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COMPETITIVE REACTIVITY AS A PROBE FOR REACTION COORDINATES IN GAS-PHASE ION–MOLECULE CHEMISTRY†

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Using the method of competitive reactivity of two functional groups in the same molecule, anionic elimination reactions show considerable kinetic selectivity for small differences in leaving group thermochemistry, in structures of the general type $YCH_2CH_2CH_2Z$, where Y and Z are good anionic leaving groups. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

When ions and neutral molecules encounter each other in the gas phase, they can form a complex that is more stable than the isolated species, because of the strong interaction energies between them. In addition, the activation energies for such species reacting in the gas phase are usually smaller than those in solution, because the energy price of desolvating the site of reaction need not be paid. These two situations often combine to make the transition state for exothermic gas-phase ion–molecule reactions more stable than the reactants.[1] Such a potential energy surface means that many of these gas-phase reactions proceed at near-collision rates. Some ion–molecule reactions do proceed more slowly, however. This occurs due to the reaction complex actually proceeding via passage through the vibrationally excited states above the potential energy surface, as described by the RRKM model.[2] As exemplified by the 'double minimum' model of Kebarle and Brauman,[1] RRKM theory is generally accepted at present as the best explanation for rate constants of gas-phase ion–molecule reactions that are less than the collision rate constant.

For sufficiently exothermic reactions, even an appreciable intrinsic[3] transition-state barrier may affect the rate constant only slightly. An example of this in the gas phase is the case of haloethanes reacting with methoxide:

$$CH_3CH_2Cl + MeO^- \rightarrow Cl^- + CH_2{=}CH_2 + MeOH \quad (1)$$

$$CH_3CH_2Br + MeO^- \rightarrow Br^- + CH_2{=}CH_2 + MeOH \quad (2)$$

When carried out in the cell of an ion cyclotron resonance (ICR) spectrometer, we find that both reactions proceed at near-collision rate,[4] within a factor of two of each other. These reactions, with methoxide as base, are -33 and -42 kcal mol^{-1} (1 kcal=4·184 kJ) exothermic, respectively.[5,6] Even when a weaker base, such as $CF_3CH_2O^-$, is utilized, the bromide elimination is still only a factor of 5·0 faster than the chloride reaction.[7]

Based on the 'double minimum' model,[1] ion–molecule reactions follow the rate expression

$$k_{obs} = k_{coll}\,(k_2/k_{-1})$$

where k_{coll} is the collision rate constant for the ion and neutral[4] entering into the ion–molecule complex, k_2 is the rate constant for passage from the ion–molecule complex over the transition state and k_{-1} is the reverse of k_{coll}, i.e. the unimolecular break-up of the complex back into reactant ion and neutral, through the orbiting transition state.[1] For reactions (1) and (2), the observed rate constant is dominated by k_{coll}; the structural effects on the kinetics of the k_2/k_{-1} term are minimal, being manifest only as a small difference between two large numbers.

In order to probe such cases, where there is little macroscopic selectivity, we have utilized a method that provides information on relative transition-state barrier heights in rapid gas-phase reactions: intramolecular competition between two functional sites, proceeding from the same collisional complex. This technique has been used in the gas phase to examine the effect of thermochemistry on the branching ratios in the unimolecular breakup of an excited complex[8] and on chemically activated complexes.[9] This competitive channel method has also been used

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previously for elimination reactions such as (3)[10, 11] and in site selectivity between different functional groups.[12]

In the present study, attack by a base at the central C–H bond of 1,3-disubstituted propanes, $YCH_2CH_2CH_2Z$, can lead to elimination of either leaving group:

$$X^- + YCH_2CH_2CH_2Z \rightarrow Y^- + CH_2{=}CHCH_2Z \quad (3)$$

$$\rightarrow YCH_2CH{=}CH_2 + Z^- \quad (4)$$

The 1,3-disubstituted framework was chosen as the best one for revealing intrinsic leaving group abilities, without interference from other structural effects. A 1,2-disubstituted ethane system results in different substituents being present on the carbon losing the proton. In that case, loss of the better carboxylate leaving group implies a less stable incipient carbanion leading to it, owing to the polar and polarizability effect of the other leaving group being at that site. Likewise, a 1,1-disubstituted system would result in the non-departing leaving group affecting the stability of the developing double bond. It also would require that conformationally different hydrogens be removed for the loss of each leaving group. In the 1,3-system chosen here, it is exactly the same proton loss that leads to each leaving group's departure, and the distance between the leaving groups is such that their differential effects on the alkene's stability will be negligible.

