phenoxide ion < morpholine < *N*-methylmorpholine).

The steric effect is seen to be slightly smaller in the deprotonation of $T_A^{\pm}$ derived from **1**-NO$_2$, as one would expect for the slightly less crowded mononitro adduct. For example, k_{2p}^{A} is about 3-fold higher for **1**-NO$_2$ than for **1**-(NO$_2$)$_2$ despite the slightly more favorable $\Delta pK = pK_a^{AH} - pK_a^{\pm}$ for **1**-(NO$_2$)$_2$ (2.89) vs. 2.35 for **1**-NO$_2$. On the other hand there is no significant difference between **1**-NO$_2$ and **1**-(NO$_2$)$_2$ with respect to catalysis by phenoxide or substituted phenoxide ions. This could be due, in part, to experimental error in k_{2p}^{B}; k_{-2p}^{BH} was only determined at one pH value (compared to k_{-2p}^{AH}, which is the average from determinations at four different pH values), and k_{2p}^{B}, which is calculated as $k_{-2p}^{BH}K_a^{\pm}/K_a^{BH}$, is very sensitive to the uncertainties in $pK_a^{\pm}$, which are relatively large in the case of **1**-NO$_2$. It should also be noted that since the phenoxide ions are less bulky than morpholine, discrimination between **1**-NO$_2$ and **1**-(NO$_2$)$_2$ should be less pronounced than for k_{2p}^{A} and thus could be masked by the experimental uncertainties.

Other systems where proton-transfer rates are depressed by steric crowding in $T_A^{\pm}$ include the amine adducts of 1,1-dinitro-2,2-diphenylethylene[15] and of 1,3,5-trinitrobenzene.[20] We note that these are the systems where eq 5 appears to hold, i.e., where coordination of *n*-butylamine and piperidine with an electrophile has, surprisingly,[21] the same effect on pK_a. Possibly this is, at least in part, because the stronger solvation of $RR'NH_2^+$ (two H bonds to solvent) compared to $RR'R''NH^+$ (one H bond), which usually leads to $pK_a(RR'NH_2^+) > pK_a(RR'R''NH^+)$, is sterically hindered. This interpretation also fits with the observation that with the less crowded amine adducts of β-nitrostyrene eq 5 breaks down.[47]

Experimental Section

Materials. α-Cyano-4-nitrostilbene (**1**-NO$_2$) and α-cyano-2,4-dinitrostilbene (**1**-(NO$_2$)$_2$) were prepared by known procedures.[17,48] **1**-NO$_2$ was recrystallized from ethanol, mp 177–178 °C (lit.[48] mp 175–176 °C); **1**-(NO$_2$)$_2$ was recrystallized from glacial acetic acid, mp 161–162 °C (lit.[17] mp 160–161 °C). (4-Nitrophenyl)acetonitrile (**2**-NO$_2$) and (2,4-dinitrophenyl)acetonitrile (**2**-(NO$_2$)$_2$) were available from a previous study.[13] Piperidine, morpholine, *n*-butylamine, *N*-methylmorpholine, and *p*-cyanophenol were purified as described before.[15] Reagent grade Me$_2$SO was stored over 4-Å molecular sieves prior to use. All other chemicals were reagent grade and were used without further purification.

Reaction Solutions, pH Measurements, and Spectra. The procedures used were essentially those described earlier.[15]

Rate and Equilibrium Measurements. We followed the general procedures described earlier[5,15] except that the evaluation of τ_1^{-1} was, in part, performed by direct computer interface with our stopped-flow apparatus. In the pH-jump experiments involving the adducts of **1**-(NO$_2$)$_2$, the pH jump had to be applied within 1–2 min after generating T_A^- because T_A^- decomposes in strongly basic solution into benzaldehyde and **2**-(NO$_2$)$_2^-$ and into an additional product with λ_{max} at 360 and 500 nm. The nature of this species was not further investigated but we suspect it is a product of the hydrolysis of the cyano group of **1**-(NO$_2$)$_2$.

Acknowledgment. This work was supported by Grants No. CHE-77-27998 and CHE-80-24261 from the National Science Foundation. We thank Professor William P. Jencks for comments on this manuscript.

Registry No. **1**-NO$_2$, 3695-95-2; **1**-(NO$_2$)$_2$, 19051-22-0; **1**-NO$_2$ (morpholine adduct), 85613-79-2; **1**-(NO$_2$)$_2$ (morpholine adduct), 85613-83-8; **1**-NO$_2$ (anionic piperidine adduct), 85613-82-7; **1**-(NO$_2$)$_2$ (anionic morpholine adduct), 85613-81-6; **1**-(NO$_2$)$_2$ (anionic piperidine adduct), 85613-80-5; **3**-H, 1214-54-6; **3**-OMe, 15795-54-7; **3**-NMe$_2$, 15795-57-0; *n*-butylamine, 109-73-9; piperidine, 110-89-4; morpholine, 110-91-8; morpholinium, 45422-42-2; *N*-methylmorpholinium, 57133-78-5; *p*-cyanophenol, 767-00-0; phenol, 108-95-2; *p*-chlorophenol, 106-48-9; water, 7732-18-5; *N*-methylmorpholine, 109-02-4; *p*-cyanophenoxide, 767-00-0; *p*-chlorophenoxide, 24573-38-4; phenoxide, 3229-70-7; hydroxide, 14280-30-9.

Supplementary Material Available: Kinetic and equilibrium data, Tables S1–S6 (8 pages). Ordering information is given on any current masthead page.

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[47] $pK_a^{\pm}(\text{pip}) = 8.30$, $pK_a^{\pm}(n\text{-BuNH}_2) = 8.62$.[14]

[48] Schonne, A.; Braye, E.; Bruylants, A. *Bull. Soc. Chim. Belg.* **1953**, *62*, 155.

α- and β-Carbon Substituent Effect on S_N2 Reactivity. A Valence-Bond Approach

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Abstract: The α- and β-carbon substituent effect, on S_N2 reactivity and reactivity–selectivity, is discussed by using a (previously described) correlation diagram model of S_N2. The reaction barrier (E) is a fraction (f) of the energy gap ($I_{N:} - A_{RX}$) between the two curves which intersect to yield the reaction profile. $I_{N:}$ is the ionization potential of the nucleophile (N:) and A_{RX} is the electron affinity of the substrate (RX). The fraction (f) of $I_{N:} - A_{RX}$ which enters the activation barrier depends inter alia on the degree of delocalization of the three-electron bonds, e.g., $(R\cdots X)^-$. The more delocalized the three-electron bond, the larger the f. Thus, reactivity trends arise from the interplay between the electron surge aspect ($I_{N:} - A_{RX}$) and the bond-interchange aspect (e.g., the degree of delocalization of the three-electron bonds) of the S_N2 transformation. It is shown that α-halo substitution (on R) delocalizes the three-electron bond and effects a small improvement in the acceptor ability of the substrate, and therefore it slows down S_N2 reactivity. The largest delocalization is effected when the α-substituent(s) is (are) identical with the leaving group. In these cases, one observes the strongest rate retardation. π-acceptor α-substituents improve the substrate acceptor ability markedly without greatly delocalizing the three-electron bonds. Therefore, these substituents will enhance reactivity but *mainly toward powerful nucleophiles*. The effects of other α-substituents (e.g., CH$_3$O, Ph, SiR$_3$, etc.) and β-substituents (e.g., F, Cl, Br, RO, etc.) are also discussed in this light. The reactivity reversals often reported in the literature are suggested to be manifestations of the gap–slope interplay.

The effect of α- and β-carbon substitution on the S_N2 reactivity of CH$_3$X derivatives (eq 1) poses a variety of intriguing trends which *in totality* remain enigmatic.

$$\text{N:} + \text{YCH}_2\text{–X} \rightarrow \text{N–CH}_2\text{Y} + \text{:X} \qquad (1)$$

Already in the twenties Petrenko-Kritschenko[1] had observed that α-halogenation deactivates the reactivity of various halides toward nucleophilic reagents. Thus, CH$_3$X (X = Cl, Br, I) was found to be more reactive than its polyhalogenated derivatives, CH$_2$X$_2$, CHX$_3$, and CX$_4$, and similarly CH$_3$CH$_2$X, PhCH$_2$Cl, and HO$_2$CCH$_2$X were found to be respectively more reactive than CH$_3$CHX$_2$ (X = Cl, Br, I), PhCH$_2$Cl$_2$, and HO$_2$CCHX$_2$ (X = Cl, Br).

In the course of the years several other groups have reported similar trends. Backer and van Mels[2] observed that α-halogenation of potassium bromoacetate results in a diminished reactivity toward potassium sulfite and that α-Br (i.e., KO$_2$CCHBr$_2$) tempers S_N2 reactivity better than does α-Cl (i.e., KO$_2$CHClBr). Davies et

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al.[3] found that CH_3CH_2Cl reacts more than 5 times as fast as CH_2Cl_2 with trimethylamine in aqueous acetone (90%) and likewise 3-bromopropyl bromide is more than 10 times as reactive as methylene bromide (CH_2Br_2).

Hine was the first to study the halo effect in a systematic manner. Early on, Hine[4a] and Hine and Dowell[4b] showed that the S_N2 reactivity order of the chloromethanes toward alkali is $CH_3Cl > CH_2Cl_2 > CCl_4$ and that $CHCl_3$ appears overly reactive only because it undergoes proton abstraction by the base. Later on, in a series of studies, Hine[5] has demonstrated quite clearly that α-halogenation decreases the rate of S_N2 reactions and for a given leaving group the deactivating power of the α-halo substituent follows the order I > Br > Cl > F, so that in practice, *in each series the lowest reactivity occurs when the α-substituent becomes identical with the leaving group.* Hine further concluded, from his kinetic measurements, that the substituent effect is electronic rather than only steric and that it is exerted through the heat of activation.[6]

The retarding effect of halogen is exerted even when the substitution is performed at the β-position.[7] Thus, β-haloethyl bromide reacts 7–10 times slower than ethyl bromide toward potassium phenoxide,[7a] while 1,2-dibromoethane reacts much slower than ethyl bromide[7b,c] toward thiosulfate, etc. The deactivating power of the β-halogen follows the order $F \geq Br \geq Cl \geq I$ and it is larger than the deactivation exerted by β-CH_3 and β-CH_3CH_2 substitution.

