)^{\ddagger}$	$\Delta q(C^2)^{\ddagger}$	$\Delta q(Z-Ph)^{\ddagger}$	$\Delta q(Z-Ph)^{\circ}$	$\Delta q(C^1)^{\circ}$	$\Delta q(C^2)^{\circ}$	$\Delta q(Z-Ph)^{\circ}$	$\Delta q(Z-Ph)^{\circ}$
Cl	OH	-0.10	0.32	0.03	0.37	0.24	-0.12	0.23	-0.30	0.38	-0.17	0.03	-0.24
	CH ₃	-0.10	0.33	0.03	0.35	0.24	-0.13	0.23	-0.27	0.40	-0.19	0.03	-0.23
	F	-0.10	0.34	0.03	0.33	0.25	-0.14	0.23	-0.27	0.40	-0.19	0.03	-0.23
	H	-0.11	0.34	0.03	0.32	0.25	-0.14	0.23	-0.25	0.41	-0.20	0.06	-0.26
	Cl	-0.10	0.34	0.03	0.33	0.25	-0.14	0.23	-0.26	0.40	-0.20	0.06	-0.27
	CN	-0.11	0.35	0.04	0.30	0.25	-0.15	0.23	-0.24	0.41	-0.21	0.06	-0.25
CN	OH	-0.11	0.32	0.02	0.38	0.24	-0.11	0.22	-0.30	0.38	-0.17	0.02	-0.24
	CH ₃	-0.11	0.33	0.02	0.36	0.25	-0.12	0.22	-0.27	0.40	-0.19	0.03	-0.24
	F	-0.11	0.34	0.03	0.34	0.25	-0.13	0.22	-0.27	0.41	-0.19	0.03	-0.24
	H	-0.11	0.34	0.03	0.33	0.25	-0.14	0.22	-0.25	0.41	-0.20	0.03	-0.23
	Cl	-0.11	0.34	0.03	0.34	0.25	-0.13	0.22	-0.26	0.41	-0.20	0.03	-0.24
	CN	-0.11	0.35	0.03	0.31	0.25	-0.15	0.22	-0.24	0.42	-0.21	0.05	-0.25

Table 3. Heats of formation (ΔH_f), entropies (S), Gibbs free energies of reaction (ΔG°) and of activation (ΔG^{\ddagger}) in kcal mol⁻¹

Z	Y	ΔH_f			S ^a			ΔG^{\ddagger}	ΔG°
		R	TS	P	R	TS	P		
OH	OH	76.98	118.89	117.92	128.71	130.01	132.38	41.52	39.85
	CH ₃	114.73	154.80	154.27	134.03	134.16	137.43	40.03	38.53
	F	81.43	120.48	119.47	127.97	128.70	131.56	38.83	36.97
	H	124.75	163.31	162.23	123.82	124.24	127.35	38.43	36.43
	Cl	119.77	158.29	157.26	130.76	131.27	134.22	38.37	36.46
	CN	163.23	199.70	198.70	132.58	132.95	135.95	36.36	34.47
CH ₃	OH	112.87	156.64	154.27	133.39	135.08	137.43	43.27	40.20
	CH ₃	150.61	192.58	190.09	138.98	138.82	141.90	42.02	38.61
	F	117.29	158.25	155.83	132.56	133.53	136.10	40.67	37.48
	H	160.62	201.09	198.61	128.63	129.02	131.86	40.35	37.03
	Cl	155.63	196.07	193.63	135.24	136.28	139.11	40.13	36.85
	CN	199.07	237.48	235.07	137.49	137.71	140.68	38.34	35.05
F	OH	78.48	123.18	119.47	127.57	128.17	131.56	44.52	39.80
	CH ₃	116.27	159.08	155.83	133.00	132.60	136.10	42.93	38.64
	F	83.08	124.93	121.94	126.79	126.94	130.31	41.81	37.81
	H	126.38	167.65	164.59	122.67	122.58	125.98	41.30	37.22
	Cl	121.40	162.72	159.70	129.49	129.58	132.95	41.29	37.27
	CN	164.98	204.27	201.28	131.43	131.30	134.65	39.33	35.34
H	OH	121.36	166.64	162.23	123.33	123.74	127.35	45.16	39.67
	CH ₃	159.11	202.56	198.61	129.30	128.10	131.86	43.81	38.74
	F	125.84	168.35	164.59	122.56	122.66	125.98	42.48	37.73
	H	169.16	211.12	207.40	118.46	118.26	121.95	42.02	37.20
	Cl	164.17	206.15	202.45	125.35	125.30	128.73	41.99	37.27
	CN	207.67	247.65	243.96	127.21	126.94	130.75	40.06	35.23
Cl	OH	116.29	161.56	157.26	130.28	130.74	134.22	45.13	39.80
	CH ₃	154.07	197.47	193.63	135.63	135.06	139.11	43.57	38.52
	F	120.86	163.28	159.70	129.50	129.55	132.95	42.41	37.81
	H	164.17	206.03	202.45	125.35	125.19	128.73	41.91	37.27
	Cl	159.19	201.08	197.55	132.21	132.18	135.60	41.90	37.35
	CN	202.74	242.60	239.10	134.10	133.91	137.31	39.92	35.40
CN	OH	157.62	205.14	198.70	132.04	131.96	135.95	47.54	39.91
	CH ₃	195.43	241.03	235.07	137.43	136.21	140.68	45.96	38.67
	F	162.32	207.00	201.28	131.29	130.90	134.65	44.80	37.96
	H	205.61	249.66	243.96	127.17	126.59	130.75	44.22	37.28
	Cl	200.64	244.78	239.10	133.98	133.50	137.31	44.28	37.47
	CN	244.30	286.42	281.09	135.92	135.23	139.29	42.33	35.79

