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THEORETICAL STUDIES ON THE TRANSITION-STATE IMBALANCE IN MALONONITRILE ANION-FORMING REACTIONS IN THE GAS PHASE AND IN WATER

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Semiempirical MO theoretical studies were carried out on the nucleophilic addition of phenoxide nucleophiles to 1,1-dicyano-2-arylethenes in the gas phase and in water using the AM1 method and the Cramer–Truhlar solvation model SM2.1. The gas-phase α^n and β^n values are 0·81 and 0·65, respectively, leading to the positive imbalance of $I = 0{\cdot}16$; the electric polarization and dispersion interactions of water incorporated in the SM2.1 model reduce both the α^n and β^n values to 0·61 and 0·36, giving $I = 0{\cdot}25$. The two Brønsted coefficients obtained theoretically in water agree satisfactorily with the experimental values ($\alpha^n_{corr} = 0{\cdot}55$ and $\beta^n = 0{\cdot}35$) obtained with amine bases. The small imbalance found both theoretically ($I = 0{\cdot}25$) and experimentally ($I \approx 0{\cdot}20$) can be ascribed to (i) a near-zero distance factor, $\Delta d = d_p - d_{TS} \approx 0$ and (ii) the small extent of negative charge localization by strucutral reorganization in the transition state. © 1997 John Wiley & Sons, Ltd.

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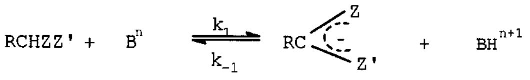
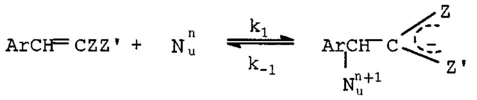
INTRODUCTION

Similarities in the structure–reactivity behavior between proton transfer involving activated carbon acids [equation (1)] and nucleophilic addition to activated alkene [equation (2)]:


(1)


(2)

have been well documented.[1] For example, ‘imbalances’ in structure-reactivity coefficients such as Brønsted α and β values exhibit a qualitatively similar dependence on the activating substituents ZZ′ in both types of reactions.[1] The transition-state imbalances are often defined as $I_p = \alpha_{CH} - \beta_B$ for the proton transfers and $I_n = \alpha^n_{nuc} - \beta^n_{nuc}$ for nucleophilic additions, where α_{CH} and α^n_{nuc} ($= \mathrm{d}\log k_1/\mathrm{d}\log K_1$) are the Brønsted α values obtained by varying a substituent, R, in the carbon acid and Ar in the alkene, respectively, and the β_B and $\beta^n{}_{nu}$ ($= \beta^n_{nuc}/\beta_{eq}$) are those obtained by varying the pK_a of the base (B) and nucleophile (Nu), respectively. These imbalances, I_p and I_n, are known to increase similarly with increasing resonance stabilization of the activating substituents ZZ′. Quantitatively, however, the effect of ZZ′ on imbalances (I) show significant differences between reactions (1) and (2); the magnitude of the imbalance for the nucleophilic addition to alkenes, I_n, is considerably smaller than that for the corresponding deprotonation of carbon acids, I_p, $I_p > I_n$. The main reason for this quantitative difference is believed to be the requirement of rehybridization of the carbon bearing the ZZ′ group in the TS for the deprotonation process. In the TS for reaction (2), the carbon is likely to maintain its sp^2 hybridization, thereby facilitating the shift of the negative charge into the ZZ′ group, whereas in the TS for reaction (1) the carbon is more sp^3-like and causes more delay in the development of resonance in the ZZ′ group, thereby leading to a greater α_{CH} value.[1]

A particularly interesting feature has emerged from studies of substituent effects involving malononitriles: an abnormally small imbalance has been observed for the deprotonation of malonitrile derivatives, ZZ′ = (CN)$_2$. For example, for the reaction of ArCH$_2$CH(CN)$_2$ with RCOO$^-$ as bases, $\alpha_{CH} \approx \beta_B \approx 1{\cdot}0$ and thus $I \approx 0$.[2] Similar results have been reported for some other deprotonations of malononitrile derivatives.[2] In line with the similarities between the

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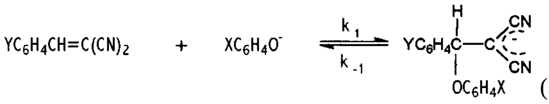
reaction types (1) and (2) noted above, abnormally small imbalances, albeit above zero, are also found in the nucleophilic addition to a dicyano-activated alkene.[3]

In our previous theoretical studies involving deprotonations of ketonic[4] and sulfonic carbon acids,[5] we have shown that the distance factor $\Delta d = d_p - d_{TS}$, where d_p and d_{TS} are the distances between substituent and anionic charge center in the product and transition state (TS), repectively, plays an important role in determining the magnitude of the imbalances, *I*. It occurred to us that the abnormally small *I* values observed for the malononitrile derivatives might be related to the distance factor. It is thought that in the imbalances with negative *I*, the site where the bulk of the negative charge ultimately resides (oxygen atoms of nitro, sulfonyl or carbonyl groups) is futher away from the substituent in the TS than in the product anion, Δd ($= d_p - d_{TS}) < 0$, whereas it is closer in the TS than in the product anion ($\Delta d > 0$) for positive *I*.[1d] This can be readily visualized using a hypothetical adiabatic transition in which the TS is balanced with $\alpha_{CH} = \beta_B$ at all stages of reaction coordinate. If the substituent is closer to the anionic center in the TS than in the product, α_{CH} will be greater, leading to a positive *I*, whereas if it is further away α_{CH} will be smaller than β_B and *I* will be negative. Hence the underlying cause of the imbalance is believed to be the same in all cases, and the change in the sign of *I* is due to a different location of the substituent relative to the anionic charge center within the molecule.

