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THE ROLE OF THE TRANSITION STATE BOND ORDER AND REACTION ENERGY IN METHYL NUCLEOPHILIC SUBSTITUTIONS

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Abstract - A general intersecting-state model has been applied to the calculation of the energy barriers for methyl nucleophilic substitutions in vapour phase and solution in terms of force constants and lengths of reactive bonds, reaction energy and the bond order of the transition state, $n^{\ddagger}$. In the vapour phase the current reactions have been found to have a $n^{\ddagger}$ value close to unity ($n^{\ddagger}$=0.93). This is attributed to the involvement of a pair of nonbonding electrons of the substituents, which acquires a bonding character at the transition state. In liquid solutions such a pair of electrons is not completely available to increase $n^{\ddagger}$, due to interactions with solvent molecules. The calculated values depend on the hard-soft nature of the substituents and the accepting properties of the solvent being higher for soft groups and solvents of low acceptor number. Solvent effects on reaction rates are interpretable in terms of the effect of solvent polarity on the transition state bond order and the reaction energy. Vapour phase reactions with delocalized nucleophiles have been found to have $n^{\ddagger}$=3/2 and the reaction energy has an inverted effect on the energy barriers, in contrast with the current reactions where this effect is a normal one.

The classical S_N2 nucleophile substitution on methyl substrates is still a very active field of research in physical organic chemistry in spite of a considerable number of experimental and theoretical studies[1-6] since the basic work of Hughes, Ingold and Patel in 1933.[7] A renewed interest recently arose for the development of approaches to interconnect the well known solution data with the more recent findings in the vapour phase.[1] With this aim several theoretical calculations have been carried out through *ab initio* approaches or even with simple models such as the theory of Marcus. To unravel trends of reactivity within a family of related molecules, theoretical models, which sacrifice rigour to gain simplicity, are often better than the *ab initio* calculations. Simple theoretical models such as that of Marcus are therefore particularly adequate in physical organic chemistry. Furthermore it was shown by Wolfe et al.[8] that the calculations of the Marcus barriers from the intrinsic self-exchange barriers and the exothermicity of the reactions, are in excellent agreement with the *ab initio* calculations. However, it remains to be understood the large variation (ca. 120 kJ mol^{-1}) in the intrinsic energy barriers, and why such reactions should show as dramatic solvent effects.[6] With this aim we have applied a recently developed intersecting-state model[9] to unravel some mechanistic aspects of nucleophilic displacements on methyl. This model which encompasses Marcus and BEBO theories as particular cases, and gives a simple rationale for the Hammond postulate and the linear free energy relationships, has provided some new insights on the mechanisms of these reactions.

Theoretical Model

The theory has been described in detail elsewhere[9] and only the essential will be stated here. Aliphatic nucleophilic substitutions involve the making and breaking of one chemical bond. Let us assume that the potential energy curves of these reactive bonds can be represented by harmonic oscillators. Within an intersecting-state model the transition state corresponds to the crossing point of the harmonic curves and one can write

$$(1/2)f_r x^2 = (1/2)f_p (d-x)^2 + \Delta E^o \qquad (1)$$

where f_i are the stretching force constants, ΔE^o is the reaction energy, x is the bond extension of the reactant and d is the displacement of the minima of the potential energy curves. The parameter d represents also the sum of the bond extensions of reactant and product, $d = (l^{\ddagger} - l_r)+(l^{\ddagger} - l_p)$. The activation energy of the reaction is given by

$$\Delta E^{\ddagger} = (1/2)f_r x^2 \qquad (2)$$

where x is estimated from eq (1) once d is known. The sum of the bond extensions was shown[9] to be proportional to the sum of the equilibrium bond lengths of reactant and product

$$d = \eta(l_r + l_p) \qquad (3)$$

where η is the reduced bond extension. This equation has a simple physical meaning: when an equilibrium bond length is small its bond extension is small, but when it is large, the bond extension is also large.