The selectivity revealed by this method is related to the well known solution-phase approach of comparing rate- versus product-determining steps in a reaction mechanism. The ratio of products provides information about barriers in the second (product-determining) step even though the macroscopic kinetics are largely insensitive to such barriers.[13] In the gas-phase 'double minimum' model, there will be some small difference in rate constant, but the ratio of the two products from this method will be a much more sensitive measure of the barriers than the overall rate constant.

EXPERIMENTAL

These experiments were carried out using a previously described ion cyclotron resonance mass spectrometer (ICR-MS).[14] All experiments were carried out at room temperature (cell temperature *ca* 305 K). Any anions produced by dissociative attachment by the substrate were ejected by double resonance immediately after the grid pulse.

General procedure for the synthesis of disubstituted compounds. A monoester alcohol or monochloro alcohol was first prepared, then the second ester group was added. Propionyl chloride, isobutyryl chloride, chloroacetyl chloride, difluoroacetyl chloride and trifluoroacetic anhydride (all from Aldrich) were used in this context. Preparative gas chromatography utilizing 20% Carbowax 20M on Chromosorb P afforded pure end products.

Propane-1,3-diol was reacted with acetyl chloride utilizing a 1·5 : 1 molar ratio of diol to acid chloride so as to minimize diacetylation. The extent of reaction was followed by thin-layer chromatography utilizing silica gel and dichloromethane as the solvent. The 3-acetylpropan-1-ol was then separated from the excess propanediol and diacetylated product via column chromatography utilizing 70–230′ mesh silica gel and dichloromethane as the solvent to yield the pure monoacetyl alcohol. The monoacetyl alcohol was reacted with the appropriate acid chloride or acid anhydride to yield the diesters of interest.

Ester chlorides. 3-Chloropropan-1-ol was reacted with the corresponding acid or acid chloride to give the products needed.

C-2 diesters. Pure 2-acetoxyethanol was obtained via separation from a commercially available mixture of it plus ethane-1,2-diol and 1,2-diacetoxyethane (Fluka) by preparative gas chromatography as above. When isolated, the acetoxyethanol was reacted with the requisite acid chloride to give the C-2 diesters.

All commercially available reagents were used without further purification (except as noted above). Gas chromatography–mass spectrometry and ^1H and ^{13}C NMR and ICR–mass spectrometry were utilized to establish purity of the products.

Care was taken to ensure that the elimination substrates were free of traces of carboxylic acid. If any acid were present, the greater rate for proton transfer from the acid to the attacking base, compared with the production of the carboxylate via elimination,[10] resulted in leaving group ratios that were not accurate. This could easily be detected, however, because clean substrate gave a product ratio of the two leaving groups that was invariant with time as the total intensity of leaving group signal increased. If carboxylic acid were present, its conjugate base ion was present in large amounts at short times, with the competitive leaving group increasing relative to it at longer times.

Methoxide was produced by thermal electron dissociative attachment of *in situ* generated methyl nitrite.[15] Fluoride was formed by dissociative attachment of nitrogen trifluoride at 4·2 eV. Isoamyl nitrite furnished isoamyl alkoxide with 0 eV electrons, and acetic anhydride gave acetate similarly.