The effect of π-donor and σ-acceptor substituents other than halides is also known. Thus, Ballinger et al.[8a] reported that α-methoxy enhances the rate of the S_N2 reaction[8b] toward potassium iodide in acetone, so that CH_3OCH_2Cl reacts $\sim 10^5$ as fast as CH_3Cl. Similarly, α-acetoxy and α-benzoxy (α-RCOO; R = CH_3, Ph) also improve S_N2 reactivity, while when put in the β-position, they, as well as other groups (PhO, RO, ...), exert a retarding effect.[7d,e]

A curious effect has been observed for the bulky α-$(CH_3)_3Si$ substituent.[9] Witmore and Sommer[9a] reported that, toward ethoxide in ethanol, neopentyl chloride reacts slower than $(CH_3)_3SiCH_2Cl$ but that hexyl chloride reacts faster than the latter. On the other hand, Eaborn and Jeffrey[9b] found that with the better nucleophile, potassium iodide in acetone, $(CH_3)_3SiCH_2Cl$ reacts even faster (×20) than propyl chloride, with a difference of $\sim$2.7 kcal/mol in the activation barriers.

Much contradiction and ambiguity surround the effect of π-acceptor substituents such as carbonyls (RCO), nitriles (NC), and aryls.[10-13] Early results by Slator and Twiss[11a] and by Conant et al.[11b-d] demonstrated that α-PhCO and α-NC exert a significant rate enhancement, such that $NCCH_2Cl$ and $PhCOCH_2Cl$ react $\sim 10^4$–10^5 times as fast as simple alkyl chlorides, with potassium iodide in acetone. This rate enhancement effected by the π-acceptor substituents has been traced to an "electronic origin" in a beautifully designed experiment by Bartlett and Trachtenberg.[12]

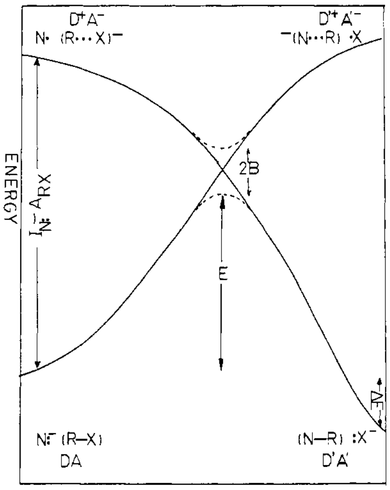

Figure 1. Correlation diagram describing the formation of the energy profile for the reaction $N^-{:} + R-X \rightarrow N-R + {:}X^-$. $N^-{:}$ and $X^-{:}$ are D and D', while R–X and R–N are A and A'. $I_{N:} - A_{RX}$ is the energy gap between the curves at the reactants' end. E is the reaction barrier. ΔE is the reaction energy.

While it has been accepted as a scientific truth that π-acceptor α-substituents accelerate S_N2 reactivity, there were other results which cast some doubt on whether the effect of these substituents is really so clear cut.[13] Thus, Ross et al.[13a] reported that $PhCH_2Br$ reacts more than 10 times as fast as $PhCOCH_2Br$ with amines but that with KI in acetone the reactivity order is inverted—$PhCOCH_2Br$ being considerably more reactive. Similar results were reported by Pearson et al.,[13b] who observed a decrease in the relative reactivities of $RCOCH_2X$ and RX (X = Cl, Br) as the nucleophile becomes less powerful. In a more recent study, Halvorsen and Songstad[13c] have shown systematically that the rate ratio of $PhCOCH_2Br$ vs. CH_3I is large mainly for powerful anionic nucleophiles, but it becomes smaller than 1 for neutral and less reactive nucleophiles (e.g., triethylamine).

The S_N2 reactivity of the benzyl system p-$YC_6H_4CH_2X$ (Y = H, NO_2) exhibits a closely related phenomenon. Thus, Songstad,[14a] Jencks,[14b], and others[15] have emphasized that p-NO_2 increases the S_N2 rate only when powerful nucleophiles are used, whereas with weak nucleophiles, p-NO_2 actually retards (relative to H) the reactivity of the benzyl system.

In contrast to these reactivity reversals the α-sulfonyl group (RO_2S) invariably retards S_N2 reactivity as was shown in the thorough study by Bordwell and Cooper.[16]

To summarize, we are faced with problems which are related

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to reactivity as well as to reactivity–selectivity. These are as follows: (a) There seems to be a symmetrization effect, so that as the number of identical leaving groups on the same carbon increases S_N2 reactivity decreases (e.g., CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4). (b) Strong σ-electron withdrawing substituents at either α- or β-carbons decelerate S_N2 reactivity, while π-donor α-substituents (e.g., RO) as well as π-acceptor substituents can accelerate the reactions. (c) The relative reactivity of α-substituted substrates to the unsubstituted ones is dependent upon the nucleophile. When the substituent is a π-acceptor group, the relative reactivity (substituted/unsubstituted) can be reversed as the nucleophile is gradually made less powerful.[17] This is clearly a reactivity–selectivity problem.

Our aim in this paper is to attempt understanding this collage of data. To achieve that we use the previously described curve-crossing model[18] to generate the S_N2 barrier and to derive reactivity factors which determine its height. As was shown[18e,f] these reactivity factors can be linked with well-defined thermochemical quantities and thereby allow a coherent discussion of substituent effect on S_N2 reactivity.

Theory

Consider the S_N2 reaction

$$\underset{D}{N^-:} + \underset{A}{R{-}X} \rightarrow \underset{A'}{N{-}R} + \underset{D'}{:X^-} \tag{2}$$

Let the nucleophiles, N^-: and X^-:, be the electron donors (D, D′), while the substrates, R–X and R–N, assume the role of electron acceptors (A, A′). The reaction profile obtains from a state correlation diagram[18e,f,g] which reflects the bond interchange and electron surge inherent in the S_N2 transformations: This is shown in Figure 1. The state correlation is $(DA)_r \rightarrow (D'^+ A'^-)_p$ and $(D^+A^-)_r \rightarrow (D'A')_p$, where r and p are reactants and products.

Our focus is the barrier's height rather than the makeup of the transition state.[18b] For this purpose, it is sufficient to know the electronic nature of the four *anchor states* of the interesecting curves.[18h] In valence-bond (VB) terms $(DA)_r$ and $(D'A')_p$ are the ground-state reactants (*r*) and products (p), in which the substrates have R–X and N–R two-electron bonds, e.g.

$$R{-}X \approx a(R{\cdot}{\uparrow}{\downarrow}{\cdot}X) + b(R^+ :X^-) \qquad a^2 + b^2 = 1 \tag{3}$$

$(D^+A^-)_r$ and $(D'^+A'^-)_p$ are the corresponding valence charge transfer forms of reactants and products. In each form, an electron has been transferred from the nucleophile to the substrate, thereby generating the corresponding $(R{\cdots}X)^-$ and $(R{\cdots}N)^-$ *delocalized* three-electron bonds,[18e,f] e.g.[19]

$$(R{\cdots}X)^- = a(R{\cdot}\ :X^-) + b(R^-\!:\ {\cdot}X) \qquad a^2 + b^2 = 1 \tag{4}$$

In between these four *anchor states* there arises a barrier owing to the avoided crossing of the interesecting curves. The height of the barrier (*E*) above the reactant encounter complex, $(DA)_r$, is seen to be a fraction (*f*) of the energy gap between the intersecting curves (at the reactant side) less the avoided crossing, *B*, i.e.

$$E = f(I_{N:} - A_{RX}) - B \tag{5}$$

$I_{N:}$ is the vertical ionization potential of the nucleophile, while A_{RX} is the vertical valence electron affinity of the substrate, at the reactant (R–X) geometry.[20] If an approximate constancy of *B* for a reaction series is assumed,[18e,f] then variations in the height of the barrier depend only on *f* and on $I_{N:} - A_{RX}$.

f is the fraction of the energy gap ($I_{N:} - A_{RX}$) which enters into the activation barrier, and the size of *f* depends on the functional forms of the intersecting curves. Two major electronic effects join to dominate the size of *f*.[21] The first is the reaction energy, ΔE (Figure 1), which can be taken as a good approximation for the reaction enthalpy, ΔH. As the reaction becomes more exothermic, the $(D^+A^-)_r \rightarrow (D'A')_p$ correlation curve is "pulled down" and descends more steeply, causing a smaller fraction (*f*) of the energy gap, $I_{N:} - A_{RX}$, to enter the activation barrier. This is the well-known Bell–Evans–Polanyi (B–E–P) relationship.[22,18f]

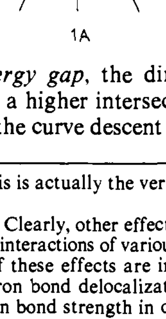
For *a given* $\Delta E(\Delta H)$, the size of *f* is set by the steepness of the curves as they descend from the charge transfer anchor states to meet at the intersection point (Figure 1).[18f] The $(D^+A^-)_r \rightarrow (D'A')_p$ descent involves *localization* of $(R{\cdots}X)^-$ to $(R{\cdot}\ :X^-)$ and, simultaneously, formation of the N–R two-electron bond via the mixing in of the carbocationic form, $[(N:^-\ R^+)\ :X^-]$.[18f] The descent of the second curve in Figure 1 involves analogous effects. These effects, which attend the descent of the curves, are shown schematically in eq 6a and 6b:

$$N{\cdot}\ (R{\cdots}X)^- \rightsquigarrow N{\cdot}\ (R{\cdot}\ :X^-) \rightsquigarrow (N{-}R)\ :X^- \tag{6a}$$

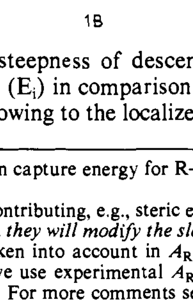
$$X{\cdot}\ (R{\cdots}N)^- \rightsquigarrow X{\cdot}\ (R{\cdot}\ :N^-) \rightsquigarrow (X{-}R)\ :X^- \tag{6b}$$

The steepness of the curve descent depends, then, on the ease with which $(R{\cdots}X)^-$ and $(R{\cdots}N)^-$ undergo localization *under the characteristic geometric distortions along the reaction coordinate (i.e., flattening of the R moiety and bond elongation)*, as well as on the strength of the coupling of N· with $(R{\cdots}X)^-$ and of X· with $(R{\cdots}N)^-$. As the three-electron bonds become increasingly delocalized (e.g., large b^2 in eq 4), the curves will descend initially less steeply *because all of the factors which cause the descent become less effective*. Thus, the localization (eq 6) of $(R{\cdots}X)^-$ and $(R{\cdots}N)^-$ becomes increasingly less facile owing to the greater amount of delocalization energies which must be lost now as the three-electron bonds get localized along the reaction coordinate. Simultaneously, the increased delocalization impairs also the two-electron bond formation owing to the large carbanionic character of R (large b^2 in eq 4) which prohibits efficient coupling of N· with $(R{\cdots}X)^-$ and of X· with $(R{\cdots}N)^-$.