^aIn cal · mol⁻¹ K⁻¹ at 298 K

and both bond cleavage and bond making are nearly complete.

In accordance with these bond length changes accompanied with the activation process, the positive charge is now transferred to the Z-ring from the Y-ring which is now almost devoid of the positive charge; reference to Table 2 reveals that the positive charge increases at C² and Z-ring whereas it becomes depleted at C¹ and Y-ring in the TS. In other words, electronic charge is transferred by the migrating ring (Z) toward the remaining phenyl ring (Y) in the TS. Thus in quite contrast to the trend of stability of the initial state, **3**, which is stabilized by a stronger donor Y ($\delta\sigma_Y < 0$), the TS is stabilized by a stronger acceptor Y ($\delta\sigma_Y > 0$).

Energetics

The heats of formation, ΔH_f , entropies, S, and Gibbs free energy of reaction, ΔG^0 , and of activation, ΔG^\ddagger , are summarized in Table 3. The barriers to rotation around the C²—C³ bond in the initial state, **3**, are shown in Table 4. The

Table 4. Rotational barrier ($\Delta H^\ddagger = \Delta H_f(90^\circ) - \Delta H_f(R)$) of the Y-ring in kcal mol⁻¹

Z	Y	ΔH^\ddagger
OH	OH	11.60
	CH ₃	9.85
	F	9.68
	H	9.04
	Cl	9.13
	CN	7.80
CH ₃	OH	11.48
	CH ₃	9.74
	F	9.58
	H	8.61
	Cl	9.03
	CN	7.70
F	OH	11.91
	CH ₃	10.11
	F	9.94
	H	8.93
	Cl	9.38
	CN	8.01
H	OH	11.62
	CH ₃	9.87
	F	9.70
	H	8.72
	Cl	9.15
	CN	7.80
Cl	OH	11.83
	CH ₃	10.05
	F	10.23
	H	8.87
	Cl	9.32
	CN	8.34
CN	OH	12.14
	CH ₃	10.32
	F	10.13
	H	9.10
	Cl	9.56
	CN	8.17

data in Table 4 show that a stronger donor Y and a stronger acceptor Z have a higher barrier to rotation due to the more stabilized (on-form) resonance structure, **3'**. The barrier heights of 8-12 kcal mol⁻¹ may be ascribed mostly to the resonance structure, **3'**, in which partial double bond is formed between C² and C³, albeit steric effect is, no doubt, responsible partially.

Since the initial state, **3**, is stabilized by a stronger donor Y ($\delta\sigma_Y < 0$) and a stronger acceptor Z ($\delta\sigma_Z > 0$) whereas the TS (TS3) is stabilized by a stronger acceptor Y ($\delta\sigma_Y > 0$) and a stronger donor Z ($\delta\sigma_Z < 0$), the activation free energy, ΔG^\ddagger , becomes the highest for a stronger donor Y ($\delta\sigma_Y < 0$) coupled with a stronger acceptor Z ($\delta\sigma_Z > 0$) and the lowest for a stronger acceptor Y ($\delta\sigma_Y > 0$) coupled with a stronger donor Y ($\delta\sigma_Y < 0$).

Linear Free Energy Relationships

The Gibbs free energies of activation are used to derive the Hammett's reaction constants, ρ^\ddagger , using eq. (7) with σ^\ddagger due to strong resonance effect.¹¹ In order to assess resonance contribution, the substituent effects are further dissected into inductive (or field), \mathcal{F} , and resonance, \mathcal{R} , parts by fitting the free energy data to the Swain-Lupton¹² dual substituent parameter (SLDSP) equation,¹³ eq. (8). The results of these linear free energy relationship analyses are presented in Table 5. We note that as expected from the above discussion, ρ_Z^\ddagger is negative while ρ_Y^\ddagger is positive reflecting positive and negative charge development in the Z and Y-rings, respectively, in the TS. Again the importance of resonance contribution is demonstrated by the greater magnitude of r , the ratio of r/f ranging from 1.3 to 1.5. Since the Z-ring is directly linked to both the migration origin (C¹) and migration terminus (C²) in the TS, the susceptibility of resonance development of the positive charge to para-substituents is relatively large, 1.5 (Z-ring) vs 1.3 (Y-ring). It is to be noted that in the Z-ring the positive charge is resonance delocalized whereas in the Y-ring resonance structure is destroyed in the TS.

