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Effects of the Leaving Group and of Ion Pairing on the Stereochemistry of E2 Reactions. An ab Initio Study

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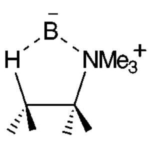
Computational studies of the stereochemistry of E2 reactions of ethyl derivatives, EtX, at MP2/6-31+G*//MP2/6-31+G* give the following results (X, base, $\Delta\Delta H^{\ddagger}$(syn − anti in kcal mol^{-1})): F, OH^-, 6.3; F, LiOH, −21.4; F, NaOH, −11.6; Cl, OH^-, 8.0; Cl, LiOH, −18.7; Cl, NaOH, −12.4; NMe_3^+, OH^-, −11.1; NMe_3^+, LiOH, 3.7. The activation barriers are much higher for the ion-paired bases than for hydroxide, reflecting their much weaker basicity. As deduced from results in solution, ion pairing of the base promotes syn elimination with negative leaving groups (F^-, Cl^-) but the reverse is true for neutral leaving groups (NMe_3). The effects are strikingly larger in the gas phase than the typically modest ones found in solution. The effects of the leaving group and the base on the nature of the transition structure are discussed.

Introduction

The substantial literature on the stereochemistry of base-promoted elimination reactions in solution has been reviewed on a number of occasions.[1,2] An intrinsic preference for anti elimination is found in most cases, but the preference is sometimes only modest and can be overridden by structural and environmental factors. The purpose of the present investigation is to examine by means of ab initio calculations how ion pairing of the base and changes in the leaving group affect the stereochemistry of elimination in the gas phase.

Ion pairing has been implicated as a major factor when changes in stereochemistry of elimination are produced by changes in the base or the solvent. Plausible rationalizations for these changes were offered some time ago when it was proposed that syn elimination from onium salts proceeded via species such as **1**.[3,4]

Syn eliminations from substrates such as halides and tosylates were proposed to proceed via species such as **2**.[5,6] Subsequent evidence from the Czech group and others is consistent with this basic picture, although interpretation of the results can sometimes be complicated by ion-pair exchange equilibria, especially in the case of the onium salts.[7,8] The influence of ion association on stereochemistry and other aspects of elimination reactions has been reviewed.[9]



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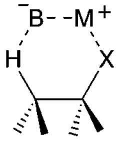

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Numerous ab initio studies of E2 reactions have been reported in recent years, though the first such study goes back a full 20 years.[10] Particularly relevant to the present study are the thorough investigations of Gronert, who did calculations on a wide variety of bases and substrates,[11−16] Other studies have applied DFT methods,[11,17,18] investigated the relation between structure and kinetic hydrogen isotope effects,[19−21] and examined the E2−S_N2 competition.[22,23] Most of the studies in which stereochemistry was examined involved ethyl derivatives, and a substantial preference (>5 kcal mol^{-1}) for anti elimination was found. Ion-paired bases, which are known to promote syn elimination with neutral leaving groups in solution, were not included in any of the investigations.

Computational Methods

The calculations utilized Gaussian 94[24] and Gaussian 98.[25] The work utilized the standard basis set 6-31+G*. Correlation corrections utilized the Møller−Plesset method.[26−30] The enthalpies (ΔH) reported in the tables are corrected to constant pressure and for zero-point-energy differences from MP2/6-31+G*//MP2/6-31+G* calculations scaled to 0.95 to account for the overestimation of frequencies by Hartree−Fock meth-

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ods.[31,32] The enthalpies were further corrected to 298 K for the contributions of the translational, rotational, and vibrational partition functions.[33] The vibrational contribution is not based on scaled frequencies, because inspection of numerous frequency calculations makes it doubtful that low-lying calculated frequencies (the only ones that contribute significantly to the vibrational partition functions) bear a predictable relation to experimental frequencies.[34]

Results and Discussion

The level of calculation employed here, MP2/6-31+G*, has been shown to yield reasonable results on elimination reactions.[11−16] While it lacks quantitative accuracy on gas-phase acidities of fluoroethanes, the relative values are much better.[35]