The overall effect is shown in **1A** vs. **1B** below. Thus, *for a given energy gap*, the diminished steepness of descent in **1A** generates a higher intersection point (E_i) in comparison with **1B** in which the curve descent is steeper owing to the localized nature



1A



1B

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[17] There may be some relation between these reactivity reversals and the reversals in nucleophilicity and leaving group ability in some cases. See: (a) Bunnett, J. F. *J. Am. Chem. Soc.* **1957**, *79*, 5969. (b) Bunnett, J. F.; Reinheimer, J. D. *J. Am. Chem. Soc.* **1962**, *84*, 3284.

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[19] The three-electron bond is written for convenience as $(R{\cdots}X)^-$. Alternative presentaions are $(R{\dot{-}}X)^-$ and $(R{\therefore}X)^-$. See ref 18f.

[20] This is actually the vertical electron capture energy for R–X + e → $(R{\cdots}X)^-$.

[21] (a) Clearly, other effects are also contributing, e.g., steric effects and nonbonded interactions of various kinds, and *they will modify the slope factor f*. Some of these effects are implicitly taken into account in A_{RX} and the three-electron bond delocalization, since we use experimental A_R, A_X, and two-electron bond strength in our scheme. For more comments see ref 18f. For other effects see also: (b) Hoffmann, R.; Howell, J. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 3047. (c) Kost, D.; Aviram, K. *Tetrahedron Lett.* **1982**, *23*, 4157.

[22] (a) Bell, R. P. *Proc. R. Soc. London, Ser. A* **1936**, *154*, 414. (b) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1936**, *32*, 1340. (c) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1938**, *34*, 11.

Table I. Calculated R–X Bond Electron Affinities (A_{RX}) and Degrees of Three-Electron Bond Delocalization (b^2, S) for Alkyl Halides[a]

R–X	A_{RX}	b^2	S	A_{R}	$D_{\mathrm{R-X}}$
(1) CH_3–Cl	−30.0	0.250	1	1.8	84
(2) $ClCH_2$–Cl	−14.0	0.268	$2^{1/2}$	15.0	74
(3) FCH_2–Cl	−26.0	0.280	~1[b]	13.0	84
(4) Cl_2CH–Cl	−5.7	0.292	$3^{1/2}$	30.0	73
(5) Cl_3C–Cl	+6.5	0.337	2	50.0	70
(6) CH_3–Br	−21.0	0.246	1	1.8	71
(7) $BrCH_2$–Br	−3.3	0.263	$2^{1/2}$	17.0	61
(8) CH_3–I	−10.0	0.240	1	1.8	56
(9) ICH_2–I	+3.8	0.271	$2^{1/2}$	19.0	50
(10) $(HO)CH_2$–Cl	−21.0	0.239	~1	−0.5	75
(11) $(FCH_2)CH_2$–Br	−7.2	0.338	~1	36.0	68

[a] A_{RX}, A_{R}, and D_{RX} are in kcal/mol. Sources of A_{R} and D_{RX} are in ref 32 (see Appendix). [b] S = 1.0257 owing to ~5% delocalization into the CF linkage (see Appendix).

of the three-electron bonds. Note that such variations in f imply changes in the curves functional forms.

The height of the reaction barrier (E in Figure 1) is therefore set by the interplay of the energy gap and functional forms (hereafter slopes) of the intersecting curves. This interplay gives rise, in principle, to *two types of reactivity* patterns: *one is gap-controlled and is dominated by the donor–acceptor abilities of the reactants* ($I_{\mathrm{N:}} - A_{\mathrm{RX}}$), *the other is slope-controlled and is dominated* (for a given ΔH) *by the degree of delocalization of the three-electron bonds* $(\mathrm{R}\cdots\mathrm{X})^-$ *and* $(\mathrm{R}\cdots\mathrm{N})^-$.[18f] As we shall see, this interplay is also a root cause of unusual reactivity–selectivity patterns.

Note that the slope factor f in eq 5 has an added mechanistic implication to it. Excluding steric effects,[21a] *a large f will generally mean a transition state having a relatively high carbanionic character, whereas a small f will point to a transition state with more carbocationic character.* With these qualitative tools we turn to analyze the experimental data.

α- and β-Halo Effect on S_N2 Reactivity. For a given nucleophile and leaving group the reaction energy (enthalpy) as well as solvation energy is expected to remain approximately constant upon α- or β-carbon substitution (e.g., eq 1). Therefore, the α- (β-) substituent effect on S_N2 reactivity will be dominated mainly by the substrate electron affinity, A_{RX}, and the extent of three-electron bond delocalization.[21]

To determine these reactivity factors we use the quantum-thermochemical relations which we derived before.[18f] The details are given in the Appendix. As a general rule, the closer the electron affinities of R and X (A_{R}; A_{X}) the more delocalized the $(\mathrm{R}\cdots\mathrm{X})^-$ three-electron bond, *having more of the carbanionic form* $\mathrm{R}^-\!: \cdot\mathrm{X}$ *mixed in.* The substrate electron affinity depends on the electron affinity of X (A_{X}), on the C–X two-electron bond energy, $D_{\mathrm{R-X}}$, and on the three-electron bond energy, $D_{\mathrm{R\cdots X}}$, as indicated in eq 7:

$$A_{\mathrm{RX}} = A_{\mathrm{X}} - D_{\mathrm{R-X}} + D_{\mathrm{R\cdots X}} \qquad (7)$$

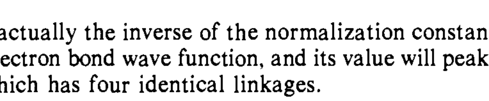
The results for various substrates are shown in Table I. b^2 is the weight of the carbanionic contribution, $\mathrm{R}^-\!: \cdot\mathrm{X}$ in the three-electron bond (eq 4). S is a symmetry factor which depends on the number of identical leaving groups possessed by the substrate.

Inspecting the electron affinities of the substrates, A_{RX}, we see that successive α-halogenation improves the acceptor ability of the substrate as indicated by the increase in A_{RX} in each series (entries 1–5, 6, 7, and 8, 9). This trend is in accord with reduction potential data[23a] and with gas-phase electron transmission spectroscopic data[23b] as well as with the propensity of CCl_4 to partake in electron transfer reactions (relative to the lower halides).[23c] In comparison between the different series (e.g., entries 1 and 2 vs. 6 and 7 vs. 8 and 9) one finds that the substrates with the larger halogens are always better electron acceptors than the corresponding ones with the smaller halogens. This is, once again, in agreement with reduction potential data[23a] and with the relative ease in which R–X's (X = I, Cl) partake in electron transfer reactions.[23d]

In the light of eq 7, the trends in A_{RX} (entries 1–9, Table I) are set by the weakening of the C–X two-electron bond ($D_{\mathrm{R-X}}$) upon successive α-halogenation (not fluorination though) and by the increase of the R electron affinity (A_{R}) which brings about stronger mixing of $\mathrm{R}^-\!: \cdot\mathrm{X}$ into $\mathrm{R}\cdot :\mathrm{X}^-$ (eq 4).

The stabilization of R^-: (larger A_{R}) is also the cause of the increasing three-electron bond delocalization across the RX linkage, as indicated by the values of b^2 in Table I. For example, the $(\mathrm{C}\cdots\mathrm{Cl})^-$ three-electron bond in CH_2FCl is more delocalized than that of CH_3Cl, since $A_{\mathrm{CH_2F}} > A_{\mathrm{CH_3}}$. Similarly, successive chlorination of methane leads to a greater delocalization and strengthening of the $(\mathrm{C}\cdots\mathrm{Cl})^-$ bond since $A_{\mathrm{CCl_3}} > A_{\mathrm{CHCl_2}} > A_{\mathrm{CH_2Cl}} > A_{\mathrm{CH_3}}$. This trend is in full accord with what is known about three-electron bonds.[24] Thus, Sprague and Williams,[25a,b] Mishra and Symons,[25c] and Fujita et al.[25d] have reported that $(CH_3X)^-$ is unstable[24g] and decomposes immediately to $H_3C\cdot$ and $:X^-$, while anions which are α-substituted with halogens or σ-electron electron-withdrawing substituents are much more stable,[25e,f] e.g., $(F_3C–X)^-$ (X = Br, I); $[(F_3C)_3C–I]^-$; $(C_6F_5–X)^-$ (X = Br, I, Cl).

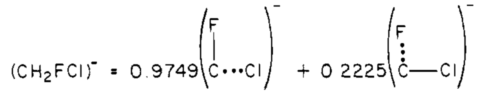
Table I exhibits yet another effect. This is the symmetrization effect which brings about interlinkage delocalization of the three-electron bond and is indicated in the table by S. For example, the S value for $(CH_2Cl_2)^-$ is $2^{1/2}$ to account for the two identical CCl linkages over which the three-electron bond is delocalized, so its wave function reads



$$(\mathrm{CH_2Cl_2})^- = 1/2^{1/2}\left(\overset{\mathrm{Cl}}{\overset{|}{\mathrm{C}}}\cdots\mathrm{Cl} + \overset{\mathrm{Cl}}{\overset{\vdots}{\mathrm{C}}}-\mathrm{Cl}\right)^- \qquad (8)$$

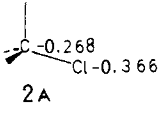
Thus, S is actually the inverse of the normalization constant of the three-electron bond wave function, and its value will peak for $(CCl_4)^-$, which has four identical linkages.