The parameter η is related to the chemical bond order at the transition state, $n^{\ddagger}$, and to the so called "configuration entropy", λ, proposed by Agmon and Levine,[10]

$$\eta = \frac{a' \ln 2}{n^{\ddagger}} + \frac{a'}{2}\left(\frac{\Delta E^o}{\lambda}\right)^2 \qquad (4)$$

a' is a constant (a' = 0.156) and λ has the dimensions of an energy.

In eq (4) the first term $a'\ln 2/n^{\ddagger}$ allows one to estimate the intrinsic energy barriers at $\Delta E^o = 0$. The second term takes into account any effect of the reaction energy on the displacement d of the potential energy curves. At the transition state, the reaction energy has to be accommodated internally. If the activated complexes have few ways and, consequently, a small capacity to store ΔE^o ($\lambda << |\Delta E^o|$) this energy has to be stored in the reactive bonds, through further bond extensions. In consequence η and d both increase with an increase in $|\Delta E^o|$. However if the activated complexes have many ways and a large capacity to store energy ($\lambda >> |\Delta E^o|$) then no reaction energy will be stored in the reactive bonds and d is independent of ΔE^o. The latter situation corresponds to the theory of Marcus.

For vapour phase reactions involving the making and breaking of the chemical bonds of diatomic molecules, the present model gives a good estimation of the activation energy of chemical reactions for one stretching mode in reactants and one in products. However for reactions of complex molecules in the gas phase or for reactions in condensed media, there are many more degrees of freedom. These can be treated on a statistical basis using free energies, and in eqs (1), (2) and (4) E should be substituted by G.

When there is conservation of the total bond order along the reaction coordinate, the transition state bond order is $n^{\ddagger} = 1/2$ (at $\Delta G^o = 0$) because for single bonds $n_i + n_r = 1$. However when the reactant or the product possess nonbonding or antibonding electrons in low energy molecular orbitals, such electrons can acquire a bonding character at the transition state and $n^{\ddagger}$ increases. For example, for hydrogen transfer reactions in the vapour phase, such as $H + HX \rightarrow H_2 + X$, where X is an halogen atom which possess pairs of nonbonding electrons, one of such pairs can acquire a bonding character at the transition state and then $n^{\ddagger} = 1$.[9] This nonconservation of the bond order of the chemical reactions can be viewed in terms of simple molecular orbital diagrams[11]; for $\{HHX\}^{\ddagger}$ the electronic configuration $1\sigma^2\, 2\sigma_b^2\, 2\sigma_a^2(nb)\, 1\pi^3(nb)$ leads to $n^{\ddagger} = 1$ for each one of the chemical bonds. For a reaction $H + X_2 \rightarrow HX + X$ the halogen diatomic molecule possess a pair of antibonding electrons which acquires a bonding character at the transition state and the average bond order of the two transition state bonds is $n^{\ddagger} = 3/2$.[9]

In our model both parameters $n^{\ddagger}$ and λ allow one to define the concept of a reaction series. A series of similar reactions is characterized in terms of a constant $n^{\ddagger}$ and λ.

Gas phase reactions

Brauman and coworkers[3,4] have undertaken a kinetic study of the reactions of several anions with methane derivatives in the vapour phase. The rates of reaction, k_r, are smaller than the rates of collision. We have considered the reactions as concerted processes with an activation free energy barrier given by $k_r = k_c \exp(-\Delta G^{\ddagger}/RT)$. With such values, d and η values which reproduce $\Delta G^{\ddagger}$ can be estimated from eqs (1) to (3) (Table 1); the force constant and bond length data were taken from ref. 12. Since the reactions under study are very exothermic processes, reasonable fits can be obtained for the normal and the inverted region ($\Delta G^o < -f_p d^2/2$). To distinguish between these two possibilities we have to examine the quadratic dependence of η on ΔG^o, predicted by eq (4).

Figure 1 presents the linear relationship between η and $(\Delta G^o)^2$ in the normal region for several current nucleophilic substitution reactions of CH_3Y. The intercept is $\eta(o)=0.116$, which corresponds to a transition state bond order close to unity ($n^{\ddagger} = 0.93$). In the inverted region the intercept is much lower, $\eta(o) = 0.055$ and $n^{\ddagger} = 2$. The presence of X or Y groups with nonbonding electrons lead one to expect a transition state bond order of unity[9] and consequently we consider that the reactions 1 to 7 of Table 1 have a normal free energy dependence ($\Delta G^o > -f_p d^2/2$).