Table 1 records well depths, barrier heights, ΔH_{TS}, relative to the separated reactants, and overall heats of reaction for the reactions of ethyl fluoride, ethyl chloride, and ethyltrimethylammonium ion with hydroxide ion and with lithium and sodium hydroxides. The ion−dipole complexes between hydroxide ion and the ethyl halides are lower in energy than the reactants by about the expected amount. It is interesting that three of the dipole−dipole complexes are of comparable stability, though in these cases the base associates with the leaving group via the metal ion rather than with a β-hydrogen. The EtF−NaOH complex is actually lower in energy by 2.4 kcal than the separated reactants, but the ZPE and partition function contributions raise its enthalpy above that of the reactants. Its low stability presumably arises from the lower affinity of the fluorine for sodium than for lithium ion. It is noteworthy that the ion−ion complex between ethyltrimethylammonium ion and hydroxide ion is as stable as a strong covalent single bond. The complexes listed are the most stable ones. No effort was made to find others in view of the fact that most ion−dipole complexes (and probably the one ion−ion complex as well) vary little in energy with changes in the relative orientations of the components.

Table 1. E2 Reactions of C_2H_5X with OH^- and M^+OH^- Studied at MP2/6-31+G*//MP2/6-31+G*[a]

X, base	ΔH_{well}	ΔH_{TS}(anti)	ΔH_{TS}(syn)	$\Delta H_{products}$[b]
F, OH^-	−16.7	−9.4	−3.1	−34.9
F, LiOH	−16.6	24.8	3.4	−21.4
F, NaOH	2.5	17.9	6.3	−16.2
Cl, OH^-	−17.8	−11.9	−3.9	−50.5
Cl, LiOH	−14.8	25.2	6.5	−25.1
Cl, NaOH	−14.1	18.0	5.6	−26.7
NMe_3^+, OH^-	−111.9	−91.7	−102.8	−129.9
NMe_3^+, LiOH	−18.6	9.1	12.8	−16.4

[a] Enthalpies in kcal mol^{-1}. [b] Products are as follows: $CH_2{=}CH_2$ in all cases, plus $XHOH^-$ for X = F or Cl, base = OH^-; H_2OMF for X = F or Cl, base = MOH; NMe_3 + H_2O for X = NMe_3^+, base = OH^-; $H_2OLiNMe_3$ for X = NMe_3^+, base = LiOH.

As expected, ethyl fluoride and chloride with hydroxide ion strongly prefer anti elimination by 6.2 and 8.0 kcal mol^{-1}, respectively. This situation is dramatically reversed when the hydroxide is ion paired with lithium or sodium ion. Now syn is preferred over anti elimination by 21.4 kcal for the fluoride and 18.7 kcal for the chloride when the base is lithium hydroxide. The preference is lower when the base is sodium hydroxide, but still more than 10 kcal.

When trimethylammonio is the leaving group, syn elimination is preferred with the free hydroxide ion by 11.1 kcal. This result is in contrast to a very recent calculation on ethyltrimethylammonium ion plus acetate ion where there is still a weak (3.3 kcal) preference for anti elimination.[36] This is probably because the delocalized charge of acetate ion does not interact as strongly with the trimethylammonio group as the concentrated charge of hydroxide ion. A preference for anti elimination is found when lithium hydroxide is the base, but only by 3.7 kcal. The results so far confirm a number of deductions from the solution phase experiments cited above. The preference for anti elimination is higher for better leaving groups (Cl > F or NMe_3^+). Ion pairing promotes syn elimination, though the effect in the absence of solvent is strikingly greater than the modest effects found in solution (usually no more than a few tenths of a kcal). Conditions that promote ion pairing of the base disfavor syn elimination from onium salts. All of these results are consistent with the transition structures for syn elimination depicted in **1** and **2**.