In comparison with, e.g., $(CH_2Cl_2)^-$, the anionic valence state of CH_2FCl is

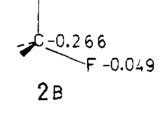


$$(\mathrm{CH_2FCl})^- = 0.9749\left(\overset{\mathrm{F}}{\overset{|}{\mathrm{C}}}\cdots\mathrm{Cl}\right)^- + 0\ 2225\left(\overset{\mathrm{F}}{\overset{\vdots}{\mathrm{C}}}-\mathrm{Cl}\right)^- \qquad (9)$$

thus having S value of ~1. Using these data (eq 8 and 9) and the b^2 values, one obtains the following charge distribution for $(CH_2Cl_2)^-$, **2A**, and $(CH_2FCl)^-$, **2B** (see Appendix):



2A



2B

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(23) (a) Weinberg, N. L., Ed. "Techniques of Electroorganic Synthesis"; Wiley: New York, 1975; Vol. 5, Part II, pp 827–839. (b) Burrow, P. D.; Modelli, A.; Chiu, N. S.; Jordan, K. D. *J. Chem. Phys.* **1982**, *77*, 2699. (c) Meyers, C. Y.; Kolb, V. M. *J. Org. Chem.* **1978**, *43*, 1985. (d) Ashby, E. C.; DePriest, R. N.; Goel, A. B. *Tetrahedron Lett.* **1981**, *22*, 1763.

(24) (a) Goodard, W. A., III; Dunning, T. H., Jr.; Hunt, W. J.; Hay, J. P. *Acc. Chem. Res.* **1973**, *6*, 368. (b) Harcourt, R. D. *J. Am. Chem. Soc.* **1978**, *100*, 8060. (c) Musker, K. W. *Acc. Chem. Res.* **1980**, *13*, 200. (d) Asmus, K.-D. *Acc. Chem. Res.* **1979**, *12*, 436. (e) Symons, M. C. R. *Pure Appl. Chem.* **1981**, *53*, 223. (f) Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753. (g) Clark, T. *J. Chem. Soc., Chem. Commun.* **1981**, 515. (h) Harcourt, R. D. *J. Chem. Educ.* **1968**, *45*, 779. (i) Harcourt, R. D. *Aust. J. Chem.* **1975**, *28*, 881. (j) Harcourt, R. D. *Aust. J. Chem.* **1978**, *31*, 199. (k) Harcourt, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5195.

(25) (a) Sprague, E. D.; Williams, F. *J. Chem. Phys.* **1971**, *54*, 5425. (b) Sprague, E. D.; Takeda, K.; Wang, J. T.; Williams, F. *Can. J. Chem.* **1974**, *52*, 284. (c) Mishra, S. P.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1973**, 239. (d) Fujita, Y.; Katsu, T.; Sato, M.; Takahashi, K. *J. Chem. Phys.* **1974**, *61*, 4307. (e) Shiotani, M.; Williams, F. *J. Am. Chem. Soc.* **1976**, *98*, 4006. (f) Hasegawa, A.; Shiotani, M.; Williams, F. *Faraday Discuss. Chem. Soc.* **1977**, *63*, 157. (g) Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1980**, *102*, 2860. (h) Symonds, M. C. R. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 783. (i) Riederer, H.; Hüttermann, J.; Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1978**, 313.

Clearly, the anionic state $(CH_2FCl)^-$ is practically localized in the CCl linkage.

The ability of a α-halo substituent (Y) to delocalize the three-electron bond into its own linkage with carbon is seen from eq 7 to depend mostly on the two-electron bond strength (D_{R-Y}), because all the halides have approximately equal $D_{R\cdots Y}$ and A_Y.[18f] The stronger the two-electron bond of the α-halo (C–Y) relative to that of the leaving group (C–X), the less able the α-substituent (Y) to delocalize the three-electron bond into its own linkage (C–Y). Therefore, for $(CH_2YI)^-$, for example, the degree of three-electron bond delocalization will follow the order $(CH_2FI)^- < (CH_2ClI)^- < (CH_2BrI)^- < (CH_2I_2)^-$. Thus, the degree of symmetrization of the three-electron bond is minimal ($S \simeq 1$) for $(CH_2FI)^-$ and maximal ($S = 2^{1/2}$) for $(CH_2I_2)^-$. Whereas in the former the three-electron bond is virtually localized in the CI linkage ($S \approx 1$) with a minor contribution from the CF linkage, in the latter full symmetrization is obtained ($S = 2^{1/2}$) and the three-electron bond is equally distributed over the two identical CI linkages, with intermediate degrees for the other members of the series.

The symmetrization effect leads to an increase in the resonance stabilization of the three-electron bond. But, more importantly, the symmetry effect delocalizes the extra electron of the three-electron bond over all the identical linkages and *away* from any one specific carbon-leaving group linkage *and thereby leads to a significant retardation of the N–R two-electron bond making with the nucleophile* (eq 6a). The full potential of the two-electron bonding (N–R) can now be realized only when the extra electron finally resides in one of the CX linkages, in the direction of the attacking nucleophile.

In summary, the S values (Table I) indicate the ability of the α-substituent to delocalize the three-electron bond into its own linkage and *away from the carbon–leaving group linkage*, while b^2 indicates the weight of the carbanionic form $R^{-}\!: \cdot X$ in the carbon–leaving group linkage. Hence, both indices indicate degrees of three-electron delocalization but in a different sense; while b^2 refers to the *intralinkage delocalization*, S refers to the *interlinkage delocalization.*

The effect of the three-electron bond delocalization becomes obvious in the light of **1A** vs. **1B** and of eq 5. Delocalization will retard the descent of the curves from their high anchor points (Figure 1), and as a result a larger fraction (f) of the energy gap ($I_{N:} - A_{RX}$) will enter the activation barrier. (**1A** vs. **1B**) Put differently, *for a given nucleophile, N:, f (eq 5) will be larger for the α-halo-substituted substrates than for the unsubstituted ones* (CH_3–X). The heavier the delocalization the larger the f, with the largest value occurring for the most symmetrically α-substituted substrate, CX_4. Thus, for a given nucleophile f in eq 5 is proportional to both b^2 and S of Table I:

$$f \propto b^2 \qquad f \propto S \tag{10}$$

At the same time that f (eq 5 and 10) increases upon α-halo substitution e.g., $ClCH_2$–Cl, the substrate becomes a better electron acceptor (A_{RX}, Table I), so that for a given nucleophile, $I_{N:} - A_{RX}$ also decreases (relative to the unsubstituted CH_3–X case). Clearly, there is here a *clash* between the two factors which dominate the height of the barrier (eq 5). If the gap effect ($I_{N:} - A_{RX}$) dominates, then one expects the α-halo-substituted substrates, which are better electron acceptors than the unsubstituted ones, to react faster. On the other hand, if the slope effect dominates, one expects the reverse. Our previous experience[18e,f] with eq 5 reveals that large changes in f tend to override changes in $I_{N:} - A_{RX}$.[26a] For example, the reaction system H^-/CH_3–H which has a symmetrized and a heavily delocalized three-electron bond (large f) reacts much slower than F^-/CH_3–F or Cl^-/CH_3–Cl, although the latter two have higher $I_{N:} - A_{RX}$ values (see Appendix I).[18e,f,27]

Inspecting the experimental data in the light of the two reactivity factors (eq 5) leads to the same conclusion: that the changes in f dominate the α-halo effect. Thus, the order of reactivity toward KI in acetone is CH_3Br (CH_3CH_2Br) > FCH_2Br > $ClCH_2Br$ > $BrCH_2Br$ and toward sodium methoxide in methanol it is $CH_3Br > FCH_2Br > CH_3CH_2Br > ClCH_2Br > BrCH_2Br$ and $CH_3I > ClCH_2I > ICH_2I$.[5] Similarly, toward the powerful nucleophile sodium thiophenoxide in methanol the observed order is $CH_3I > FCH_2I > ClCH_2I > BrCH_2I \approx ICH_2I$.[5b] In all cases, the CH_2Cl_2 system is by far the least reactive among the CH_2YX substrates, having an activation barrier ~13 kcal/mol higher than that of CH_3Br and ~10 kcal/mol higher than that of CH_3Cl. Additional such data are mentioned in the introductory section. We see therefore, for a given leaving group, *the α-halo substituent slows down the reaction in proportion to its ability to delocalize away the three-electron bond into its own linkage with carbon, i.e., I > Br > Cl > F.*[28]

Thus, *the totality of the data* clearly emphasizes the impact of the three-electron bond delocalization on reactivity. It follows that *making the substrate a better electron acceptor does not guarantee enhanced S_N2 reactivity if at the same time the three-electron bond gets increasingly delocalized.*[26] This conclusion and others could have been, in fact, derived directly from eq 5. Let us compare the relative reactivity of CH_3–X and YCH_2–X toward various nucleophiles ($N:^-$). By deriving an expression for the change in the barrier,[26] one can see that *when $I_{N:} - A_{RX}$ is large, an increase in f can override an attendant decrease in $I_{N:} - A_{RX}$ and raise the energy barrier. Only when $I_{N:} - A_{RX}$ is small, then an increase in f may not be sufficient to override an attendant decrease in $I_{N:} - A_{RX}$, and as a result improvement of the donor–acceptor relationship of the reactants may eventually lead to enhanced S_N2 reactivity despite the increasing delocalization of the three-electron bond.*

In conclusion, eq 5 anticipates the potential rate retarding effect of increasing three-electron bond delocalization. But, more important, *it predicts that as one improves the nucleophile, the rate retardation exerted by delocalized three-electron bonds will gradually diminish, allowing the acceptor ability of the substrate to take expression.* This could be a reason why CH_2I_2 is not the least reactive in the YCH_2I (Y = F, Cl, Br, I) series toward the powerful nucleophile thiophenoxide.[5b]

The larger the increase in f, the smaller the chances that improving the acceptor ability of the substrate will result in a higher S_N2 reactivity. Thus, the largest retardation effect is expected upon changing the substrate from CH_3X to CH_2X_2 (CHX_3, CX_4)—a change which involves the largest increase in f because of the jump in the symmetrization factor (eq 10). This is indeed what one finds when one compares the "jumps" in the reaction barriers obtained upon switching from CH_3X to CH_2X_2[4,5] to the much smaller differential barriers which attend smaller changes in f (e.g., CH_3Br vs. CH_2FBr).