In order to examine the origins of such an abnormality, we carried out theoretical studies on the nucleophilic addition of phenoxide bases to substituted benzylidenemalononitriles (BMN) [equation (3)] in the gas phase and in water using the AM1 method[6] coupled with the Cramer–Truhlar solvation model, SM2.1.[7]



(3)

X = H, p-Cl, p-CN, p-CHO or p-NO$_2$

Y = p-NH$_2$, p-CH$_3$, H, P-Cl, p-CHO, p-CN or p-NO$_2$

CALCULATIONS

The semiempirical MO method AM1[6] was used throughout this work. Complex reaction systems (more than 20 heavy atoms are involved) precluded the use of more accurate *ab initio* methods. All stationary point structures including transition states were fully optimized and were characterized by harmonic frequency calculations. The Gibbs free energies of reaction, $\Delta G°$, and of activation, $\Delta G^‡$, were obtained by incorporating entropy terms at 298 K. The solvent effects (in water) were accounted for by use of the SM2.1 model of the Cramer–Truhlar method.[7] This quantum statistical continuum-dielectric model includes local-field terms representing solvent electric polarization, cavity creation, dispersion interaction and change in solvent structure, and these terms are treated self-consistently with a solute electronic Hamiltonian. In this work, we performed single-point calculations with the gas-phase geometries owing to the excessive computation times required. That the

Table 1. Solvent effects calculated using the Cramer–Truhlar solvation model (AM1–SM2.1) on the identity S_N2 reactions of (Y)-benzyl chlorides with Cl^- anion in the aqueous phase[a]

Phase	Y	ΔH_f[b] Substrate	Reactants	TS	$\Delta H^{\neq}$[c]	ρ_Y
Gas	H	6·91	−30·75	−27·60 (i444·6)[d]	3·15	
(no solvent)	*p*-Cl	−0·71	−38·37	−37·38 (i449·8)	0·99	8·74
	p-CN	38·78	1·12	−1·68 (i455·6)	−2·83	(*r*=0·96)
	p-NO$_2$	11·09	−26·57	−33·71 (i466·0)	−7·14	
Aqueous[e]	H	5·25	−109·32	−88·09	21·23	
(single point)	*p*-Cl	−2·04	−116·61	−95·62	20·23	0·96
	p-CN	33·93	−80·64	−60·34	20·30	(*r*=0·99)
	p-NO$_2$	5.84	−108.73	−88.44	20.29	
Aqueous[f]	H	5·20	−109·37	−88·17 (i385·4)[d]	21·20	
	p-Cl	−2·08	−116·65	−95·74 (i295·3)	20·91	0·98
	p-CN	33·89	−80·68	−60·44 (i172·6)	20·24	(*r*=0·99)
	p-NO$_2$	5·71	−108·86	−88·64 (i33·3)	20·22	

[a] Cl^-: heat of formation (ΔH_f) in the gas phase = −37·66 kcal mol^{-1}. $\Delta H_f + \Delta G_{sol}$ in the aqueous phase = −114·57 kcal mol^{-1}.
[b] Heat of formation, ΔH_f, in kcal mol^{-1}.
[c] In kcal mol^{-1}.
[d] Only one imaginary frequency for the transition state is given in parentheses.
[e] Results of single-point calculations (SM2.1/AM1//AM1).
[f] Fully optimized values (SM2.1/AM1//SM2.1/AM1).

Table 2. Solvent effects calculated using the Cramer–Truhlar solvation model (AM1–SM2.1) on the identity S_N2 reactions of (Y)-benzyl fluorides with F^- anion in the aqueous phase[a]

Phase	Y	ΔH_f[b] Substrate	Reactants	TS	$\Delta H^{\neq}$[c]	ρ_Y
Gas	H	31·48	−28·04	−4·06 (i434·3)[d]	23·98	
(no solvent)	*p*-Cl	−38·47	−35·03	−14·94 (i426·6)	20·09	11·02
	p-CN	0·40	3·84	19·80 (i433·1)	15·96	(r=0·97)
	p-NO_2	−27·26	−23·82	−13·60 (i438·9)	10·76	
Aqueous[e]	H	−32·13	−135·32	−69·16	66·16	
(single point)	*p*-Cl	−39·40	−142·59	−76·78	65·81	1·40
	p-CN	−3·38	−106·57	−41·67	64·90	(r=1·00)
	p-NO_2	−31·44	−134·63	−69·92	64·71	
Aqueous[f]	H	−32·15	−135·34	−69·65[d]	65·69	
	p-Cl	−39·42	−142·61	−77·35	65·26	1·44
	p-CN	−3·41	−106·60	−42·20	64·40	(r=1·00)
	p-NO_2	−31·55	−134·74	−70·58	64·16	

[a] F^-: heat of formation (ΔH_f) in the gas phase = 3·44 kcal mol^{-1}. $\Delta H_f + \Delta G_{sol}$ in the aqueous phase = −103·19 kcal mol^{-1}.

[b–f] See Table 1

[g] Only one imaginary frequency is not given.

use of the results of such single-point calculations is justified was tested for the identity S_N2 reactions of $YC_6H_4CH_2X + X^-$, with X = F and Cl and Y = H, *p*-Cl, *p*-CN and *p*-NO_2, as shown in Tables 1 and 2. The $\Delta H^{\neq}$ values by the single-point calculations (SM2.1/AM1//AM1) agree within 0.1 and 0.5 kcal mol^{-1} (1 kcal = 4·184 kJ) with those of the fully opitimized calculations (SM2.1/AM1//SM2.1/AM1) for X = Cl and F, respectively. The calculated Hammett ρ values are also in good agreement between the two methods, differing by only *ca* 2–3%.