Another obvious point from Table 1 is that barriers are much higher for lithium and sodium hydroxides than for free hydroxide. This is primarily a consequence of the much lower basicity of hydroxide ion when ion paired with an alkali cation. The basicity of hydroxide ion (Table 2, expressed as the heat of ionization of its conjugate acid) when coordinated with lithium and sodium ions, is diminished by some 150 and 130 kcal, respectively. As shown in Table 3, coordination also strongly stabilizes the transition structures for elimination, but less strongly than it stabilizes the base. In the case of experiments it is often difficult to decide how much of a change in activation energy arises from a change in the reactants

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Table 2. Effect of Coordination with Alkali Cations on the Heat of Ionization of Water

	ΔH(acid)^a		
acid	MP2/6-31+G*	G2(MP2)	literature
H_2O	395.2	390.3	390.7^b
$LiOH_2^+$	234.3	238.0	–
$NaOH_2^+$	254.3	259.3	–

^{a} Enthalpies in kcal mol^{-1}. ^{b} Lias, S. G.; Bartmess, J. E.; Liebman, J. L.; Holmes, R. D.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data Suppl.* **1988**, *17*, as updated by NIST Databases 19a,b, National Institute of Standards and Technology, Gaithersburg, MD 20889. The most up-to-date versions of these databases are available at the web site http://webbook.nist.gov/chemistry.

Table 3. Effect of Adding M$^+$ to Reactant and Transition Structure in E2 Reactions of Ethyl Fluoride and Chloride at MP2/6-31+G*

reactants	product	ΔH(reaction)^a
Li$^+$ + OH$^-$	LiOH	−184.3
Li$^+$ + syn-F-TS$^-$	Li-syn-F-TS	−177.8
Li$^+$ + anti-F-TS$^-$	Li-anti-F-TS	−150.1
Li$^+$ + syn-Cl-TS$^-$	Li-syn-Cl-TS	−173.9
Li$^+$ + anti-Cl-TS$^-$	Li-anti-Cl-TS	−147.1
Na$^+$ + OH$^-$	NaOH	−154.3
Na$^+$ + syn-F-TS$^-$	Na-syn-F-TS	−145.0
Na$^+$ + anti-F-TS$^-$	Na-anti-F-TS	−127.0
Na$^+$ + syn-Cl-T^{S-}	Na-syn-Cl-TS	−144.8
Na$^+$ + anti-Cl-TS$^-$	Na-anti-Cl-TS	−124.3

^{a} In kcal mol^{-1}.

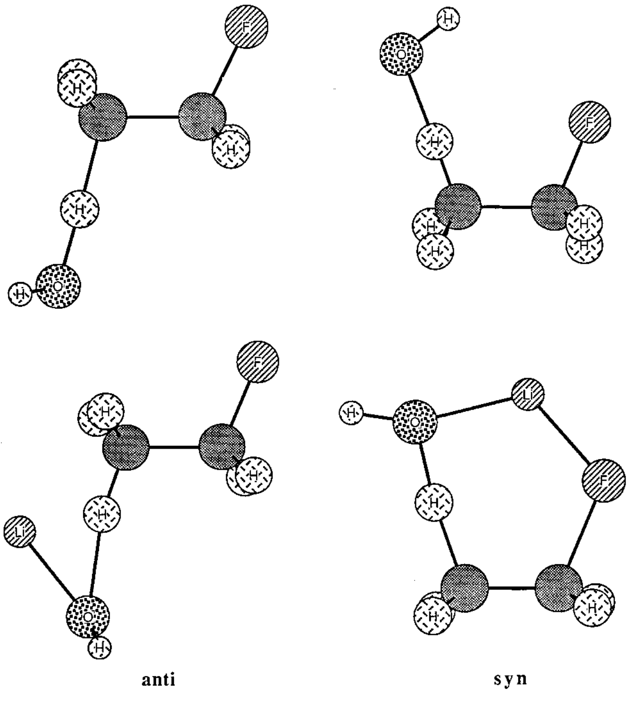

Figure 1. Transition structures (anti left, syn right) for the reaction of ethyl fluoride with hydroxide ion (top line) and lithium hydroxide (bottom line).