We can attempt to rationalize, in this light, the effect exerted by substituents which are weak σ-acceptors and strong π-donors such as α-RO (R = H, alkyl). From entry 10 in Table I we see that a prototype of such substituents enhances the electron affinity of the substrate (relative to CH_3–Cl in entry 1), while only

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(26) (a) This can be deduced from the expression for the change in the barrier (ΔE): $\Delta E = (I_{N:} - A_{RX})\cdot\Delta f + f\cdot\Delta(I_{N:} - A_{RX})$. (b) As long as $I_{N:} - A_{RX}$ is large the change in the barrier (ΔE) is dominated by the change in f, making the substrate with the more delocalized three-electron bonds less reactive.

(27) (a) For gas-phase barriers, see: Tanaka, K.; Mackay, G. I.; Payzant, J. D.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643.; Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4019. (b) For solution data see: McLennan, D. J. *Aust. J. Chem.* **1978**, *31*, 1897.; Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 85. (c) For computational results see: Dedieu, A.; Veillard, A. *J. Am. Chem. Soc.* **1972**, *94*, 6730. Wolfe, S.; Mitchell, D. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7694.

(28) For other interpretations of the α-halo effect, see MO analyses in ref 6b and 21c. The analogy of Wofe et al. (ref 6b) to pyramidal inversion barriers constitutes an equivalent (though not a complete) MO expression of the effect exerted by a delocalized three-electron bond on the slopes of the curves (see drawings **1A** vs. **1B**). In general, substituents which increase the nitrogen inversion barrier will also cause the bond elongation and the flattening of the carbon configuration in $(R\cdots X)^-$ to be more difficult. A straightforward extension of the analogy between S_N2 barriers and pyramidal inversion barriers *is not always possible* though. For example, while F increases the nitrogen inversion barrier more than Cl and Br do, the effect on S_N2 barriers is the opposite (Br > Cl > F).

marginally affecting the delocalization of the three-electron bond (compare b^2 values in entries 1 vs. 10). This effect, by itself, is sufficient to render $ROCH_2–Cl$ more reactive than $CH_3–Cl$. However, our model[18b] also predicts that since the ionization potential of $ROCH_2$ is generally very low,[32d] the carbocationic configuration (N^-: $ROCH_2^+$:Cl^-) will be strongly mixed into the intersection point in Figure 1, therefore endowing the transition state with a considerable carbocationic character.[8b] Thus, in applying the model to borderline cases ($S_N2–S_N1$), one must keep in mind that while the indices A_{RX} and b^2 usually predict the correct reactivity trend, they are not sufficient, by themselves, to assess the full mechanistic impact of the substituent.

The effect of β-substituents becomes clear now. From entry 11 in Table I, β-fluoro substitution leads to some improvement of the acceptor ability of the CBr linkage, but at the same time it heavily delocalizes the three-electron bond ($b^2 = 0.324$) owing to the large value of $A_{FCH_2CH_2}$. This strong delocalization effect leads to a decreased reactivity as was found experimentally by Hine and Brader for a variety of β-σ-acceptor substituents such as β-X (F, Cl, Br, I) and β-RO.[7] Note that the difference between α-RO and β-RO merely reflects the balance between the π-donor ability and the σ-acceptor ability of the substituent. Thus, dominance of the π effect in the α position leads to a slight decrease in A_R (entry 10, Table I), whereas dominance of the σ effect in the β-position is expected to increase A_R and, thereby, to delocalize the three-electron bond $(R{\cdots}X)^-$. The same considerations apply for α- vs. β-fluorine.[29] Thus, the π effect tempers the σ acceptance at the α-position, making $A_{FCH_2} < A_{FCH_2CH_2}$, and accordingly, one expects that retardation of the S_N2 rate will be larger in the β-position (unless the leaving group is F).

We can see that the concept of gap–slope interplay inherent in eq 5 is useful—allowing us to pattern some of the experimental facts. No doubt, steric and lone pair repulsion effects of the substituents are important too,[21] but considering the totality of evidence, these effects do not seem to play the major role in governing all of these reactivity trends.

Let us couch our considerations in a somewhat more quantitative treatment of eq 5. So as to remove complications arising from possible variations in ΔH, let us consider the identity reaction with $\Delta H = 0$:

$$X^-: + R–X \rightarrow X–R + :X^- \tag{11}$$

Previously[18f] we have found that $f = 0.25k$[30] reproduces nicely the experimental trends in these intrinsic barriers. k is the ratio of the b^2 values for a given three-electron bond to a standard "weak" three-electron bond. Since $b^2 \approx 0.25$ for weak three-electron bonds (Table I entries 1, 6, and 8), then, in general, $f = b^2$ for identity reactions.

Table II. Reactivity Indices and Relative Barriers for Identity S_N2 Reactions[a]

$X^-/R–X$	$I_{X:^-} - A_{RX}$[b]	f	E_{rel}	E_{rel} (expt)
(1) $Cl^-/CH_3–Cl$	113	0.250	0.00	0.0[c]
(2) $Cl^-/FCH_2–Cl$	109	0.280	+2.27	
(3) $Cl^-/ClCH_2–Cl$	97	0.373	+8.51	~(+10.0)[d]
(4) $Cl^-/Cl_2CH–Cl$	89	0.500	+16.10	>(+10.0)[e]
(5) $Br^-/CH_3–Br$	99	0.246	0.00	0.0
(6) $Br^-/BrCH_2–Br$	81	0.372	+5.90	+5.8;[d] +4.9[f]
(7) $Br^-/(FCH_2)CH_2–Br$	85	0.338	+4.10	⩾(+1.3)[g]
(8) $I^-/CH_3–I$	81	0.240	0.00	0.0
(9) $I^-/ICH_2–I$	67	0.383	+6.34	+3.9;[f] +(2.8–3.8)[h]

[a] Using eq 5. [b] $I_{X:}$ values for Cl^-, Br^-, and I^- (in kcal/mol) are 83, 78, and 71. [c] Barrier for $Cl^-/CH_3–Cl$ in acetone from ref 27b. [d] From ref 5a. The nucleophile is I^- (in acetone). [e] Estimated from data in ref 4. [f] From ref 5a. The nucleophile is CH_3O^- (in methanol). [g] From ref 7a. The nucleophile is PhS^- (in methanol). [h] From ref 7c. The nucleophile is I^- (in ethanol).

Table III. Calculated R–X Bond Electron Affinities and Degrees of Three-Electron Bond Delocalization for $CH_3–X$ and $NCCH_2–X$ (X = Cl, Br, I)[a]

R–X	A_{RX}	b^2	D_{R-X}	A_R
(1) $CH_3–Cl$	−30.0	0.250	84	1.8
(2) $NCCH_2–Cl$	−5.5	0.321	69	35.0
(3) $CH_3–Br$	−21.0	0.246	71	1.8
(4) $NCCH_2–Br$	+4.7	0.320	56	35.0
(5) $CH_3–I$	−10.0	0.240	56	1.8
(6) $NCCH_2–I$	+15.2	0.328	40	35.0

[a] A_{RX}, D_{R-X}, and A_R are in kcal/mol. D_{R-X} values are from ref 32b, c. A_{NCCH_2} is from ref 34.

To take into account the additional delocalization brought about by symmetrization of the three-electron bond, we use $f = b^2k'$ where k' is obtained[31] from the ratio of the symmetrization factor (S) in a given case to a standard case having $S = 1$. Thus, a general form for f is

$$f = b^2S \tag{12}$$

Note that this form follows from the qualitative considerations and is in the spirit of eq 10.[31]

Using this recipe for f, we have calculated relative barriers for a few reactions and the results are exhibited in Table II side by side with experimental data.

The calculated data models quite well the observed α-halo effect and the symmetrization effect (entries 1–4, 5 and 6, and 8 and 9), and so it does with respect to the β-halo effect (entries 7 vs. 5). An interesting trend which we have just discussed and is predicted in the table is the decrease in the α-halo retarding effect as one increases the donor–acceptor abilities of the reactants.[26b] Thus, for the lesser donor–acceptor pairs $Cl^-/H_3C–Cl$ and $Cl^-/H_2ClC–Cl$ the α-halo substituent is predicted to increase the barrier by 8.51 kcal (entries 1 and 3), whereas in the $Br^-/R–Br$ and $I^-/R–I$ systems (entries 5 and 6 and 8 and 9), which constitute better donor–acceptor pairs, the predicted effect is 5.9–6.34 kcal. This prediction finds support in the experimental trend, as shown in the table.

The above results and the predicted qualitative trends give us some confidence that eq 5 indeed captures the physical sense of the problem, and we turn to other substituents.

π-Acceptor Substituents

The effects attending the substitution of a hydrogen, on the α-carbon in R–X, by a π-acceptor group are demonstrated in Table III by comparing $NCCH_2–X$ with $CH_3–X$. Substituents such as CN are seen to stabilize R^-: (large A_R) and thereby to delocalize the three-electron bonds of R, i.e., both $(R{\cdots}X)^-$ and $(R{\cdots}N)^-$.

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(29) The balance of σ and π effect of fluroine in alkyl anions is discussed in: (a) Sullivan, S. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 1160. (b) Faird, R.; McMahon, T. B. *Can. J. Chem.* **1980**, *58*, 2307.

(30) The value $f = 0.25$ obtains from a model of two intersecting parabolas.[18f] But note, eq 5 (which is assumptions free) can have $f = 0.25$ from other curve types with appropriate steepness parameters. Thus $f = 0.25$ should not be equated with a harmonic approximation.