RESULTS AND DISCUSSION

The energetics for the nucleophilic additions of phenoxide anions, $XC_6H_4O^-$, to 1,1-dicyano-2-arylethenes (benzylidenemalononitriles, BMN), $YC_6H_4CH{=}C(CN)_2$, in the gas phase at 298 K are summarized in Table 3. The rate is faster (or $\Delta G^{\neq}$ is lower) with a stronger electron-donating X (or with a weaker electron-withdrawing X) on the phenoxide anion nucleophile and/or electron-withdrawing Y on BMN, as expected from a typical nucleophilic addition process. The entropy terms vary very little with regard to the substituent X and/or Y. Therefore, in the calculations of the $\Delta G^{\neq}$ and $\Delta G°$ values in water by incorporating solvation effects (Cramer–Truhler model AM1–SM2.1)[7] (Table 4), we disregarded the entropy changes. The relevant structure–reactivity coefficients, ρ, α and β, for reaction (3) at 298 K in the gas phase and in water are given in Tables 5 and 6, respectively.

Table 5 reveals that the Brønsted α^n (or $\rho_Y^n = \rho_Y^{kim}/\rho_Y^{eq}$; ρ^n is the normalized ρ value, ρ^{kin}/ρ^{eq}) value is 0.81 (average value), which is greater than the Brønsted β^n (or $\rho^n{}_X = \rho^{kin}{}_X/\rho^{eq}{}_X$) value (average of 0·65) by *ca* 0·16, i.e. the transition-state imbalance, $I_n (= \alpha^n - \beta^n)$, in the gas-phase reaction is positive and the magnitude (0·16) is relatively small. This is in reasonable agreement with the experimental I_n value in water of *ca* 0·20,[3] although the individual AM1 α^n and β^n values in the gas phase are larger than the corresponding experimental values ($\alpha^n_{corr} \approx 0·55$ and $\beta^n = 0·35$)[3] in water. Our AM1 strucure–reactivity coefficients in water ($\alpha^n = 0·61$, $\beta^n = 0·36$ and $I_n = 0·25$) (Table 6) are, however, in good agreement with the corresponding experimental values in water obtained using piperidine and morpholine as bases[3] instead of the phenoxide ions used in the current theoretical studies. This agreement is an indication that the Cramer–Truhlar SM2.1 model[7] is satisfactory in simulating solvation reorganization in the TS in water. The experimental value of $\alpha^n \approx 0·55$ is that corrected for distortion effect due to the developing positive charge on the amine nitrogen.[3] In the present work, there is no need for such correction since phenoxide anion bases are used. The better agreement of our AM1 values in water with the corresponding experimental values in water seems to result from approximately the same magnitude of decrease in ρ^{kin} and ρ^{eq}, probably owing to local solvent electric polaization and dispersion interaction with charged solute (reaction system) when the solvation energies are taken into consideration with the Cramer–Truhler SM2.1 model;[7] the $\Delta\rho$ $(= |\rho_{water}| - |\rho_{gas}|)$ values are *ca* −3·8 and −3·2 for ρ_X^{kin} and −4·1 and −4·4 for ρ_Y^{kin} and ρ_Y^{eq}. Since the solvation effect leads to decreases in both ρ^{kin} land ρ^{eq} by approximately the same magnitude and since $\alpha^n = \rho_Y^{kin}/\rho_Y^{eq}$ and $\beta^n = \rho_X^{kin}/\rho_X^{eq}$, the net result is a decrease in α^n and β^n due to a greater proportional decrease in ρ^{kin} (which has a smaller magnitude than ρ^{eq}) than ρ^{eq} in water. Thus the solvent effect calculated with the quantum statistical continuum-dielectric model, Cramer–Truhler SM2.1,[7] which includes local-field terms representing solvent electric polarization and dispersion interaction, appears to be satisfactory for the type of reaction studied in this work.

It is commonly assumed that the Brønsted β value (β_B and β^n) in reaction types (1) and (2) is not only a measure of positive charge development on the base (amines or oxyanions) but also an approximate measure of progress of reaction along the reaction coordinate [the extent of proton transfer in reaction (1) and of bond making by the nucleophile in reaction (2)].[1, 8, 9] In contrast, however, α (α_{CH} and α^n) represents a measure of negative charge development on the substrate but is not a measure of the degree of proton transfer [in reaction (1)] or of bond making by the nucleophile [in reaction (2)]. The α value represents simply the extent of strucutral and solvational reorganization in the TS.[1, 8, 9]

Our AM1 results therefore suggest that O—C bond formation is *ca* 65% complete ($\beta^n \approx 0.65$), whereas negative charge development on C_2 (Scheme 1) felt by the substituent Y is stronger by *ca* 15% ($I_n \approx 0{\cdot}15$) than that which would result in a hypothetical synchronous case ($\alpha^n = \beta^n$). Recent high-level *ab initio* studies[10] of the carbon-to-carbon proton transfer from the acetaldehyde (and also from the proto-

Table 3. Gas-phase AMI-calculated energetics (kcal mol^{-1}) for the nucleophilic addition reactions of (Y)-1,1-dicyano-2-arylethenes with (X)-phenoxide anions