Table 1. Bond Extensions for Methyl Transfer $X^- + CH_3Y \rightarrow XCH_3 + Y^-$ Reactions in the Vapour Phase[a]

Reaction	X^-	Y^-	$f_r/10^3$[f]	$f_p/10^3$[f]	$\Delta G^{\ddagger}$[a,g]	ΔG^o[a,b,g]	$1/A^o$[c]	η normal	η inverted
1	CH_3O^-	Cl^-	2.2	3.0	2.94	-175.6	3.193	0.124	0.092
2	t-BuO$^-$	Cl^-	2.2	3.0	5.68	-146.3	3.193	0.122	0.077
3	CH_3O^-	Br^-	1.9	3.0	2.24	-204.8	3.364	0.125	0.096
4	t-BuO$^-$	Br^-	1.9	3.0	2.96	-179.7	3.364	0.121	0.087
5	F^-	Cl^-	2.2	3.6	3.42	-117.0	3.146	0.118	0.065
6	CD_3S^-	Cl^-	2.2	2.2	8.65	-121.2	3.584	0.121	0.071
7	CN^-	Br^-	1.9	3.5	11.36	-146.3	3.397	0.120	0.055
a[d]	HCC^-	Br^-	1.9	2.7	4.52	-246.6	3.482	0.144	0.104
b	HCC^-	Cl^-	2.2	2.7	9.2	-213.2	3.312	0.150	0.095
c	$PhCH_2^-$	Cl^-	2.2	2.7	11.35	-213.2	3.312	0.154	0.092
d	$CH_3CO_2^-$	Br^-	1.9	3.0	10.5	-71.1	3.364	0.137	0.074
e[e]	pMe-ArCH_2^-	Br^-	1.9	2.7	2.75	-252.5	3.483	0.140	0.109
f[e]	ArCH_2^-	Br^-	1.9	2.7	4.16	-246.2	3.483	0.143	0.104
g[e]	mF-ArCH_2^-	Br^-	1.9	2.7	6.78	-223.6	3.483	0.143	0.094
h[e]	mCN-ArCH_2^-	Br^-	1.9	2.7	11.6	-200.6	3.483	0.145	0.082

[a] Data of ref. 3 except where stated otherwise; $\Delta G^{\ddagger}$ estimated from the reaction efficiency; [b] Assumed to be identical to ΔH^o; [c] $1=(l_r + l_p)$; [d] Reactions with inverted region behaviour (a to h); [e] Data of ref. 4; [f] kJ mol^{-1} A^{o-2}; [g] kJ mol^{-1}.

Other reactions (a to g on Table 1) do not follow the same dependence of Figure 1, and consequently represent a different reaction series. Such reactions are also associative processes, but involve delocalized nucleophiles.[3] These reactions do not follow the linear dependence of η on $(\Delta G^o)^2$ in the normal region. However, such a dependence is found in the inverted region (Figure 2). The intercept $\eta(o) = 0.071$ corresponds to the type-III ($n^{\ddagger} = 3/2$) hydride reactions since $n^{\ddagger} = 1.52$. Another pair of electrons from the delocalized nucleophiles is siphoned into the reactive bonds of the activated complexes. With substituted aromatic nucleophiles further electron siphoning can occur at the transition state as we have shown with sigmatropic shift reactions.[13] This is particularly notable with m-CN-ArCH_2^-.

All these facts support the view that the energy barriers for the methyl transfer reactions with delocalized nucleophiles are due to an inverted region effect. Under normal conditions we would have expected that these reactions would be faster than those previously considered, but a decrease in d due to an increase in $n^{\ddagger}$, moves the reaction from the normal to the inverted region and increases the energy barrier. This is the first case that we are aware of an inverted region effect, for reactions outside the field of electron transfer processes.