(31) From overlap considerations there is a loss of bonding with a nucleophile (N) in $N{\cdot}(CH_2X_2)^-$ relative to $N{\cdot}(CH_3X)^-$. This requires $k' > 1$ so that f is proportional to S in one way or another. While it is easy to derive the connection between the loss of bonding and the slopes of the curves, the quantitative calculation in each case is much more complex. Therefore, we prefer eq 12, which allows us to treat all the possible cases in a coherent manner and is found to yield correct trends.

(32) (a) A_R values are from: Ellison, C. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556 (CH_3). From ΔH (ACID) data in: Bartmess, J. E.; McIver, R. T., Jr. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2 (CH_2F, CH_2Cl, $CHCl_2$, CCl_3, CH_2Br, CH_2I, FCH_2CH_2, C_6H_5). (b) D_{R-X} values from: Sanderson, R. T. "Chemical Bonds and Bond Energy"; Academic Press: New York, 1976 ($H_3C–Cl$, $H_3C–I$, $H_3C–Br$, $C_6H_5–Cl$). deB Darwent, B. "Bond Dissociation in simple molecules"; NSRDS-NBS 31: Washington, DC, 1970 ($H_2ClC–Cl$, $HCl_2C–Cl$, $Cl_3C–Cl$, $H_2BrC–Br$, $H_2IC–I$). (c) Additional sources of bond energy which were used to calibrate other D_{R-X} values appearing here are: Benson, S. W. *J. Chem. Ed.* **1965**, *42*, 502. Kerr, J. A.; Parsonage, M. J.; Trotman-Dickenson, A. F. "Handbook of Chemistry and Physics", CRC Press: Cleveland, OH, 1976; p F-204. (d) A_{HOCH_2} was estimated from data in: Pross, A.; DeFrees, D. J.; Levi, B. A.; Pollack, S. K.; Radom, L.; Hehre, W. J. *J. Org. Chem.* **1981**, *46*, 1693, coupled with experimental bond energies. $IP_{HOCH_2} = 7.6$ eV in comparison with 9.84 eV for CH_3. See: Griller, D.; Lossing, F. P. *J. Am. Chem. Soc.* **1981**, *103*, 1586.

Table IV. Calculated Relative Barriers for the Reaction $N^-: + YCH_2-X \rightarrow N-CH_2Y + :X^-$ (X = Halides; Y = H, CN)

$N^-:/R-X$	$I_{N:} - A_{RX}$[a]	f	E_{rel}[a]
(1) Cl^-/CH_3-Cl	113.0	0.250	0.00
(2) $Cl^-/NCCH_2-Cl$	88.5	0.321	+0.16
(3) Br^-/CH_3-Br	99.0	0.246	0.00
(4) $Br^-/NCCH_2-Br$	73.3	0.320	−0.90
(5) I^-/CH_3-I	81.0	0.240	0.00
(6) $I^-/NCCH_2-I$	55.8	0.328	−1.14
(7) HO^-/CH_3-Cl	74.0 (−46)[b]	0.296[c]	0.00
(8) $HO^-/NCCH_2-Cl$	49.5 (−46)[b]	0.385[c]	−3.63

[a] Values in kcal/mol. $I_{HO:} = A_{HO\cdot} = 44$ kcal/mol. [b] ΔH in parentheses. Barriers are calculated by using the equation derived in ref 18f: $E = f'(I_{N:} - A_{RX})^2/[(I_{N:} - A_{RX}) - \Delta H] - B$. Thus, $f = f'(I_{N:} - A_{RX})/[I_{N:} - A_{RX} - \Delta H]$, i.e., $f \propto (1/|\Delta H|)$. See the discussion in the text. $\Delta H = A_{HO} - A_{Cl} + D_{C-Cl} - D_{C-OH}$. We assume the α-CN affects D_{C-OH} as it does D_{C-Cl}, or very approximately so. [c] These are f' values; $f' = [b^2(C\cdots Cl)(C\cdots OH)]^{1/2}$.

This can be seen by comparing, for example, the b^2 values of $(NCCH_2\cdots X)^-$ with those of $(CH_3\cdots X)^-$. Hand in hand with stabilizing $R^-:$, π-acceptor substituents markedly weaken the two-electron bond by ≥ 15 kcal/mol (compare D_{R-X} values in Table III).[33] The combination of these two effects leads to a great improvement of the bond acceptor ability as can be witnessed by comparing the A_{RX} values in, e.g., entries 1 vs. 2 in Table III. This improvement in A_{RX}, caused by α-CN, is much more significant than the effect exerted by either an α-halogen or a β-halogen (compare with Table I).

The relative S_N2 reactivity of $NCCH_2-X$ vs. CH_3-X is, again, endowed with the, previously discussed, clash between the gap and the slope factors.[26] Since CN leads to a great improvement of the bond acceptor ability, there is now a real opportunity for a superior reactivity of the good acceptor substrate, $NCCH_2-X$. In general, the likelihood of such a trend increases as the gap factor, $I_{N:} - A_{RX}$, decreases without overly increasing the slope factor, f.[26] Specifically, this depends on the nature of both the nucleophile (N) and the leaving group (X). Whenever the nucleophile is either a poor electron donor (high $I_{N:}$ in the reaction medium[35a]) or/and it tends to form heavily delocalized three-electron bonds, the reaction will be dominated by the slope factor, and CH_3-X will usually react almost as fast as or even faster than $NCCH_2-X$. On the other hand, whenever the nucleophile is a good electron donor and/or it does not form overly delocalized three-electron bonds, the reaction will be dominated by the gap factor $(I_{N:} - A_{RX})$[26] and may eventually grant superiority to the better acceptor substrate, $NCCH_2-X$.[35b]

In a similar manner,[26] our model predicts that for a given nucleophile the superiority of $NCCH_2-X$ over CH_3-X will be established more easily for X's which improve the acceptor ability of the substrate (higher A_{RX}) without markedly delocalizing its $(R\cdots X)^-$ three-electron bond.

Table IV presents a quantitative application of these considerations in terms of eq 5 for various identity reactions of CH_3-X and $NCCH_2-X$. By comparing entries 1 and 2 entries 3 and 4 and 5 and 6, we can see that as the gap factor decreases, i.e., the donor–acceptor relationship of the reactants is improved, the relative reactivity switches from being slope (f)-controlled where CH_3-Cl reacts faster or as fast as $NCCH_2-Cl$ (entries 1 and 2) to being gap-controlled where $NCCH_2-X$ reacts faster than CH_3-X (X = Br, Cl in Table IV). In entries 7 and 8 we show how by markedly improving the donor ability of the nucleophile and increasing reaction exothermicity, the relative reactivity of the same two substrates can be inverted. Thus, while toward Cl^- the relative reactivity is $CH_3-Cl \geq NCCH_2-Cl$, toward the better (gas phase) nucleophile HO^- the relative reactivity is inverted, becoming $NCCH_2-Cl > CH_3-Cl$.

While we are not enamored with the numerical results, it is clear that the qualitative model and its quantitative application, *both appear to capture* the physical trend[13a,c] and to attribute it to well-defined properties of the reactants. For example, the low reactivity ratios of $PhCOCH_2-Br$ vs. CH_3-I which are obtained with neutral nucleophiles[13a] can be attributed to the, sometimes, poor donor ability of the nucleophile (e.g., pyridine) and to the propensity of such nucleophiles to form heavily delocalized three-electron bonds as shown in eq 13:[35a]

$$(R\cdots N) = a(R\cdot\ :N) + b(R^-:\ \cdot N^+) \qquad (b^2 = \text{large}) \quad (13)$$

These three-electron bonds are stabilized by electronic delocalization (as in eq 4) as well as by electrostatic interactions and therefore they become especially delocalized whenever $R^-:$ is stable such as when $R = PhCOCH_2$. Thus, the low reactivity ratio, $k[PhCOCH_2-Br]/k[CH_3-I]$, with some neutral nucleophiles[13a] derives from the intrinsic tendency of $R = PhCOCH_2$ to form more delocalized three-electron bonds than does $R = CH_3$ and is therefore a manifestation of the gap–slope clash. As the donor ability of the nucleophile is improved (e.g., thiourea, $NCSe^-$) and its propensity to form overly delocalized three-electron bonds is decreased (e.g., Cl^-),[35a] reactivity becomes gap-controlled, granting superiority to $PhCOCH_2-Br$—the better acceptor substrate. Thus both reactivity trends appear to be manifestations of the gap–slope clash.

It is instructive to highlight the difference between α-halo and α–π-acceptor substitution. The change in f (three-electron bond delocalization) attending α-halo substitution is large in comparison with its effect on the substrate electron affinity (A_{RX}), especially when symmetrization of the three-electron bond occurs (e.g., in $ClCH_2-Cl$, Table I). Therefore, the change in f overrides the improvement in A_{RX} and superior reactivity of CH_2Cl_2 over CH_3Cl is not very likely to occur. On the other hand, the changes in f attending π-acceptor substitution are not as large in comparison with the large enhancement of the acceptor ability of the substrate (Table III), and therefore superior reactivity of, e.g., $NCCH_2-Cl$ can occur.

The qualitative insight projected by eq 5 and the following discussion make now a substantial amount of data understandable. Thus, the often small relative reactivity observed for $PhCH_2-X$ vs. CH_3-X (also H_2CCHCH_2-X vs. CH_3-X)[7d,e] may arise from the opposing effects brought about by α-Ph substitution (also α-vinyl). On the one hand, α-Ph delocalizes the three-electron bond by virtue of increasing A_R ($A_{PhCH_2} = 20.0$ kcal/mol) and, thereby, it increases f (eq 5) through the slope effect. On the other hand, it weakens the C–X two-electron bond, making the substrate a better electron acceptor and decreasing the energy gap ($I_{N:} - A_{RX}$ in eq 5). The net result is a small rate enhancement.