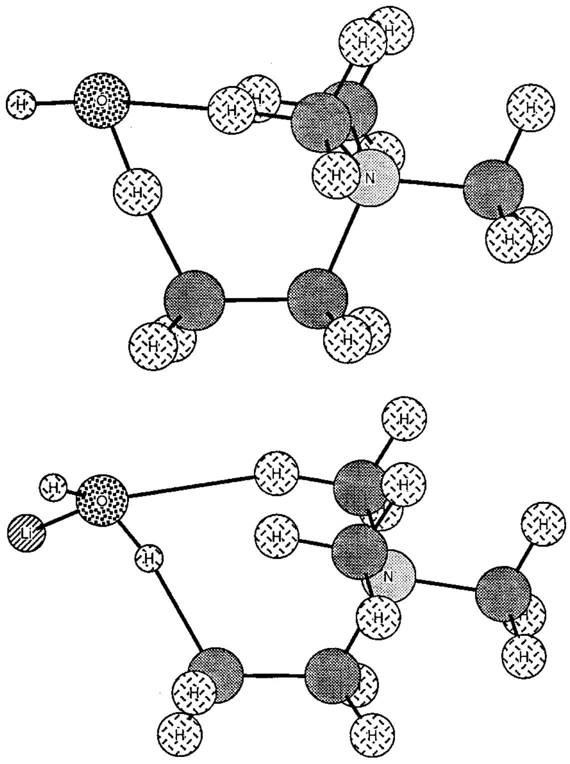

Figure 2. Transition structures for syn elimination from ethyltrimethylammonium ion promoted by hydroxide ion (top) and lithium hydroxide (bottom).

and how much from a change in the transition structure, but it is easy to make this distinction with appropriate computational data.

The marked changes in heats of activation noted above are accompanied by significant changes in structure. Figure 1 shows transition structures for anti and syn elimination from ethyl fluoride promoted by hydroxide ion (top line) and lithium hydroxide (bottom line). The anti elimination with hydroxide ion shows the expected structure with the departing fluoride ion and proton very close to 180° from each other, though rehybridization at the carbon atoms has barely started. The syn elimination shows both C−H and C−F bonds distinctly shorter, and eclipsing has caused the dihedral angle to depart markedly from the 0° required for maximization of overlap. The transition structure for syn elimination promoted by lithium hydroxide is clearly stabilized by association of the lithium ion with the departing fluoride and also shows more rehybridization at the carbon atoms than even the anti elimination with hydroxide. The H−C−C−F dihedral angle is held close to 0° by stereoelectronic effects and by the cyclic structure, which together overwhelm the unfavorable eclipsing effect. The anti transition structure with lithium hydroxide is very reactant like. The H−C−C−F dihedral angle is close to 180° because this arrangement is now favored by both stereoelectronic and eclipsing effects. The transition structures for reaction of ethyl fluoride with sodium hydroxide and for ethyl chloride with both metal hydroxides are not shown, but display very similar overall patterns.

Transition structures for syn elimination in reactions of ethyltrimethylammonium ion with hydroxide and lithium hydroxide are shown in Figure 2. In both cases a cyclic structure in which hydroxide ion associates with both the departing hydrogen and the leaving group is evident. The association is closer with the free hydroxide ion. It suffices to enforce a nearly eclipsed H−C−C−N dihedral angle, which is not the case with lithium hydroxide. The association of the base in both cases is with a peripheral methyl hydrogen of the trimethylammonio group. The positive charge of the trimethylammonio group is found by both NPA and Mulliken charges to be entirely in the peripheral hydrogens, not in either the nitrogen or carbon atoms. Even with lithium hydroxide some stabilization must be afforded by the association

Table 4. E2 Reactions of C_2H_5X with OH^- and M^+OH^-. Bond Length Changes between Reactant and Transition Structure