The values of λ for the reactions of Figures 1 and 2 are quite high (λ = 580 kJ mol^{-1} and 960 kJ mol^{-1}) when compared with the ones for the hydride reactions (145 to 77 kJ mol^{-1}).[9] This implies that the dependence of η on ΔG^o is very weak for methyl transfers and that the activated complexes are not very tight.

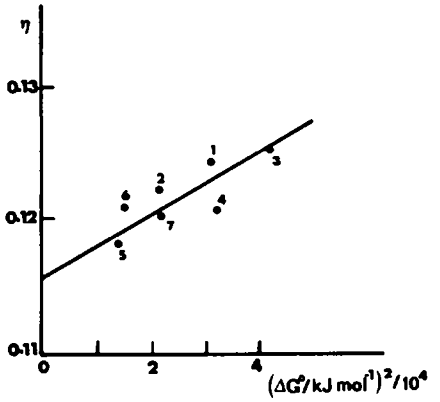

Figure 1. Linear dependence of the reduced extensions, η, and (ΔG°) for methyl transfer reactions in the vapour phase. Legend for the reactions in Table 1.

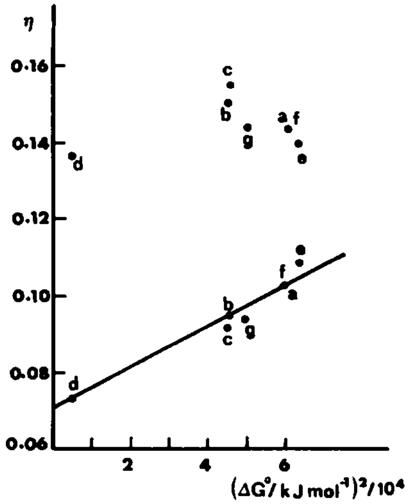

Figure 2. η versus $(\Delta G^{o})^2$ for methyl transfers with delocalized nucleophiles; bottom plot: inverted region; top plot: normal region. Legend in Table 1.

Brauman et al.[3,4] have interpreted the gas phase methyl transfer reactions in terms of the theory of Marcus on a double minimum potential energy surface. For very exothermic reactions this situation can be represented by the following kinetic scheme

$$X^- + CH_3Y \underset{k_{-c}}{\overset{k_c}{\rightleftarrows}} X.CH_3.Y^- \xrightarrow{k_1} XCH_3 + Y^-$$

where $X.CH_3.Y^-$ represents a large-dipole complex which can be observed under certain conditions.[14] The observed rate constant is simply $k_{obs} = k_c k_1/(k_{-c}+k_1)$. When $k_1 << k_{-c}$ it is $k_{obs} = k_c k_1/k_{-c}$ and $k_{obs} = A\ \exp|-(\Delta G^{\ddagger}_{int}+\Delta G_{int})/RT|$ where A is a preexponential factor, ΔG_{int} is the energy of the intermediate complex and $\Delta G^{\ddagger}_{int}$ the activation free energy for the decomposition of the same intermemediate. As long as the presence of the intermediate does not alter the energy of the transition state, the apparent activation free energy with respect to reactants is simply $\Delta G^{\ddagger} = \Delta G^{\ddagger}_{int}+\Delta G_{int}$ and the formation of the intermediate complex will not be revealed in the apparent energy barriers of the reaction[§]. However the formation of such an intermediate can have some effect on the synchronous nature of the reaction.

Conservation of total bond order, $n_r + n_p = 1$, is only valid for synchronous processes.[13] The loss of the synchronous character of the reaction would lead to $n_r + n_p < 1$ and consequently the transition state bond order will have $n^{\ddagger} < 1/2$. When there is an increase in the total bond order at the transition state, $n_r + n_p = m$ $(m>1)$, the loss of the synchronous character of the reaction would lead to $n_r + n_p < m$. For the normal methyl transfer reactions the transition state bond order is not unity, but slightly smaller ($n^{\ddagger} = 0.93$). Although this may be due to the relatively small experimental errors in $\Delta G^{\ddagger}$, it seems more likely that it corresponds to some loss of the synchronous character of the normal methyl transfer reactions and consequently, to the formation of a weakly stable intermediate complex with k_1, comparable to k_{-c}. Under this assumption, e.g. for the complex $(CH_3O.CH_3Br)^-$ the binding energy is estimated to be $\Delta G = -1.7$ kJ mol^{-1} (300 K) in agreement with the accepted view that, along the reaction path, there is a double-well potential with an energy barrier. The value of the potential-well is comparable to values calculated by Carrion and Dewar[6] for similar complexes. The scatter of points in Figure 1 can also be due to small differences on the binding energy of these charge-dipole complexes.