		Heat of formation (ΔH_f)								
X	Y	R	TS	P	$\Delta H^{\neq}$ [a]	$-T\Delta S^{\neq}$ [b]	ΔH° [c]	$-T\Delta S^{\circ}$ [b]	$\Delta G^{\neq}$ [d]	ΔG° [e]
H	*p*-NH$_2$	59·09	56·57	43·28	−2·52	11·02	−15·81	12·04	8·50	−3·67
	p-CH$_3$	54·19	50·40	36·41	−3·79	11·52	−17·78	12·09	7·73	−5·69
	H	63·04	57·87	43·84	−5·17	11·32	−19·20	12·08	6·15	−7·12
	p-Cl	55·55	48·99	34·50	−6·56	11·31	−21·05	12·05	4·75	−9·00
	p-CHO	32·32	24·06	9·26	−8·26	11·50	−23·06	12·33	3·24	−10·73
	p-CN	94·94	85·73	70·77	−9·21	11·35	−24·17	12·13	2·14	−12·04
	p-NO$_2$	68·01	55·19	39·54	−12·82	11·43	−28·47	12·22	−1·39	−16·25
p-Cl	*p*-NH$_2$	44·76	44·97	33·77	0·21	11·74	−10·79	12·23	11·95	1·44
	p-CH$_3$	39·86	38·78	26·93	−1·08	11·85	−12·93	12·28	10·77	−0·65
	H	47·77	46·25	34·36	−1·52	11·74	−13·41	12·21	10·22	−1·20
	p-Cl	41·22	37·47	25·14	−3·75	11·73	−16·08	12·21	7·98	−3·87
	p-CHO	17·99	12·63	−0·28	−5·36	11·90	−18·27	12·44	6·54	−5·83
	p-CN	80·61	74·32	61·52	−6·29	11·73	−19·09	12·20	5·44	−6·89
	p-NO$_2$	53·68	43·93	30·45	−9·75	11·81	−23·23	12·32	2·06	−10·91
p-CN	*p*-NH$_2$	74·41	78·12	69·16	3·71	12·02	−5·25	12·36	15·73	7·11
	p-CH$_3$	69·51	71·89	62·36	2·38	12·19	−7·15	12·41	14·57	5·26
	H	77·42	79·38	69·79	1·96	11·99	−7·63	12·17	13·95	4·54
	p-Cl	70·87	70·72	60·70	−0·15	11·97	−10·17	12·36	11·82	2·19
	p-CHO	47·64	45·95	35·61	−1·69	12·15	−12·03	12·56	10·56	0·53
	p-CN	110·26	107·69	97·20	−2·57	11·97	−13·06	12·37	9·40	−0·69
	p-NO$_2$	87·33	77·46	66·30	−5·87	12·06	−17·03	12·43	6·19	−4·60
p-CHO	*p*-NH$_2$	12·31	16·23	7·20	3·92	12·03	−5·11	12·20	15·95	7·09
	p-CH$_3$	7·41	10·02	0·39	2·61	12·22	−7·02	12·28	14·83	5·26
	H	15·32	17·50	7·83	2·18	12·00	−7·49	12·19	14·18	4·70
	p-Cl	8·77	8·85	−1·28	0·08	11·93	−10·05	12·17	12·01	2·12
	p-CHO	−14·46	−15·94	−26·40	−1·48	12·12	−11·94	12·41	10·64	0·47
	p-CN	48·16	45·81	35·20	−2·35	11·97	−12·96	12·19	9·62	−0·77
	p-NO$_2$	21·23	15·59	4·27	−5·46	12·04	−16·96	12·24	6·58	−4·72
p-NO$_2$	*p*-NH$_2$	35·07	43·30	37·07	7·60	12·10	2·00	12·23	19·70	14·23
	p-CH$_3$	30·17	37·04	30·32	6·87	12·24	0·15	12·40	19·11	12·56
	H	38·08	44·54	37·76	6·46	12·11	−0·32	12·25	18·57	11·93
	p-Cl	31·53	36·02	28·84	4·49	12·08	−2·69	12·23	16·57	9·54
	p-CHO	8·3	11·34	3·86	3·04	12·23	−4·44	12·40	15·27	7·96
	p-CN	70·92	73·13	65·50	2·21	12·13	−5·42	12·24	14·34	6·82
	p-NO$_2$	43·99	43·11	34·84	−0·88	12·17	−19·15	12·30	11·29	3·15

[a] $\Delta H^{\neq} = \Delta H_f(\mathrm{TS}) - \Delta H_f(\mathrm{R})$, where R and TS denote reactant and transition state, respectively.

[b] At 298 K.

[c] $\Delta H^{\circ} = \Delta H_f(\mathrm{P}) - H_f(\mathrm{R})$, where P denotes product.

[d] $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$.

[e] $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$.

nated acetaldehyde cation) to its enolate ion (to its acetaldehyde enol) have indicated that the fractional C—C π bond formation is roughly equal to the amount of negative charge build-up. The percentage changes in bond orders in the TS, $\%\Delta n^{\neq}$ defined by[11]

$$\%\Delta n^{\neq}=100\times\frac{\exp(-r^{\neq}/a)-\exp(-r_{R}/a)}{\exp(-r_{p}/a)-\exp(-r_{R}/a)} \qquad (4)$$

where $r^{\neq}$, r_R and r_P are bond lengths in the TS, reactant and product, respectively, gave 25–50, 27–46, 36–53 and 39–57% for r_1, r_2, r_3 and r_4, respectively, using the parameter $a=0{\cdot}6$[12] (Table 7). The degree of structural reorganization depends on the substituents, X and Y. Bonds r_1 and r_2 are stretched whereas r_3 and r_4 are compressed as the reaction progresses. The bond order changes in Table 7 reveal that a weaker nucleophile with a stronger electron acceptor (X = *p*-NO$_2$) and/or a stronger electron donor in the substrate (Y = *p*-NH$_2$) lead to a greater extent of bond order changes, $\%\Delta n^{\neq}$. This indicates that a weaker nucleophile and/or a stronger donor *Y* lead to a later TS along the reaction coordinate, which is of course a direct consequence of a lower exothermicity (or a higher endothermicity) (Table 3). Thus the reaction series studied in this work follows the Bell–Evans–Polanyi (BEP) principle,[13] which asserts that the TS shifts to a later position along the reaction coordinate as the reaction becomes more endothermic (or less exothermic). The $\%\Delta n^{\neq}$ values suggest that structural

Table 4. Gibbs free energy changes, $\Delta G^{\neq}$ and $\Delta G°$, in kcal mol^{-1}, for reaction (3) in water at 298 K

