Tetrahedron Letters,Vol.23,No.51,pp 5467-5470,1982 0040-4039/82/515467-04$03.00/0
Printed in Great Britain

IS CHARGE DEVELOPMENT A MEASURE OF S_N2 TRANSITION STATE STRUCTURE?

Addy Pross*[1a] and Sason S. Shaik[1b]

Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600, Australia

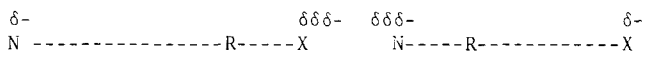
and Department of Chemistry, Ben Gurion University of the Negev, Beer-Sheva, Israel

Summary. Application of the configuration mixing model to the S_N2 reaction illustrates that charge development in an S_N2 reaction is not linearly related to the position of the transition state along the reaction coordinate.

There is an intuitive belief in chemistry that the extent of charge development in a transition state is dependent on the earliness or lateness of that transition state. For example, in the S_N2 reaction of an anionic nucleophile with a neutral substrate (eq. 1), most of the negative charge would be expected to be localised on the nucleophile for an early

$$N^- + RX \longrightarrow NR + X^- \qquad (1)$$

transition state, as indicated in 1, while for a late transition state most of the charge would be localised on the leaving group, as indicated in 2.



1 2

This belief presumably stems from the Leffler-Hammond postulate[2] which attributes to the transition state characteristics intermediate between those of reactants and products. Thus "early" transition states are expected to have reactant-like charge distributions, while "late" transition states are expected to exhibit product-like charge distributions.

In this communication we wish to suggest that the above supposition is often invalid and that charge development in the transition state, in general, is unrelated to the position of the transition state along the reaction coordinate. For an S_N2 reaction on CH_3X, for example, about equal negative charge on both nucleophile and leaving group is expected for the entire range of

transition states - from "early" through to "late".

In recent papers[5] we have shown that reaction profiles may be built up using the method of linear combination of valence-bond configurations. This approach was utilised for substitution,[3a,b,e,f] elimination[3c] and proton-transfer reactions.[3d] Application of this method to a simple S_N2 reaction[3e,f] suggested that two key configurations are involved in determining the reaction profile. These are the reactant configuration, 3, and the product configuration, 4.

A schematic plot of these two configurations as a function of the reaction coordinate is illustrated in Fig. 1. Using this model, it is apparent that the position of the transition state along the reaction coordinate will be in the vicinity of the intersection point of the two VB configuration curves. Thus the wave function, ψ_{TS} describing the transition state will reflect the fact that both configurations are of equal energy at the crossing point by having equal weights as indicated in eq. 2.

$$\psi_{TS} = \frac{1}{\sqrt{2}} \left[(N:^- \; R\cdot \; \cdot X) + (N\cdot \; \cdot R \; :X^-) \right] \qquad (2)$$

On the basis of eq. 2, the charge on the nucleophile and the leaving group will be the same and equal to 0.5. Consideration of small contributions of higher energy configurations may modify the value of 0.5 somewhat but is not expected to significantly disturb the charge equality.[4]

The important point is that the above conclusion holds regardless of the position of the transition state along the reaction coordinate. Making the nucleophile more powerful, or replacing the leaving group by a better one, will lead to a lowering of the energy of configuration 4 relative to 3. This is indicated in Fig. 1 by the broken line. Of course, the transition state is now "earlier" in accord with the Bell-Evans-Polanyi principle;[5] however electron transfer also takes place "earlier" so that the transition state is still described by eq. 2 in which ~0.5 electronic charge has been transferred. We see therefore that charge distribution within an S_N2 transition state is not directly related to the position of the transition state along the reaction coordinate, and in any event is certainly not expected to be a linear function of the geometric change along that coordinate.

The idea that charge redistribution is not linearly related to the geometric change along the reaction coordinate has support from other reaction types. The reaction of an alkali metal, e.g. K with a halogen atom, e.g. Br, to give the ion pair, e.g. KBr, has long been represented using VB configurations, $M\cdot \; \cdot X$ and $M^+ \; X^-$.[6] The M----X distance at which electron-transfer from M to X takes place is given by the approximate equation 3,

$$I_M - A_X \approx \frac{e^2}{r} \qquad (3)$$

where I_M is the ionization potention of M, A_X is the electron affinity of X and r is the M----X distance at which the electron is transferred. The better the donor-acceptor MX pair,

the "earlier" the electron transfer, in close analogy with the S_N2 model.[7] Thus both reactions share the feature that charge transfer takes place owing to crossing of the two VB configurations, and this may occur either early or late along the reaction coordinate.

Comparison of S_N2 reactions with electron-transfer processes between metal complexes also suggests certain similarities. For these redox reactions, metal-ligand bond reorganization is required to accompany electron transfer.[8] This takes place when donor and acceptor complexes attain appropriate metal-ligand bond lengths, so that reactant and product configurations become of equal energy. It is at this point - the transition state - that the electron transfer process takes place. Here, also, as in the S_N2 case, electron transfer is centered in the transition state region regardless of the TS geometry.[9]

Acknowledgment We are most grateful to W.J. Bouma, D.P. Craig, J.A. Pople, L. Radom, and H.F. Schaefer for helpful comments and one of us (A.P.) to the Australian National University for the award of a Visiting Fellowship.