[§] The same conclusion stands even when k_1 is comparable to k_{-c}, as long as the intermediate charge-dipole complex cannot dissipate its excess energy fast enough in the gas phase.

Reactions in Water

Several methyl transfer reactions have been studied in water solutions. Albery and Kreevoy[2] have reviewed these data which can be studied in the same manner as the vapour phase processes. Table 2 summarizes the calculated data. With the exception of the very exothermic processes (CN^- and OH^-), the calculated reduced displacements are essentially free of the quadratic dependence on ΔG^o, and can be used to calculated the bond orders at the transition state through eq (4), $n(o) = 0.108/n^{\ddagger}$. The results are also presented in Table 2.

Table 2. Bond Extensions for Methyl Transfer $X^- + CH_3Y \rightarrow XCH_3 + Y^-$ Reactions in Water[a]

X^-	Y^-	$f_r/10^3$ [c]	$f_p/10^3$ [c]	$\Delta G^{\ddagger}$ [d]	ΔG^o [d]	l/Å	n	$n^{\ddagger}$
Cl^-	F^-	3.6	2.2	122	-2	3.146	0.190	0.57
Br^-			1.9	115	4	3.317	0.180	0.60
I^-			1.6	117	-5	3.586	0.180	0.60
H_2O			3.0	135	-8	2.805	0.208	0.52
OH^-			3.0	109	-94	2.805	0.219	(0.58) [b]
CN^-			2.7	106	-152	2.838	0.240	(0.58) [b]
Cl^-	Cl^-	2.2	2.2	109	0	3.534	0.179	0.60
Br^-			1.9	109	6	3.705	0.175	0.62
I^-			1.6	100	-3	3.974	0.167	0.65
H_2O			3.0	127	-6	3.193	0.200	0.54
OH^-			3.0	103	-92	3.193	0.209	(0.54) [b]
CN^-			2.7	96	-156	3.226	0.224	(0.54)[b]
I^-	Br^-	1.9	1.6	91	-9	4.145	0.162	0.67
H_2O			3.0	120	-12	3.364	0.195	0.55
OH^-			3.0	95	-98	3.364	0.201	(0.57) [b]
CN^-			2.7	90	-156	3.397	0.218	(0.57) [b]
I^-	I^-	1.6	1.6	92	0	4.414	0.154	0.70
H_2O			3.0	124	-3	3.633	0.189	0.57
OH^-			3.0	97	-89	3.633	0.193	(0.59) [b]
CN^-			2.7	92	-147	3.666	0.209	(0.59) [b]
Cl^-	NO_3^-	2.8	2.2	115	3	3.237	0.187	0.58
Br^-			1.9	109	9	3.408	0.178	0.61
I^-			1.6	103	0	3.677	0.171	0.63
H_2O			3.0	125	-3	2.896	0.204	0.53

[a] Data from ref 2; [b] Extrapolated to $\Delta G^o = 0$; [c] kJ mol^{-1} $Å^{-2}$; [d] kJ mol^{-1}

The most striking feature that comes from comparison with vapour phase data is the change in $n^{\ddagger}$. Whereas for the normal reactions in the vapour phase $n^{\ddagger} \approx 1.0$, in water solutions $n^{\ddagger}$ is close to 0.5. As we have said before, $n^{\ddagger} \approx 1.0$ is attributed to a siphoning of the electronic density of the pair of nonbonding electrons of a halogen or oxygen atom into the transition state. The fact that in water $n^{\ddagger} = 0.5$ reveals that such nonbonding pair of electrons, owing to strong interactions with the solvent, is not available to increase the total bond order of the transition state. Although this is the main feature for these reactions, there are significant differences between the substituents.