		$\Delta H_f+\Delta G_{sol}$[a]				
X	Y	R	TS	P	$\Delta G^{\neq b}$	$\Delta G^{\circ b}$
H	*p*-NH$_2$	−17·42	−2·83	−20·49	14·59	−3·07
	p-CH$_3$	−16·21	−3·32	−21·82	12·89	−5·61
	H	−8·57	4·07	−14·50	12·64	−5·93
	p-Cl	−15·25	−2·97	−21·89	12·28	−6·64
	p-CHO	−41·59	−29·84	−49·11	11·75	−7·52
	p-CN	21·35	32·93	13·66	11·58	−7·69
	p-NO$_2$	−6·05	5·45	−14·21	11·50	−8·16
p-Cl	*p*-NH$_2$	−28·11	−12·63	−28·03	15·48	0·08
	p-CH$_3$	−26·90	−13·12	−29·30	13·78	−2·40
	H	−19·26	−5·70	−21·98	13·56	−2·72
	p-Cl	−25·94	−12·73	−29·36	13·21	−3·42
	p-CHO	−52·28	−39·59	−56·58	12·69	−4·30
	p-CN	10·66	23·21	6·18	12·55	−4·48
	p-NO$_2$	−16·74	−4·24	−21·67	12·50	−4·93
p-CN	*p*-NH$_2$	3·02	19·81	6·64	16·79	3·62
	p-CH$_3$	4·23	19·34	5·43	15·11	1·20
	H	11·87	26·47	12·76	14·60	0·89
	p-Cl	5·19	19·77	5·42	14·58	0·23
	p-CHO	−21·15	−7·09	−21·77	14·06	−0·62
	p-CN	41·79	55·74	41·02	13·95	−0·77
	p-NO$_2$	14·39	28·32	13·16	13·93	−0·46
p-CHO	*p*-NH$_2$	−59·95	−43·01	−56·17	16·94	3·78
	p-CH$_3$	−58·74	−43·45	−57·40	15·29	1·34
	H	−51·10	−36·05	−50·05	15·05	1·05
	p-Cl	−57·78	−43·04	−57·40	14·74	0·38
	p-CHO	−84·12	−69·90	−84·59	14·22	−0·47
	p-CN	−21·18	−7·08	−21·81	14·10	−0·63
	p-NO$_2$	−48·58	−34·51	−49·65	14·07	−1·07
p-NO$_2$	*p*-NH$_2$	−30·78	−11·71	−22·02	19·07	8·76
	p-CH$_3$	−29·57	−12·18	−23·16	17·39	6·41
	H	−21·93	−4·73	−15·81	17·20	6·12
	p-Cl	−28·61	−11·72	−23·14	16·89	5·47
	p-CHO	−54·95	−38·57	−50·32	16·38	4·6
	p-CN	7·99	24·28	12·46	12·29	4·47
	p-NO$_2$	−19·41	−3·16	−15·40	16·25	4·01

[a] The ΔG_{sol} values obtained by single-point calculations using the gas-phase optimized geometries.

[b] $\Delta G=\Delta(\Delta H_f+\Delta G_{sol})$.

Table 5. Structure–reactivity coefficients[a] for reaction 3 in the gas phase at 298 K

Coefficient	p-NH$_2$	pCH$_3$	H	p-Cl	p-CHO	p-CN	p-NO$_2$
ρ_X^{kin} [b]	−5·83	−5·85	−6·32	−6·03	−6·14	−6·22	−6·51
ρ_X^{eq} [c]	−9·04	−9·24	−9·61	−9·40	−9·54	−9·57	−9·81
$\rho_X^n = \rho_X^{kin}/\rho_X^{eq}$	0·64	0·63	0·66	0·64	0·64	0·65	0·66
Brønsted β^n [d]	0·64	0·63	0·65	0·64	0·64	0·65	0·66
ρ_Y^{kin} [e]	—	—	5·69	5·76	5·56	5·51	4·99
ρ_Y^{eq}	—	—	7·02	7·08	6·66	6·76	6·36
$\rho_Y^n = \rho_Y^{kin}/\rho_Y^{eq}$	—	—	0·81	0·81	0·83	0·82	0·78
Brønsted α^n [f]	—	—	0·81	0·82	0·83	0·81	0·79

[a] Correlation coefficient (r) > 0·96 in all cases.

[b] σ^- and σ^o values are used. ρ^{kin} denotes the Hammett-type reaction constants for $\Delta G^{\neq}/-2{\cdot}303RT$ vs substituent constants.

[c] σ^- and σ^o values are used. ρ^{eq} denotes the Hammett-type reaction constants for $\Delta G^{o}/-2{\cdot}303RT$ vs substituent constants.

[d] Brønsted β^n values from the slopes of the plot of $\Delta G^{\neq}$ vs ΔG^{o}.

[e] σ^o values are used.

[f] Brønsted α^n values from the slopes of the plot of $\Delta G^{\neq}$ vs ΔG^{o}.

reorgnization in the TS (%$\Delta n^{\neq}$ for $r_1 \approx r_3$) lags behind the progress of reaction (%$\Delta n^{\neq}$ for r_4) by *ca* 5–10%. This lag is relatively small amount compared with that in the structural reoganization found in the TS of the deprotonation of nitroalkanes[1,14] [equation (1)]. The reason for this difference is that in the nucleophilic addition of a nucleophile to an alkene [equation (2)] the developing negative charge is not as easily localized on the carbon bearing the activating groups, (CN)$_2$, as in the deprotonation of nitroalkanes [equation (1)]. In the nucleophilic addition no rehybridization of C$_2$ (Scheme 1) is required, in contrast to the hybridization change (sp^3→sp^2) in the deprotonation.[1]

Another important reason for the small imbalance found, $I_n \approx 0{\cdot}2$ may be the small distance factor, $\Delta d = d_p - d_{TS}$ (≈ 0). As discussed in previous papers,[4,5] when the anionic charge center is closer to the substituent (Y) in the TS (d_{TS}) than in the product (d_p), $d_{TS} < d_p$, the charge felt by the substituent is disproportionately larger in the TS than it is in the product anion simply due to the positive distance factor, Δd ($= d_p - d_{TS}) > 0$; this results in an increased α^n ($= \rho^{kin}/\rho^{eq}$) simply because of an increased ρ^{kin} relative to ρ^{eq}.