The observed reversals in the k_H/k_{NO_2} in the benzyl system $YC_6H_4CH_2-X$ (Y = H, NO_2)[14,15] may also be manifestations of the gap–slope interplay. NO_2 increases the substrate electron affinity relative to H ($A_{RX} = -1.4$ and -10.5 kcal/mol for $NO_2C_6H_4CH_2-Cl$ and $C_6H_5CH_2-Cl$, respectively), but it also increases the three-electron bond delocalization ($b^2 = 0.3613$ vs. 0.2614). Therefore, as before (Table IV) $NO_2C_6H_4CH_2-Cl$ will react faster than $C_6H_5CH_2-Cl$ with powerful nucleophiles but slower with weaker ones. A similar logic applies also to the effect of α-SiR_3 substitution.[9]

The fascinating Bartlett result[12] which exhibits an enormous difference in the activation energies of **3A** and **3B** toward KI in acetone originates in the fact that the H_2C-O linkage in **3A** is deconjugated from the π system. The deconjugation lowers the effective electron affinity of the leaving group. Therefore it makes

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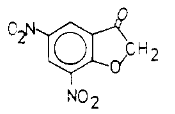
(33) The factors controlling two-electron bond strenghts were discussed in: (a) Epiotis, N. D.; Shaik, S. *J. Am. Chem. Soc.* **1977**, *99*, 4936. (b) Larson, J. R.; Shaik, S. S.; Epiotis, N. D. *Tetrahedron*, **1981**, *37*, 1205.

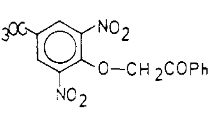
(34) Zimmerman, A. H.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 3565.

(35) (a) Relative $I_{N:}$ values in solution may be deduced from oxidation potential data (for data see ref 23a). Note the solvent would tend to *decrease* the delocalization of three-electron bonds of the type $(R\cdots N)^-$ by preferentially stabilizing the VB form $R\cdot\ :N^-$ and to *increase* the delocalization of three-electron bonds of the type $R\cdots N$ by stabilizing the VB form $R^-:\ \cdot N^+$ (see eq 13). (b) The rate enhancement (*though not the rate retardation*) exerted by a π-acceptor substituent is nicely acocunted for in ref 6b and 21c by using an MO rationale which is basically equivalent to our discussion of the substituent effect on A_{RX} (Table III). (c) Closs, G., private communication.



$\Delta H^{\ddagger} = 31.3$ kcal/mole

3A



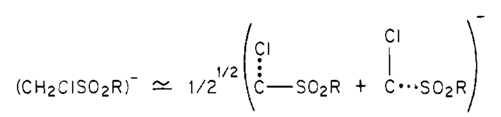
$\Delta H^{\ddagger} = 10.2$ kcal/mole

3B

3A a worse acceptor than **3B**, and simultaneously it causes enhanced delocalization of the $(\mathrm{H_2C\cdots O})^-$ bond of **3A**. These two effects join to create a great difference in the activation barriers of the two compounds.

Finally, the effect of α-$\mathrm{SO_2R'}$ substituent which was investigated thoroughly by Bordwell[16] does seem on its face as a steric or an electrostatic problem. However, the mere fact that the bulky α-$\mathrm{Si(CH_3)_3}$ substituent[9b] and α-Li[35c] (which accumulate negative charges on the α-carbon) both lead to rate enhancement casts some doubts on the *sole* dominance of the steric or electrostatic effects in staging the outstanding retardation exerted by α-$\mathrm{SO_2R'}$.

Consideration of two-electron bond energies[32b] shows that $D_{\mathrm{C\text{-}SO_2R}} < D_{\mathrm{C\text{-}Cl}}$. This will tend to equalize the acceptor abilities of the two bonds (since $A_{\mathrm{SO_2R}} < A_{\mathrm{Cl}}$, see eq 7). Therefore, when both substituents are present on the same carbon, the three-electron bond will tend to delocalize over the two linkages, much the same as in $\mathrm{CH_2Cl_2}$, i.e.



$$(\mathrm{CH_2ClSO_2R})^- \simeq 1/2^{1/2}\left(\overset{\mathrm{Cl}}{\overset{\vdots}{\mathrm{C}}}\!-\!\!-\mathrm{SO_2R} + \overset{\mathrm{Cl}}{\overset{|}{\mathrm{C}}}\cdots\mathrm{SO_2R}\right)^- \qquad (14)$$

This symmetrization effect will contribute to the rate retardation exerted by α-$\mathrm{SO_2R}$. When this substituent is put, e.g., in the γ-position of allyl chloride,[9b] the symmetrization (as well as steric) effect ceases and the substituent then improves the acceptor ability of the C–Cl bond without greatly raising its three-electron bond delocalization, much the same as does α-CN (Table III). In such a position $\mathrm{SO_2R}$ *can* enhance S_N2 reactivity if the nucleophile is strong enough (consult Table IV).

Thus we have seen that carbon substituent effect on S_N2 reactivity and reactivity–selectivity follows a rather simple logic when viewed through the eyes of the correlation diagram model. It is yet to be seen whether this model can predict other curious S_N2 phenomena.[17]

Conclusions

We have presented here a correlation diagram[18e–g] model of S_N2 which leads to a simple and compact equation for the reaction barrier in terms of a slope factor (f) and an energy gap factor ($I_{\mathrm{N:}} - A_{\mathrm{RX}}$). *The slope factor ($f$) takes into account the bond reorganization aspect of the S_N2 transformation*, and is determined jointly by the reaction enthalpy and the degree of delocalization of the three-electron bonds $(\mathrm{N\cdots R})^-$ and $(\mathrm{R\cdots X})^-$.[21] *The energy gap factor ($I_{\mathrm{N:}} - A_{\mathrm{RX}}$) reflects the electron surge aspect of the S_N2 transformation* and is determined by the donor–acceptor properties of the reactants.

Thus, the model brings under one equation some well-defined thermochemical properties of the reactants and thereby it allows one to rationalize and make verifiable predictions in a coherent manner. The equation predicts that part of the reactivity trends will respond to the donor–acceptor properties of the reactants, while others will respond better to, e.g., the degree of delocalization of the three-electron bonds and that at predictable instances relatively reactivity (e.g., of two substrates) can change its response from being e.g., three-electron bond controlled to being donor–acceptor-controlled. We have attempted to show here that these principles form a basis for understanding the effect of α- and β-carbon substituents on S_N2 reactivity.

The model has of course its limitations; some are those which accompany any attempt at generalization[18f,21] and some are more specific ones like the overemphasis on barriers rather than on rates, while others may still be found in the course of application. Yet the usefulness of any model must be judged by its ability to pattern and predict experimental trends. The present model does seem[18e,f] to meet these criteria of usefulness.

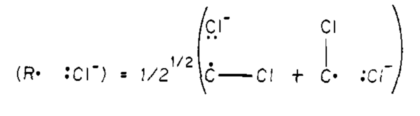
Acknowledgment. I am indebted to Professor A. Pross for the enlightening discussions. Special thanks are due to Y. Ahuvia and A. Seidman for the typing of this manuscript.

Appendix

The general quantum–thermochemical equation for estimating the energy of the anionic state $(\mathrm{R\cdots X})^-$ relative to $\mathrm{R\cdot} + \mathrm{:X^-}$ is

$$E[(\mathrm{R\cdots X})^-] = [(D_{\mathrm{R\text{-}R}}D_{\mathrm{X\text{-}X}})^{1/2} - E_{\mathrm{b,b}}] + \tfrac{1}{2}[(A_{\mathrm{X}} - A_{\mathrm{R}}) + E_{\mathrm{b,b}}] - \tfrac{1}{2}\{[(A_{\mathrm{X}} - A_{\mathrm{R}} + E_{\mathrm{b,b}})^2 + (D_{\mathrm{R\text{-}R}}D_{\mathrm{X\text{-}X}})/S_{\mathrm{R\text{-}X}}{}^2]^{1/2}\} \qquad (15)$$

$(D_{\mathrm{R\text{-}R}}D_{\mathrm{X\text{-}X}})^{1/2}$ is the energy of the $(\mathrm{R\cdot\ :X^-})$ form relative to $\mathrm{R\cdot} + \mathrm{:X^-}$.[18f] D stands for bond energy. $E_{\mathrm{b,b}}$ is the effective one-electronic matrix element of equivalent $(\mathrm{R\cdot\ :X^-})$ forms in a case where two or more identical X's are attached to the same carbon. For example, in the case of $\mathrm{CH_2Cl_2}$ $\mathrm{R\cdot\ :Cl^-}$ is actually



$$(\mathrm{R\cdot\ \ :Cl^-}) = 1/2^{1/2}\left(\overset{\mathrm{:Cl^-}}{\dot{\mathrm{C}}}\!-\!\!-\mathrm{Cl} + \overset{\mathrm{Cl}}{\overset{|}{\mathrm{C}}}\mathrm{\cdot\ \ :Cl^-}\right) \qquad (16)$$

Therefore the energy of $(\mathrm{R\cdot\ :Cl^-})$ at the R–Cl equilibrium distance is $(D_{\mathrm{R\text{-}R}}D_{\mathrm{Cl\text{-}Cl}})^{1/2}$ less the matrix element of the two forms. If the two-electron linkage is taken to be represented solely by the Heitler-London form, then the matrix element ($E_{\mathrm{b,b}}$) is simply

$$E_{\mathrm{b,b}} = \tfrac{1}{2}\langle\phi_{\mathrm{Cl}}|\hat{\mathrm{H}}|\phi_{\mathrm{Cl}}\rangle = \tfrac{1}{2}\beta(\mathrm{Cl,Cl}) \qquad (17)$$

whereas if the two-electron linkage is represented by eq 3, then

$$E_{\mathrm{b,b}} = (a^2/2)\beta(\mathrm{Cl,Cl}) + 2^{1/2}ab\beta(\mathrm{C,Cl}) \qquad (18)$$

where $\beta(\mathrm{C,Cl})$ refers to the nonbonded C, Cl interaction. It turns out that the values of $E_{\mathrm{b,b}}$ are practically invariant under eq 17 or 18; therefore, we use the simpler relation in eq 17.