Table 3 summarizes the $n^{\ddagger}$ values for several substituents. The conclusion that we can establish is that the availability of the nonbonding pair of electrons, which becomes a bonding pair at the transition state, is in the order $F^-(H_2O) < Cl^- < Br^- < I^-$. Consequently, soft anions favour the nucleophilic substitutions from an electronic point of view, whereas the hard nucleophiles do not help the reactions in solution, because they do not increase the bond order of the transition state. The smaller anions have the higher HOMO which are then more available for the interaction with the H_2O molecules.[15]

Table 3. Transition State Bond Orders of Methyl Transfer Reactions in Water

Y^-/X^-	H_2O	F^-	Cl^-	Br^-	I^-
F^-	0.52	—	0.57	0.60	0.60
Cl^-	0.54	0.57	0.60	0.62	0.65
Br^-	0.55	0.60	0.62	—	0.67
I^-	0.57	0.60	0.65	0.67	0.70
NO_3^-	0.53	—	0.58	0.61	0.63

The terms "hard" and "soft" have been criticized because of their imprecision and the difficulty of defining them quantitatively.[16] We have attempt to correlate $n^\ddagger$ with some quantitative properties of the entering and leaving groups. A reasonable non-linear correlation has been found for F^-, Cl^-, Br^- and I^- with the oxidation potential. For the same groups there is a linear correlation between $n^\ddagger$ and one of the empirical Swain-Scott parameter, n_{CH_3I} ($n_{CH_3I} = \log(k_{CH_3I+Y}/k_{CH_3I+CH_3OH})$).[17] Both correlations are independent of the group entering or leaving situation. However when one includes other ions such a NO_3^-, OH^-, CN^- they do not fit into any of the previous correlations.

Steric effects in spin exchange processes of transition metal complexes have been found to cause large variations in the transition state bond order $n^\ddagger$, which lead to variations in rates by several orders of magnitude.[18] In a similar manner one can interpret the steric effects in alkyl substitutions. For example, $(CH_3)_3CH_2X$ is about 10^{-7} times slower than the methyl system.[19] Owing to steric hindrances bond-making and bond-breaking processes cannot take place in unison and the synchronous character of the reaction is lost.

Although data on very exothermic reactions in solution are not so abundant as in the vapour phase, the dependence of η on $(\Delta G^o)^2$ shows that the configuration entropy parameter in solution ranges between $\lambda = 180$ to 250 kJ mol^{-1}. These values are smaller than the ones in the vapour phase which reveals that the activated complexes are more tightly bound species in solution than in gas phase. This involves not only the reagent and product species, but also the solvent molecules of the solvation shell.

Methyl transfer reactions have been found to obey the Marcus equation.[2-5] According to the intersecting-state model, Marcus theory corresponds to the situation where d and η are independent of ΔG^o. This requires high configuration entropies or small $|\Delta G^o|$, a situation that is quite common for the vapour phase and solution reactions. However a word of caution should be made with respect to the use of cross-reaction rate constants employed in the Marcus theory. This procedure is only valid when η depends weakly on ΔG^o and $n^\ddagger$ does not vary significantly for the different reactions.

Solvent Effects

The nature of solvent has a strong influence on the rates of nucleophilic substitution reactions.[20] For example, the S_N2 displacement (charge type 2)

$$(CH_3CH_2)_3N + CH_3CH_2I \rightarrow (CH_3CH_2)_4N^+ + I^-$$

proceeds faster in alchools than in hydrocarbons. In contrast substitution reactions between a negative or positive ion and a neutral molecule (charge type 1 and type 4) and between ions of opposite charges (charge type 3) proceed more rapidly in nonpolar than in polar solvents and, namely, are slowed by addition of water. The present model can provide some insights on these facts.