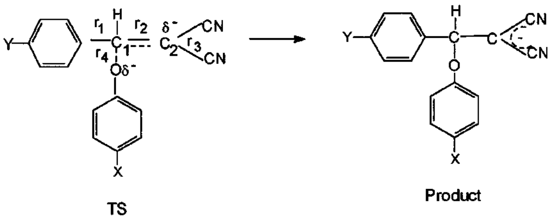
Mulliken charge distributions in the TSs and product anions are shown in Figure 1 for the deprotonation of alkanes (**I** and **II**) and for the nucleophilic addition of phenoxide (C$_6$H$_5$O$^-$) to alkens (**III** and **IV**). We note that a strong negative charge accumulation occurs in the TS on the carbon being deprotonated (C$_1$) in **I and II**, whereas it occurs on the adjacent carbon (C$_2$) in **III** and **IV**. Moreover, negative charge shifts toward the activating groups [(CN)$_2$ and NO$_2$] and the phenyl ring are greater in the latter, **III** and **IV**, than in the former, **I** and **II**. Thus, ρ^{kin} for the deprotonation of the alkanes will be greater than that for the nucleophilic addition to alkenes on two accounts: (i) the developing negative charge in the TS is nearer to the substituent in the ring and (ii) negative charge loss to the neighbouring groups (the activating groups and the ring) is smaller.

Since the difference in the charge distribution between the TS and the product ion increases with increasing π acceptor strength of ZZ′, α^n should increase for the same degree of reaction progress β^n at the TS. The observed α^n values will therefore consist of two parts, one due to delayed structural/solvational reorganization and the other to the non-zero distance factor, $\Delta d \neq 0$. In the ideal case of $\Delta d = 0$, α^n will represent the part due to the lag in structural and solvational reorganization only. When the activating groups are dicyano, ZZ′ = (CH)$_2$, as in the present work, the near-zero distance factor is almost realized. In the TS and

Table 6. Structure–reactivity coefficients[a] for reaction (3) in water at 298 K

Coefficient	p-NH$_2$	pCH$_3$	H	p-Cl	p-CHO	p-CN	p-NO$_2$
ρ_X^{kin} [b]	−2·20	−2·22	−2·19	−2·27	−2·28	−2·52	−2·35
ρ_X^{eq} [c]	−6·10	−6·19	−6·21	−6·24	−6·31	−6·28	−6·20
$\rho_X^n = \rho_X^{kin}/\rho_X^{eq}$	0·36	0·36	0·35	0·36	0·36	0·37	0·38
Brønsted β^n [d]	0·37	0·37	0·37	0·38	0·38	0·39	0·39
ρ_Y^{kin} [e]	—	—	1·52	1·47	1·38	1·41	1·38
ρ_Y^{eq}	—	—	2·47	2·44	2·13	2·35	2·30
$\rho_Y^n = \rho_Y^{kin}/\rho_Y^{eq}$	—	—	0·62	0·60	0·65	0·60	0·60
Brønsted α^n [f]	—	—	0·62	0·61	0·65	0·61	0·61

[a–f] See Table 5.

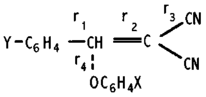


Scheme 1

product anion in Scheme 1 the anionic charge residues on C_2 so that $d_{TS} \approx d_P$ and $\Delta d \approx 0$, except that in the product anion the negative charge is delocalized over wide ranges on $C(CN)_2$ moiety and r_1 and r_2 stretch further than those in the TS (by $\Delta d = 0{\cdot}126$ Å for X = Y = H, Table 7). The Δd caused by such bond stretching will be small, however, compared with the Δd caused by the shift of negative charge center over one or two bond lengths ($\Delta d \approx 2$–3 Å, Table 7), as in the nitroalkanes (Scheme 2).

Charge distributions in the product anions in Figure 1 indicate that the negative charge is distributed evenly over the —$C(CN)_2$ moiety in **I** and **III**, whereas it is more

Table 7. Bond lengths (Å) and percentage bond order changes, $\%\Delta n^{\neq}$, in the transition states



X	Y	Bond lengths (Å)				$\%\Delta n^{\neq}$			
		r_1	r_2	r_3	r_4	r_1	r_2	r_3	r_4
H	*p*NH_2	1·467	1·388	1·410	1·973	35	31	38	43
	p-CH_3	1·468	1·386	1·411	1·992	31	29	36	41
	H	1·468	1·386	1·411	1·992	30	29	36	41
	p-Cl	1·468	1·385	1·411	2·000	29	29	36	40
	p-CHO	1·468	1·384	1·412	2·006	28	29	33	40
	p-CN	1·468	1·384	1·412	2·006	28	29	33	40
	p-NO_2	1·468	1·381	1·412	2·020	25	27	35	39
p-Cl	*p*-NH_2	1·469	1·392	1·409	1·928	39	35	41	46
	p-CH_3	1·470	1·391	1·410	1·940	35	34	39	45
	H	1·470	1·390	1·410	1·941	33	34	39	45
	p-Cl	1·470	1·389	1·410	1·948	33	33	39	44
	p-CHO	1·471	1·388	1·410	1·954	33	33	39	44
	p-CN	1·470	1·388	1·410	1·955	32	33	39	44
	p-NO_2	1·471	1·386	1·411	1·964	30	31	38	43
p-CN	*p*-NH_2	1·472	1·397	1·408	1·876	44	40	44	51
	p-CH_3	1·473	1·395	1·408	1·886	40	39	47	50
	H	1·473	1·395	1·408	1·889	39	39	46	49
	p-Cl	1·473	1·393	1·409	1·895	39	38	44	49
	p-CHO	1·474	1·393	1·409	1·899	39	38	44	49
	p-CN	1·473	1·392	1·409	1·900	37	37	44	48
	p-NO_2	1·474	1·390	1·410	1·909	36	36	43	47
p-CHO	*p*-NH_2	1·472	1·397	1·408	1·876	44	40	44	51
	p-CH_3	1·473	1·395	1·408	1·886	40	39	46	50
	H	1·473	1·395	1·408	1·866	39	39	47	52
	p-Cl	1·473	1·393	1·409	1·894	39	37	44	49
	p-CHO	1·474	1·393	1·409	1·899	39	37	44	49
	p-CN	1·474	1·392	1·409	1·901	39	36	44	48
	p-NO_2	1·474	1·390	1·410	1·909	36	36	43	47
p-NO_2	*p*-NH_2	1·475	1·402	1·406	1·816	50	45	52	57
	p-CH_3	1·476	1·400	1·407	1·828	46	44	50	55
	H	1·477	1·400	1·407	1·828	47	44	50	55
	p-Cl	1·476	1·399	1·407	1·835	45	44	50	55
	p-CHO	1·477	1·398	1·408	1·839	45	43	47	54
	p-CN	1·477	1·398	1·408	1·840	45	43	47	54
	p-NO_2	1·477	1·396	1·408	1·849	42	42	49	53