Table 5. Hammett type ρ^\ddagger values and dual substituent parameter analyses

	ρ_Y^\ddagger	f	r	r/f^0
Z=OH	2.44	1.02	1.31	1.28
Z=CH ₃	2.36	1.10	1.24	1.13
Z=F	2.45	0.94	1.34	1.43
Z=H	2.43	1.03	1.30	1.26
Z=Cl	2.46	0.96	1.34	1.40
Z=CN	2.47	0.92	1.35	1.47
$\rho_{YZ} = 0.03$				
	ρ_Z^\ddagger	f	r	r/f^0
Y=OH	-2.83	-1.10	-1.54	1.40
Y=CH ₃	-2.76	-0.85	-1.56	1.84
Y=F	-2.80	-1.03	-1.54	1.50
Y=H	-2.70	-0.90	-1.50	1.67
Y=Cl	-2.78	-1.03	-1.52	1.48
Y=CN	-2.78	-0.93	-1.55	1.67
$\rho_{YZ} = 0.03$				

⁰ $\log(k/k_H) = -(\Delta G^\ddagger / 2.303RT) = \rho^\ddagger \sigma^\ddagger$, Regression coefficients ≥ 0.99 .

¹ $\log(k/k_H) = f\mathcal{F} + r\mathcal{R}$, Regression coefficients ≥ 0.98

$$\delta \log k = -\delta \Delta G^\ddagger / 2.303RT = \rho^+ \sigma^+ \quad (7)$$

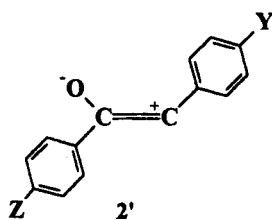
$$\delta \log k = -\delta \Delta G^\ddagger / 2.303RT = f \rho + rR \quad (8)$$

Strong dependence of the resonance structure, **3'**, on the para-substituent is shown by derived ρ_Y^+ ($\cong 1.7$) and r/f ($\cong 7$) values using rotational barriers (in ΔH^\ddagger instead of ΔG^\ddagger) in Table 4. Here again, the resonance structure is broken in the TS, the 90°-rotated state.

It is also interesting to note that the ratio of r/f for the benzylic rearrangements, eq. (1), ranges from 0.7 to 0.8 reflecting the predominant inductive (or field) effect over the resonance effect.¹⁴ In fact for this system, no important resonance structure can be assigned either in the initial state or in the bridged transition state. A quite surprising result emerged in this work is that the cross-interaction constant, ρ_{YZ} , exhibits vanishingly small value ($\rho_{YZ}=0.03$), eq. (9). The bridged TS structure, (Figure 1), which is a late one, i.e.,

$$\log(k_{YZ}/k_{RH}) = 2.44\sigma_Y^+ - 2.77\sigma_Z^+ + 0.03\sigma_Y^+\sigma_Z^+ \quad (9)$$

the migration of Z-ring is nearly complete, convinces us that the interaction between the two substituents, Z and Y, must be very strong. The negligibly small magnitude of ρ_{YZ} obtained therefore suggests strongly that the interaction of the two substituents within the initial state, **3**, is also very strong. This latter suggestion is not unreasonable in view of the strong positive charge delocalization in the initial state. The strong interactions in the TS, (large I^+_{YZ}), as well as in the initial state, (I^+_{YZ}), may well lead to a negligible change in the interaction (ΔI^+_{YZ}) on going from the initial to transition state and hence leads to a negligible ρ_{YZ} ,⁸ eq. (5). It is instructive to compare the magnitude of ρ_{YZ} for the series of gas-phase reactions theoretically investigated using the AM1 method in this laboratory: (i) For benzylic (anionic) rearrangements, $\rho_{YZ} = -0.48$.⁵ In structure **1** of eq. (1), there is no significant resonance delocalization effect. (ii) For azibenzil (neutral) rearrangements, $\rho_{YZ} = -0.53$.⁶ In structure **2** of eq. (2), there is weak resonance effect due to the vicinal $n-\sigma^*$ interaction, **2'**. There is a reversal of charge on going from the reactant (negative charge on Z-ring and positive charge on Y-ring) to the TS (positive charge on Z-ring and negative charge on Y-ring) which requires a relatively large



structural reorganization. (iii) For (cationic) rearrangements in protonated ketones, $\rho_{YZ}=0.03$. There is a strong resonance delocalization of positive charge in **3'**.

This comparison of the ρ_{YZ} values for these three rear-

angement processes together with the extent of resonance contribution in the initial state provides therefore evidence for the proportionality relation between the magnitude of ρ_{YZ} and the change in the intensity of interaction, ΔI^+_{YZ} , given by eq. (5).⁸

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