Table 4 presents the calculated bond extension parameter for methyl nucleophilic substitutions in non-aqueous solvents and Table 5 shows the corresponding transition state bond orders. According to the present model the higher $n^\ddagger$ values should be found for solvents with poor accepting properties[21], such as acetone (acceptor number, (AN = 12.5) and dimethylformamide (AN = 16). Good acceptor solvents such as water (AN = 55) and methanol (AN = 41) would lead to low $n^\ddagger$ values, close to the $n^\ddagger = 0.5$ limiting value.

Table 4. Bond Extensions for Methyl Transfer Reactions in Nonaqueous Solvents.

Solvent	X^-	Y^-	$f_r/10^3$ [c]	$f_p/10^3$ [c]	$\Delta G^\ddagger$ [b, d]	ΔG^o [b, d]	l/A^o	η
acetonitrile	Br^-	Cl^-	2.2	1.9	79	12	3.705	0.145
methanol					109	7		0.174
DMF [a]					97	22		0.157
methanol	I^-	Cl^-	2.2	1.6	104	0	3.974	0.169
DMF					92	22		0.148
acetone					89	20		0.146
methanol	I^-	Br^-	1.9	1.6	90	-6	4.145	0.159
DMF					72	0		0.140
acetone					74	10		0.136
methanol	I^-	I^-	1.6	1.6	87	0	4.414	0.150
acetone					68	0		0.132

[a] Dimethylformamide; [b] Data collected in ref 2; [c] kJ mol^{-1} A^{o-2}; [d] kJ mol^{-1}.

Table 5. Transition State Bond Orders for Methyl Transfer Reactions in Different Solvents.

Solvent	Br^-/Cl^-	I^-/Cl^-	I^-/Br^-	I^-/I^-
Water	0.62	0.65	0.67	0.70
Methanol	0.62	0.64	0.68	0.72
Dimethylformamide	0.69	0.73	0.77	—
Acetone	—	0.74	0.79	0.82

The quantitative assessment of the effect of thermodynamics on the reaction rates of methyl transfers has dominated the more recent studies of these systems. The present model has revealed the effect of many other structural factors on the reaction rates, namely the effect of bond lengths and force constants of the reactive bonds, the configuration entropy and the bond order of the transition state. Of all those factors, the important ones are in general, the reaction energy, ΔG^o, and the transition state bond order, $n^\ddagger$. In charge type 2 reactions an increase in solvent polarity decreases drastically ΔG^o, which becomes the dominating effect. Consequently, the rates increase with an increase in solvent polarity. In contrast, the transition state bond order seems to be the dominant factor for the other charge type reactions. Since $n^\ddagger$ decreases with increase in the solvent acceptor number and consequently, with an increase in solvent polarity, the rates are slower for the more polar solvents.

For some reactions solvents have only a minor effect on the reaction rates, a kind of solvent paradox.[6] This is a consequence of the almost equal effect of $n^\ddagger$ and ΔG^o on the reaction barriers. A good acceptor solvent on decreasing both $n^\ddagger$ and ΔG^o leads to opposite and compensating effects of both parameters on the reaction barriers.

In qualitative terms the nucleophilicity of halide ions for reactions in dipolar protic solvents is $I^- > Br^- > Cl^- > F^-$ reflecting the dominant effect of $n^\ddagger$. In the dipolar aprotic solvents and in the vapour phase [22]the order is reversed, $F^- > Cl^- > Br^- > I^-$, which reveals that other structural factors rather than $n^\ddagger$ dominate the reaction kinetics. This is obvious in the vapour phase, because $n^\ddagger$ is constant for all those substituents.

In liquid solutions the nucleophilicity can depend on the nature of the halide counter ion. For example the order of reactivity of the halides towards n-butyl brosylate[20] in acetone is $Cl^- > Br^- > I^-$ when $(C_4H_9)_4N^+$ is the cation of the halide salt, but is $I^- > Br^- > Cl^-$ when Li^+ is the cation. A hard cation such as Li^+ interacts more strongly with the hard anions in the ion-pairs and can reverse the order of reactivity, the variation of $n^\ddagger$ being the dominant factor.

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