localized on the two oxygen atoms in **II** and **IV**.

The anionic charge center moves from C_2 in the TS to oxygen atoms of the nitro group in the product, i.e. Δd will represent a shift of negative charge over two bond lengths, $r_{CN}+r_{NO}$. This large positive distance factor, $\Delta d \gg 0$, is the main reason for the large experimentally observed α leading to the large imbalance, *I*, for the nitroalkanes.[1,14] In general, a single intervening C—C bond between the reaction center and substituent is believed to reduce ρ by a factor of 2·8.[15] This is why the distance factors plays such an important role in determining the TS imbalances, *I*.[4, 5] It is also why a negative TS imbalance, $I=\alpha-\beta<0$, is observed when Δd is negative; α becomes disproportionately small owing to the depressed ρ^{kin} in α ($\rho^{n}=\rho^{kim}/\rho^{eq}$), despite the fact that the lag in structural and solvation reorganization should result in an increased α value relative to β.[1d,4,5] In this situation, the distance factor ($\Delta d<0$) decreases α ($\Delta\alpha<0$), whereas the lag in structural/solvational reorganization leads to an increased α ($\Delta\alpha>0$), so that the two components partially cancel each other out. This is why the α values obtained theoretically in deprotonations of ketonic and sulfonic carbon acids were so small, leading to relatively large negative imbalance, *I*.[4,5]

We therefore conclude that the near-zero imbalance, $I_n \approx 0{\cdot}20$ found for the nucleophilic addition to benzylidene-malononitrile, both experimentally and theoretically, can be

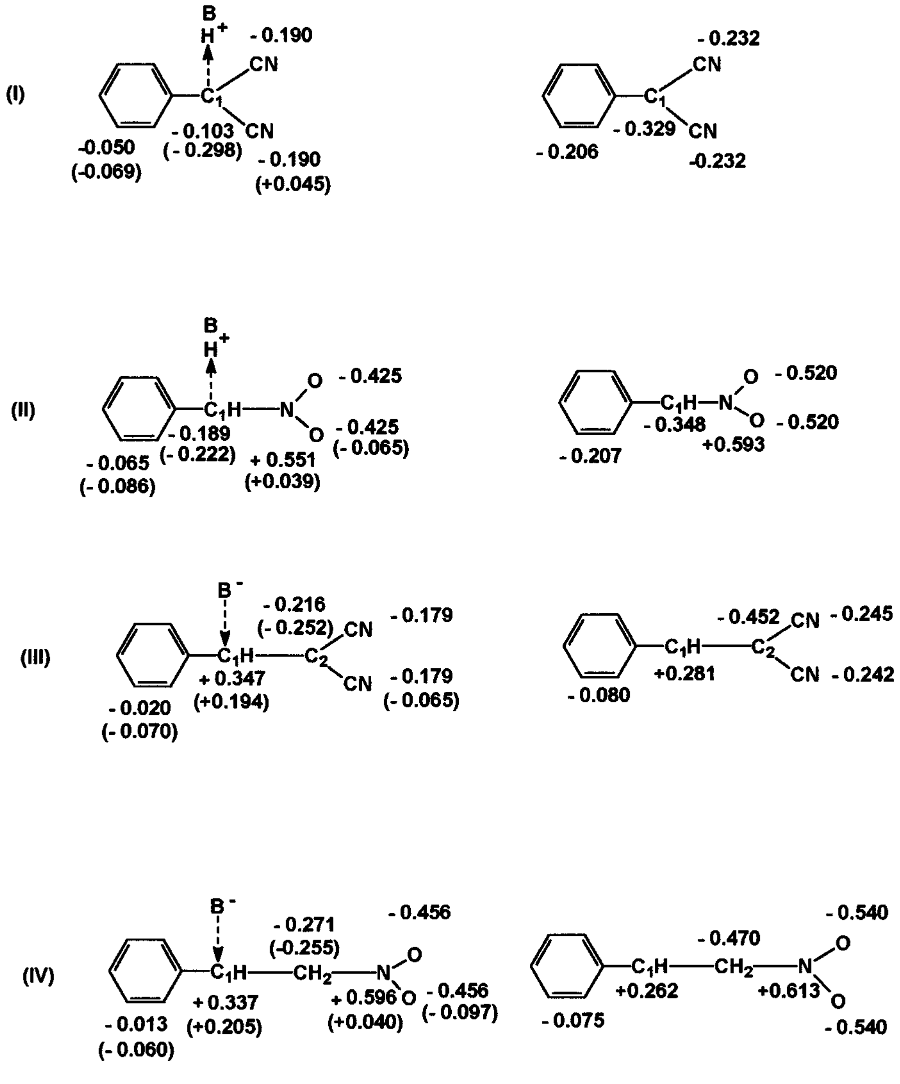
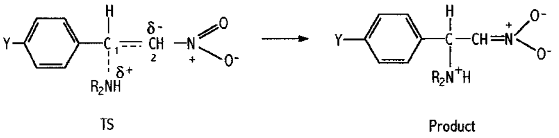


Figure 1. Charge distribution in the TS and in the product anions. Group charge except for NO_2 group. Changes in charge ($\Delta q^{\neq}=q_{TS}-q_R$) are given in parentheses. Average values are given for the two CN and O



Scheme 2

ascribed to (i) the near-zero distance factor, $\Delta d = d_p - d_{TS} \approx 0$, and (ii) the small extent of negative charge localization by structural reorganization in the TS as there no hybridization change required.