RESULTS AND DISCUSSION

To provide a thermochemical framework for discussing these reactions, ΔH_{elim} is defined as the enthalpy of the reaction

$$CH_3CH_2CH_2Y \rightarrow H^+ + CH_3CH{=}CH_2 + Y^- \quad (5)$$

evaluated from standard data compilations.[5, 6] An anionic base with a conjugate ΔH_{acid} numerically larger than this ΔH_{elim} should react exothermically in such a process. Because three species are being formed from two, there is also an entropic driving force for this elimination, up to *ca* 51 cal mol^{-1} K^{-1}. Values for these quantities are given in Table 1. To obtain the thermochemical values for reaction of

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Table 1. Thermochemistry of elimination reactions of $CH_3CH_2CH_2X$ in the gas phase[a]

X	ΔH_{elim}[b]	ΔS_{elim}[b]	ΔG_{elim}[b]	ΔH_{acid}[c]	ΔG_{acid}[c]
F	377·7	49·3	362·9	370·9	365·1
Cl	347·6	48·8	333·0	333·4	328·0
Br	339·2	48·3	324·7	323·5	318·2
I	332·4	47·4	318·2	314·4	309·3
CH_3CO_2	362·0	51·6	346·5	348·6	341·5
$CH_3CH_2CO_2$	360·9	51·0	345·6	347·5	340·4
$(CH_3)_2CHCO_2$	359·5	51·0	344·2	346·1	339·0
$ClCH_2CO_2$	348·5	51·0	333·2	336·5	329·0
F_2CHCO_2	343·4	51·0	327·7	331·0	323·8
CF_3CO_2	337·0	49·6	322·1	323·9	317·4

[a] Ionic data from Ref. 5; neutral data from Ref. 6, or estimated by group additivity.[22]
[b] Corresponding to equation (3).
[c] For the gas-phase acidity of HX.

Table 2. Leaving group ratios for gas-phase anionic elimination reactions

		Base			
Substrate[a]	$\Delta\Delta H_{elim}$[b]	MeO^-	$iAmO^-$	F^-	$MeCO_2^-$
$Br(CH_2)_3Cl$	8·4	91 : 1	95 : 1	105 : 1	> 200 : 1
$EtCO_2(CH_2)_3O_2CMe$	1·1	1·6 : 1	[d]	2·5 : 1	[e]
$iPrCO_2(CH_2)_3O_2CMe$	2·5	10 : 1	[c]	50 : 1	[e]
$CF_3CO_2(CH_2)_3O_2CMe$	24·7	> 100 : 1	[c]	[c]	[e]
$Cl(CH_2)_3O_2CCH_2Cl$	0·9	> 100 : 1	[c]	108 : 1	[c]
$F_2CHCO_2(CH_2)_3Cl$	4·2	1 : 6·2	[c]	[c]	[c]
$CF3CO_2(CH_2)_3Cl$	10·6	36 : 1	[c]	[c]	[c]
$EtCO_2(CH_2)_2O_2CMe$	1·1	1·26 : 1		2·4 : 1	
$iPrCO_2(CH_2)_2O_2CMe$	2·5	4 : 1	[c]	12 : 1	[e]

[a] Thermochemically favored leaving group is on the left.
[b] In kcal mol^{-1}; relative ΔH_{elim} values from equation (1) for the two leaving groups in the substrate.
[c] Not tried.
[d] Base and leaving group isobaric, not tried.
[e] No reaction (endothermic) for at least one leaving group.

some anionic base X^- with RY, one subtracts ΔH_{acid}(HX) from ΔH_{elim}(RY).

A point that must be addressed is the question of elimination versus substitution. If both pathways are structurally possible, substitution tends to be favored over elimination enthalpically in the gas phase,[5, 6] although as noted above, entropy favors elimination. Nevertheless, studies have shown that for anionic nucleophiles/bases of first-row elements, elimination is the preferred pathway.[16] We therefore constrained our studies to such ions here. Likewise, a second elimination from the neutral allylic species in reaction (3), to yield HZ and allene, is a possibility. This is *ca* 25 kcal mol^{-1} endothermic for all the leaving groups used in this work, however. For all bases used, with a carboxylate leaving group, the overall production of allene would be endothermic by $\geqslant 6$ kcal mol^{-1}. Even with the help of the entropy factor for the creation of another product, this makes such double elimination only marginally allowed thermodynamically. Such second eliminations, exoergic but endothermic, are known to proceed,[17] but usually circumvent the endothermicity problem by having the HZ moiety depart hydrogen bonded to the anionic leaving group, as in the following reaction:[18]

$$X^- + YCH_2CH_2CH_2Z \rightarrow [Y^- + CH_2{=}CHCH_2Z] \rightarrow CH_2{=}C{=}CH_2 + Y^- \cdots HZ \quad (6)$$