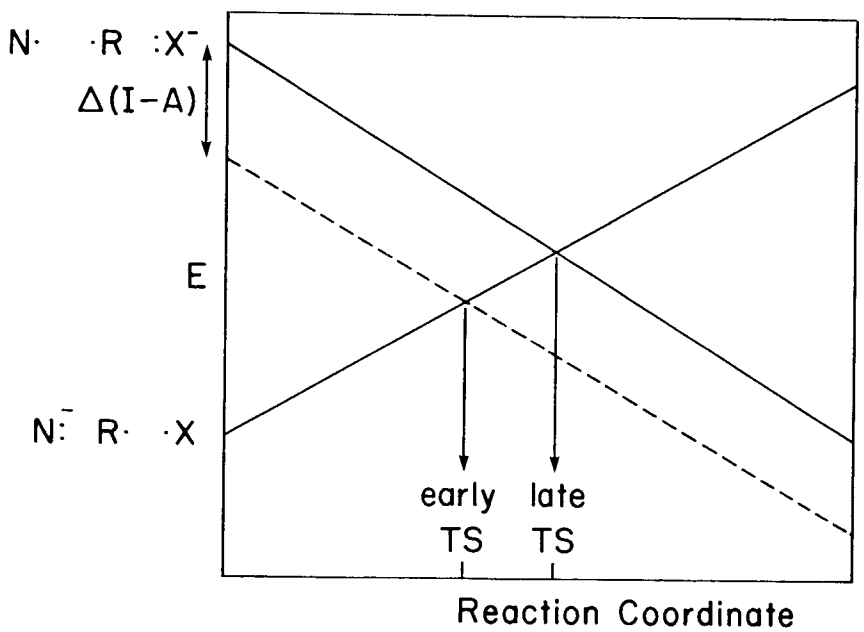


Fig. 1: Schematic energy diagram for reactant (N:⁻ R· ·X) and product (N· ·R :X⁻) configurations along the S_N2 reaction coordinate. Dotted line indicates the product configuration curve, using a better nucleophile or leaving group. While the more reactive system (dotted line) is seen to have an "earlier" transition state, ψ_{TS} (eq. 2) remains invariant.

References and Notes

(1) (a) Research School of Chemistry, Australian National University. Permanent Address: Department of Chemistry, Ben Gurion University.
(b) Department of Chemistry, Ben Gurion University.

(2) (a) Leffler, J.E. Science 1953, 117, 340.
(b) Hammond, G.S. J. Am. Chem. Soc. 1955, 77, 334.
(c) Leffler, J.E.; Grunwald, E. "Rates and Equilibria of Organic Reactions," Wiley, New York, 1963.
(d) Pross, A. Adv. Phys. Org. Chem. 1977, 14, 69.

(3) (a) Shaik, S.S. J. Am. Chem. Soc. 1981, 103, 3692.
(b) Pross, A.; Shaik, S.S. J. Am. Chem. Soc. 1981, 103, 3702.
(c) Pross, A.; Shaik, S.S. J. Am. Chem. Soc. 1982, 104, 187.
(d) Pross, A.; Shaik, S.S. J. Am. Chem. Soc. 1982, 104, 1129.
(e) Shaik, S.S.; Pross, A. J. Am. Chem. Soc. 1982, 104, 2708.
(f) Shaik, S.S. Nouv. J. Chim. 1982, 6, 159.

(4) The slight mixing in of "intermediate" configurations - the carbonium ion configuration, $N:^{-}\ R^{+}\ :X^{-}$, and the carbanion configuration, $N\bullet\ R:^{-}\ \bullet X$, will modify the value of 0.5. Mixing in of the carbonium ion configuration will tend to increase the nett negative charge on both nucleophile and leaving group while mixing in of the carbanion configuration will tend to decrease these corresponding charges. However, if we assume that the mixing in of intermediate configurations does not significantly disturb the equality of the contribution of the major contributors, 3 and 4, then the charge on the leaving group and the nucleophile in the transition state will remain the same (though not necessarily 0.5). Mixing in of the very high energy asymmetric configurations $N:^{-}\ R:^{-}\ X^{+}$ and $N^{+}\ R:^{-}\ :X^{-}$ will modify the charge equality but not to any significant extent due to the slight extent of mixing. Recall mixing in is proportional to the stability of the secondary configuration. Cases which deviate from this description are borderline S_N1-S_N2 mechanisms where the carbonium ion configuration is more dominant, and very exothermic S_N2 reactions where extreme curve skewing may shift the transition state so it no longer coincides with the intersection point of Figure 1. For curve skewing effects see, Michl, J. Photochem. Photobiol., 1977, 25, 141.

(5) (a) Evans, M.G.; Polanyi, M. Trans. Faraday Soc. 1936, 32, 1540.
(b) Bell, R.P. Proc. Roy. Soc. Ser. A 1936, 154, 414.
(c) For a more recent discussion see: Dewar, M.J.S. in "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill: New York, 1969; pp. 284-288.

(6) For example see: Laidler, K.J. "Theories of Chemical Reaction Rates" McGraw-Hill, New York, 1969; pp. 171-175.

(7) For KBr, a particularly good donor-acceptor pair, electron transfer takes place at $\sim 15\overset{\circ}{A}.^{6}$

(8) (a) Marcus, R.A. Annu. Rev. Phys. Chem. 1964, 15, 155.
(b) Marcus, R.A. J. Phys. Chem. 1968, 72, 841; 1963, 67, 853.

(9) Ab initio MO calculations which were conducted to verify the S_N2 transition state charge distribution computationally, were of little value. Charge distributions were found to be very basis set dependent highlighting the well-known deficiencies of the Mulliken population analysis. Interestingly though, for the transition state of $H^{-} + CH_3F$ at the highest level of calculation used (3-21G + CI), essentially equal charges on H and F were obtained (H: -0.67; F: -0.63) despite the asymmetric transition state.

(Received in UK 6 October 1982)