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REFERENCES

1. (a) C. F. Bernasconi, *Acc Chem. Res.* **20**, 301–308 (1987); **25**, 9–16 (1992); (b) C. F. Bernasconi, *Tetrahedron* **45**, 4017–4090 (1989); (c) C. F. Bernasconi, *Adv. Phys. Org. Chem.* **27**, 118–238 (1992); (d) C. F. Bernasconi and S. A. Hibdon, *J. Am. Chem. Soc.* **105**, 4343–4348 (1983).
2. R. P. Bell and S. Grainger, *J. Chem., Soc. Perkin Trans. 2* 1367–1370 (1976).
3. C. F. Bernasconi and R. B. Killion, Jr, *J. Org. Chem.* **54**, 2878–2885 (1989).
4. (a) D. J. Stefanidis and J. W. Bunting, *J. Am. Chem. Soc.* **112**, 3163–3168 (1990); **113**, 991–995 (1991); (b) W. K. Kim, Y. I. Chun, C. K. Sohn, C. K. Kim and I. Lee, *Bull. Korean Chem. Soc.* **18**, 193–197 (1997).
5. (a) S Wodzinski and J. W. Bunting, *J. Am. Chem. Soc.* **116**, 6910–6915 (1994); (b) W. K. Kim, W. S. Ryu, C. K. Sohn, B.-S. Lee, C. K. Kim and I. Lee, *Bull. Korean Chem. Soc.* **18**, 208–212 (1997).
6. (a) M. J. S. Dewar, E. G. Zoebisch, E. P. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.* **107**, 3902–3909 (1985); (b) *MOPAC 6·0 Program,* available from Quantum Chemistry Program Exchange (QCPE), No. 506.
7. (a) D. A. Liotard, G. D. Howkins, G. C. Lynch, C. J. Cramer and D. G. Truhlar, *J. Comput. Chem.* **16**, 422–440 (1995); (b) C. J. Cramer and D. G. Truhlar, *J. Am. Chem. Soc.* **113**, 8305–8311 (1991); (c) C. J. Cramer and D. G. Truhlar, *J. Comput. Chem.* **13**, 1089–1097 (1992); (d) C. J. Cramer and D. G. Truhlar, *J. Am. Chem. Soc.* **116**, 3892–3900 (1994); (e) D. J. Giesen, J. W. Storer, C. J. Cramer and D. G. Truhlar, *J. Am. Chem. Soc.* **117**, 1057–1068 (1995); (f) J. W. Storer, D. J. Giesen, G. D. Howkins, G. C. Lynch, C. J. Cramer, D. G. Truhlar and D. A. Liotard, in *Structure and Reactivity in Aqueous Solution. Characterization of Chemical and Biological Systems*, edited by C. J. Cramer and D. G. Truhlar, ACS Symposium Series, No. 568m Chapt. 3. American Chemical Society, Washington, DC (1994); (g) *AMSOL 5·0 Program*, available from Quantum Chemistry Program Exchange (QCPE), No. 606.
8. J. E. Leffler and E. Grunwald, *Rates and Equilibria in Organic Reactions*, p. 156. Wiley, New York (1963).
9. (a) A. J. Kresge, *Acc. Chem. Res.* **8**, 354 (1975); (b) W. P. Jeucks, *Chem. rev.* **85**, 511 (1985); (c) C. F. Bernasconi and P. J. Wenzel, *J. Am. Chem. Soc.* **118**, 10494–10504 (1996).
10. C. F. Bernasconi and P. J. Wenzel, *J. Am. Chem. Soc.* **116**, 5405–5413 (1994); **118**, 10494–10504 (1996).
11. (a) G. P. Ford and C. T. Smith, *J. Am. Chem. Soc.* **109**, 1325–1331 (1987); (b) S. S. Glad and F. Jensen, *J. Chem. Soc., Perkin Trans. 2* 871–876 (1994); (c) J. K. Lee, C. K. Kim, B.-S. Lee and I. Lee, *J. Phys. Chem.* (A) **10**, 2983–2899 (1997).
12. (a) I. Lee, C. K. Kim and B.-S. Lee, *J. Comput. Chem.* **16**, 1045–1054 (1995); (b) H. S. Johnston, *Gas Phase Reaction Rate Theory*, pp. 80–83. Ronald Press, New York (1996); (c) K. N. Houk, S. M. Gustafson and K. A. Black, *J. Am. Chem. Soc.* **114**, 8565–8572 (1992).
13. M. J. S. Dewar and R. C. Dougherty, *The PMO Theory of Organic Chemistry*, p. 212. Plenum Press, New York (1975).
14. F. G. Bordwell and W. J. Boyle, Jr, *J. Am. Chem. Soc.* **94**, 3907–3911 (1972).
15. (a) M. Charton, *Prog. Phys. Org. Chem.* **13**, 119–251 (1981); (b) I. Lee, C. S. Shim, S. Y. Chung, H. Y. Kim and H. W. Lee, *J. Chem. Soc., Perkin Trans. 2* 1919–1923 (1988); (c) M. R. F. Siggel, A. Streitwieser, Jr and T. D. Thomas, *J. Am. Chem. Soc.* **110**, 8022–8028 (1988); (d) I. Lee, *Adv. Phys. Org. Chem.* **27**, 57–117 (1992).