Although such cluster ions are frequently observed in the high-pressure flowing afterglow technique[9, 10] owing to third-body clustering reactions, in the micro-Torr and lower pressure regime of the ICR spectrometer they are only observed when very specific thermodynamic criteria are met. The elimination to the free ion must be endothermic, but the process yielding the cluster ion is exothermic. These criteria are met by the leaving groups used here; thus, the absence of such cluster ions is indicative of, although not proof of, the absence of the second elimination step.

In 1-bromo-3-chloropropane, bromide is favored as a leaving group over chloride by 8·4 kcal mol^{-1} in enthalpy, as given in Table 1. For acetate anion as base, we observe the resulting elimination product to be exclusively bromide (> 200 : 1 bromide : chloride). With hydroxide, methoxide, isoamyl alkoxide and fluoride as bases, the elimination product ratios (bromide : chloride) that result are 6 : 1, 91 : 1, 95 : 1 and 105 : 1, respectively (Table 2). These results illustrate three important points. First, intramolecular selectivity is observed for a reaction that occurs at near-collision rate. Second, the elimination process observed is not strictly governed by the thermochemistry of the leaving group alone; if it were, the bromide : chloride ratio would be *ca* 10^{14}, and would be independent of the attacking base. Third, the elimination process becomes more selective as the energy difference between attacking base and departing leaving group becomes smaller, in accordance with the axiom 'selectivity is inversely related to reactivity.'[19]

For the case of bromide versus chloride elimination, in addition to the thermochemical difference in ionic leaving group ability, there could also be effects of electronegativity, homolytic bond strength, polarizability, bond dipoles, etc., on kinetic reactivity. To minimize or eliminate these factors, the corresponding elimination reactions of several mixed diesters of the general structure $RCO_2CH_2CH_2O_2CR'$ have been examined. For these, the leaving groups are attached to the alkane structure by identical atoms and functional groups; only a 'distant' substituent affects the energetics of elimination. For acetate versus propionate and acetate versus isobutyrate, the results in Table 2 indicate that the elimination reaction is very sensitive to the relative leaving group ability. A difference in leaving group energetics of only 1·1 kcal mol^{-1} results in a propionate : acetate ratio of 2·5 : 1 when fluoride is the base. As expected, the selectivity decreases as the base becomes stronger, i.e. 1·6 : 1 with methoxide as the base. A larger

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difference in leaving group ability (isobutyrate is 2·5 kcal-mol^{-1} better as a leaving group than acetate) increases the ratio of observed leaving group ability.

We can also compare very different types of leaving groups with this method, such as chloride versus various carboxylates. Figure 1, showing a plot of $\log(X^-/Y^-)$ versus $\Delta\Delta H_{elim}$, reveals that chloride is inherently a better leaving group than carboxylate, when thermochemical differences are cancelled out. For example, chloroacetate and chloride have comparable thermochemistry as leaving groups (chloride is 0·9 kcal mol^{-1} better than chloroacetate), so we would expect a value of $\leqslant 10$ for the chloride : chloroacetate ratio if thermochemistry were the only criterion. However, chloride predominates in actual leaving group ability by $>100:1$, indicating that some other factor(s), such as electronegativity, polarizability or degrees of freedom, must be operating. Difluoroacetate is a better leaving group than chloride by 4·2 kcal/mol^{-1}, yet chloride still predominates over it by 6 : 1. The preference for chloride can be overcome eventually by thermochemistry : trifluoroacetate completely wins out over chloride, being 11 kcal mol^{-1} better thermochemically as a leaving group. From Figure 1, a comparison of the two lines at constant $\Delta\Delta H_{elim}$ indicates that chloride is intrinsically about 80 times better as a leaving group than a carboxylate of the same ΔH_{elim} value. Conversely, it takes *ca* 5 kcal mol^{-1} of increased thermochemical leaving group ability to cancel the greater intrinsic leaving group ability of chloride over the carboxylates.