According to ref 18f $\beta(\mathrm{Cl,Cl})$ at the Cl–Cl equilibrium (e) distance is given by

$$\beta(\mathrm{Cl,Cl})_{\mathrm{e}} = \left[\frac{1}{2S(\mathrm{Cl,Cl})_{\mathrm{e}}}\right]D_{\mathrm{Cl\text{-}Cl}} \qquad (19)$$

Assuming a proportionality between β and the overlap integral S, one gets for the nonbonded $\beta(\mathrm{Cl,Cl})$

$$\beta(\mathrm{Cl,Cl}) = \beta(\mathrm{Cl,Cl})_{\mathrm{e}}S(\mathrm{Cl,Cl})/S(\mathrm{Cl,Cl})_{\mathrm{e}} \qquad (20)$$

The nonbonded Cl, Cl overlap was determined over Slater AO's with $\mathrm{sp^3}$ and $\mathrm{sp^5}$ hybridizations and turns out to be almost identical: 0.0713 and 0.0708, respectively. This yields $\beta = 8.3$ kcal/mol. Similar values were obtained for $\beta(\mathrm{Br,Br})$ and $\beta(\mathrm{I,I})$: 7.4 and 6.5 kcal/mol, respectively.

Using these values and eq 15, one gets $D_{\mathrm{R\cdots X}}$, which is simply $-E[(\mathrm{R\cdots X})^-]$, and with the aid of eq 7 one finds A_{RX}. The b^2 values are obtained from the relation

$$b^2 = 0.5[1 - \Delta/(\Delta^2 + 4)^{1/2}] \qquad (21)$$

where $\Delta = |[A_{\mathrm{X}} - A_{\mathrm{R}} + E_{\mathrm{b,b}}]/(D_{\mathrm{R\text{-}R}}D_{\mathrm{X\text{-}X}})^{1/2}|$. Thus, the negative charge on the carbon in drawing **2A** (see the text) is simply b^2, while on the two Cl's it is $(1 - b^2)/2$.

When the second linkage is not identical with the main one as in $\mathrm{CH_2FCl}$, one calculates separately the two anionic states $(\mathrm{C\cdots Cl})^-$ and $(\mathrm{C\cdots F})^-$ using eq 15 with $E_{\mathrm{b,b}} = 0$. The so resulting states are allowed then to interact with an $\sim 0.5\beta(\mathrm{Cl,F})$ matrix element in analogy to eq 17. In this manner one obtains the mixing coefficients of $(\mathrm{C\cdots F})^-$ into $(\mathrm{C\cdots Cl})^-$ and eq 9 (text) follows naturally.

The results show small sensitivity to the values of the nonbonded $\beta(\mathrm{X,X})$. For example, with $\beta(\mathrm{Cl,Cl}) = 16.6$ kcal instead of 8.3 one obtains $A_{\mathrm{CH_2Cl_2}} = -11$ kcal/mol, $A_{\mathrm{CHCl_3}} = +0.1$ kcal/mol, $A_{\mathrm{CCl_4}} = +11$ kcal/mol. Changing other parameters like the value of $\beta(\mathrm{R\text{-}X})$, which is given by $0.5(D_{\mathrm{R\text{-}R}}D_{\mathrm{X\text{-}X}})^{1/2}/S_{\mathrm{R\text{-}X}}$ in eq 15, from 67.4 to 71.44 kcal/mol (the latter is the value for $\mathrm{CH_3\text{-}Cl}$) yields the following values: $A_{\mathrm{CH_2Cl_2}} = -13.28$ kcal/mol, $A_{\mathrm{CHCl_3}} = -4$ kcal/mol, and $A_{\mathrm{CCl_4}} = +9.11$ kcal/mol. Thus, changes in the

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values are expected, but the trends are invariant.

When this methodology is used, the resulting valence electron affinity of CH_4 is –65 kcal/mol and $b^2 = 0.34$. Using these values and $I_{H:} = 19.0$ kcal/mol yields a barrier of 43.12 kcal/mol, with $S = 2$ (see Table I) and $f = b^2S = 0.68$. The reasonable size of the barrier gives some confidence that our recipe for f in eq 12 is a reasonable one.[31] Note the values of A_{CH_4} in ref 18e,f refer to a localized anionic form.

All the values of A_{RX} and b^2 refer to a standard S_{R-X} overlap (0.5). For details, see ref 18f.

Registry No. CH_3Cl, 74-87-3; $ClCH_2Cl$, 75-09-2; FCH_2Cl, 593-70-4; Cl_2CHCl, 67-66-3; Cl_3CCl, 56-23-5; CH_3Br, 74-83-9; $BrCH_2Br$, 74-95-3; CH_3I, 74-88-4; ICH_2I, 75-11-6; $(HO)CH_2Cl$, 15454-33-8; $(FCH_2)CH_2Br$, 762-49-2; Cl, 16887-00-6; Br, 24959-67-9; I, 20461-54-5; $NCCH_2Cl$, 107-14-2; $NCCH_2Br$, 590-17-0; $NCCH_2I$, 624-75-9.

Photochemistry of β,γ-Enones. 7.[1] Intramolecular Competition between Di-π-methane and Oxa-di-π-methane Rearrangements. On the Intermediacy of Charge-Transfer Complexes and Zwitterions in the Di-π-methane Rearrangements

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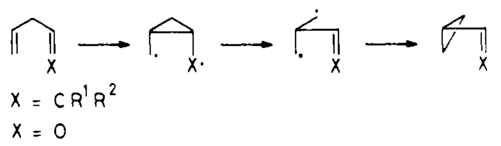
Abstract: The intramolecular competition between the di-π-methane (DPM) rearrangement and the oxa-di-π-methane (ODPM) rearrangement of 3-(3,4-dihydro-2-naphthyl)-3-methylpent-4-en-2-one (**1**), (*E*)-3-methyl-3-vinyl-5-phenylpent-4-en-2-one (**2**), and 2-cyclopent-1-enyl-2-vinylcyclopentanone (**3**) has been examined. Dienone **1** in benzene upon triplet photosensitization with 4-benzoylbiphenyl leads to the formation of one DPM isomer and two ODPM isomers in a ratio of 35:17:10. The results are consistent with a stepwise mechanism via 1,4- and 1,3-biradicals as the subsequent intermediates. The occurrence of only one instead of the expected two DPM isomers is explained in terms of the specific charge-transfer complexation in the 1,3-biradical rotamer intermediate in which the phenylene and acetyl group are "cisoid" (CTC). The preference of the DPM over the ODPM rearrangement has been explained in terms of the lower bond strength of the C═C as compared with the C═O π-bond. Dienone **2**, under similar conditions as **1**, exhibits only *E–Z* isomerization, even after prolonged irradiation. This may be explained in terms of the free rotor theory in which presumably the 1,4-biradicals of the DPM and ODPM rearrangements (E and F) are involved. Dienone **3** upon irradiation in acetone as solvent and triplet sensitizer decomposes rapidly; use of the sensitizers acetophenone, *m*-methoxyacetophenone, and benzene also leads to the formation of nonvolatile products only. No rearrangement products have been observed.

Both the DPM[2,3] and the ODPM rearrangements[3-5] are currently under investigation, and excellent reviews on these photochemical reactions were recently published. Our interest in these topics originated from our photochemical studies on the ionones and the noted absence of the ODPM rearrangement with the retro-α-ionones.[6-8] Later van der Weerdt, in a detailed study on acyclic γ-phenyl-β,γ-enones,[9] showed that the occurrence of an ODPM rearrangement, which is in competition with *E–Z* isomerization, is strongly dependent on the degree and type of α-alkyl substitution.[8] On the basis of a relation between homoconjugation and the occurrence of the ODPM rearrangement,[4,9c] it was suggested that conformational effects in β,γ-enones lead in some cases to a sufficient orbital overlap to effect the ODPM rearrangement.[9b]

Scheme I



Based on single-photon counting studies Zimmerman[2,10] showed that the rate of the DPM rearrangement is affected by the degree of α-alkyl substitution between the two unsaturated bonds. He suggested that the rate variation results from a difference in stabilization of the transition state for the conversion of the 1,4- into the 1,3-biradical intermediate. The same could apply to the ODPM rearrangement,[9] but this still awaits experimental evidence.

DPM and ODPM rearrangements occur upon triplet photosensitization of suitable 1,4-dienes and β,γ-unsaturated ketones,

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(1) For part 6, see R. H. van der Veen, C. Kruk, and H. Cerfontain, *Recl. Trav. Chim. Pays-Bas*, **101**, 272 (1982).

(2) H. E. Zimmerman in "Rearrangements in Ground and Excited States", Vol. 3, P. de Mayo, Ed., Academic Press, New York, 1980, pp 131–161.

(3) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).

(4) D. I. Schuster in "Rearrangements in Ground and Excited States", Vol. 3, P. de Mayo, Ed., Academic Press, New York, 1980, pp 167–279.

(5) K. N. Houk, *Chem. Rev.*, **76**, 1 (1976).

(6) A. van Wageningen, P. C. M. van Noort, and H. Cerfontain, *J. Chem. Soc., Perkin Trans. 2*, 1662 (1974); A. van Wageningen, J. A. J. Geenevasen, and H. Cerfontain, *Ibid.*, 1283 (1975).

(7) In a study on the acetone-photosensitized irradiation of three spiro-β,γ:δ,ε-dienones Fuchs[8] very recently reported that the 1,2-acyl shift product formation can be explained in terms of an ODPM type mechanism involving one or both double bonds.

(8) S. Abramson and B. Fuchs, *J. Chem. Soc., Chem. Commun.*, 1376 (1982).

(9) (a) A. J. A. van der Weerdt and H. Cerfontain, *J. Chem. Soc., Perkin Trans. 2*, 592 (1980); (b) A. J. A. van der Weerdt, Thesis (in English), University of Amsterdam, 1978; (c) A. J. A. van der Weerdt and H. Cerfontain, *Recl. Trav. Chim. Pays-Bas*, **96**, 247 (1977).

(10) H. E. Zimmerman and P. S. Mariano, *J. Am. Chem. Soc.*, **91**, 1718 (1969); H. E. Zimmerman and J. A. Pincock, *Ibid.*, **95**, 2957 (1973).

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