If the point for the elimination ratio from $BrCH_2CH_2CH_2Cl$ is compared with the chloride/ester line in Figure 1, it is observed that for this reaction, the C—Br bond is about 15 times more labile than the C—O bond in esters when one factors out the thermochemical driving force. Although this is not surprising in itself, when it is compared to the chloride : ester ratio of 80 derived above it implies that bromide is inherently a worse leaving group than chloride by a factor of *ca* 5, should thermochemistry be factored out! This involves the assumption that these effects are additive, which may not hold for a comparison of an atom leaving group versus a more complex structure. Brauman and co-workers[20] have found that in thermoneutral S_N2 reactions, the intrinsic Marcus barrier for bromide loss from CH_3X is *ca* 1 kcal mol^{-1} larger than for chloride loss, in agreement with our competitive results in elimination.

In all the cases, no evidence of cluster ions as shown in equation (6), or $XH\cdots Y^-$ from equation (3), was observed.

For the diesters connected by a glycol moiety, the acidic site is different for loss of each leaving group. As shown in Table 2, we observe smaller leaving group ratios for the dimethylene cases, compared with the same bases and leaving groups with the trimethylene framework. This holds for both methoxide and fluoride as bases, although the acetate : propionate ratios with fluoride as the base are similar for the di- versus tri-methylene structures. We ascribe this to the development of a partial negative charge on the acidic carbon in the product determining transition state.[10] The reaction pathway with the less favored leaving group has this charge on the carbon nearer the larger adjacent group. The resonance stabilizing effect of a carboxy group is negligible,[21] and the difference in the polar effect of an acetoxy versus a propionoxy or an isobutyroxy should likewise be small. The greater polarizability of the larger group, however, should stabilize the adjacent incipient carbanion, and thus favor loss of the smaller leaving group. This effect is not large enough to reverse the order of reactivity, but does reduce the ratio of intrinsic leaving

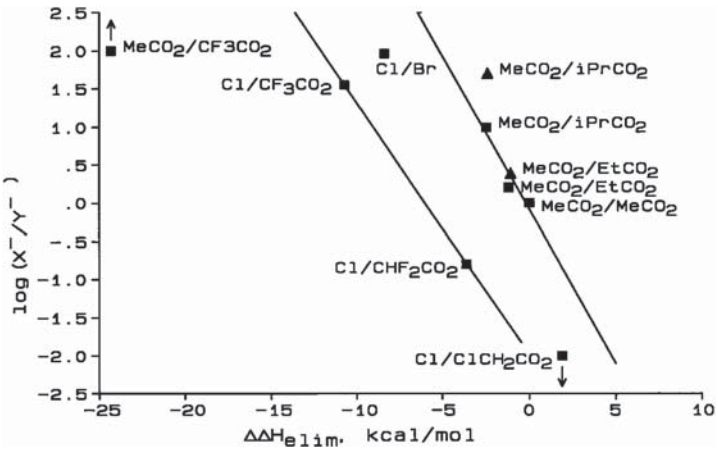

Figure 1. Logarithm of the leaving group ratio for $X(CH_2)_3Y$ versus the relative thermochemistry of elimination. Squares are for methoxide as base and triangles for fluoride. Arrows indicate maximum/minimum limits

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group ability. As with the trimethylene cases, the leaving group ratio is larger when the weaker base fluoride is used, compared with methoxide.

We are extending the use of this method to other reactions, such as substitution and proton transfer, and also attempting to factor out the relative barrier height via RRKM calculations.[1, 20]

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