X, base, stereochem[a]	Δr(CX)	Δr(CC)[b]	Δr(CH)	Δr(OH)[c]
F, OH^-, a	0.1027	−0.0492	0.3572	0.2505
F, OH^-, s	0.0599	−0.0253	0.2699	0.3138
F, LiOH, a	0.0336	−0.0199	0.5958	0.1232
F, LiOH, s	0.3484	−0.0900	0.2864	0.2822
F, NaOH, a	0.0435	−0.0252	0.6250	0.1079
F, NaOH, s	0.2856	−0.0773	0.2766	0.2957
Cl, OH^-, a	0.1728	−0.0621	0.2663	0.3353
Cl, OH^-, s	0.1061	−0.0364	0.3216	0.2630
Cl, LiOH, a	0.0531	−0.0210	0.5982	0.1198
Cl, LiOH, s	0.4595	−0.0961	0.1984	0.3806
Cl, NaOH, a	0.0711	−0.0286	0.6143	0.1095
Cl, NaOH, s	0.3854	−0.0890	0.2200	0.3545
NMe_3^+, OH−, a	−0.0142	−0.0432	0.2098	0.3780
NMe_3^+, OH^-, s	−0.0065	−0.0355	0.3800	0.2164
NMe_3^+, LiOH, a	−0.0089	−0.0313	0.4534	0.1705
NMe_3^+, LiOH, s	−0.0036	−0.0056	0.5818	0.1119

[a] anti = a, syn = s. [b] A change of −0.17 to −0.18 is expected for full double bond formation. [c] r(OH) in TS − r(OH) in water. The smaller this value, the more product-like the TS.

Table 5. E2 Reactions of C_2H_5X with OH^- and M^+OH^-. Changes in NPA Charges between Reactant and Transition Structure

X, base, stereochem[a]	Δq(X)	Δq(C1)	Δq(C2)	Δq(H)	Δq(O)
F, OH^-, a	−0.0987	−0.0182	−0.2174	0.2353	0.1742
F, OH^-, s	−0.0623	−0.0069	−0.2304	0.2306	0.2034
F, LiOH, a	−0.0346	−0.0127	−0.4072	0.2567	0.2531
F, LiOH, s	−0.2720	0.0022	−0.2443	0.2371	0.2823
F, NaOH, a	−0.0444	−0.0234	−0.3725	0.2593	0.2457
F, NaOH, s	−0.2236	0.0039	−0.2404	0.2299	0.2749
Cl, OH^-, a	−0.2710	0.1403	−0.1806	0.2197	0.1646
Cl, OH^-, s	−0.1754	0.0988	−0.2380	0.2330	0.1836
Cl, LiOH, a	−0.0884	0.0378	−0.4036	0.2595	0.2849
Cl, LiOH, s	−0.5129	0.3451	−0.2344	0.2202	0.1748
Cl, NaOH, a	−0.1175	0.0471	−0.3624	0.2588	0.2822
Cl, NaOH, s	−0.4746	0.2998	−0.2356	0.2243	0.1834
NMe_3^+, OH^-, a	−0.0226	0.0159	−0.1766	0.1860	0.1216
NMe_3^+, OH^-, s	−0.0229	0.0408	−0.2609	0.2178	0.1971
NMe_3^+, LiOH, a	−0.0160	0.0132	−0.3055	0.1956	0.2390
NMe_3^+, LiOH, s	−0.0067	0.0203	−0.3937	0.2274	0.2860

[a] anti = a, syn = s. For NMe_3^+ q(X) is the charge on nitrogen, not the charge on the whole group.

because the preference for anti over syn elimination is modest, only 3.6 kcal. The anti transition structures are not shown because they are closely analogous to those from the ethyl halides.

Examination of changes in bond lengths (Table 4) and in NPA charges[37,38] (Table 5) provides further insight into the transition structures and how they vary with changes in the leaving group, base, and stereochemistry. Elongation of the bond to the leaving group in comparable reactions is consistently greater for C−Cl than for C−F, and least of all for C−N. In fact, the C−N bond is slightly *shortened* in the transition structure, presumably due to attraction between the positive leaving group and the negative basic atom. To test whether the elimination is really concerted, an IRC calculation (at HF/6-31+G* to save time) was performed starting from the syn elimination transition structure. The species generated on the product side expels NMe_3 when allowed to optimize freely, thereby proving that there is no stable carbanion (zwitterion) on the way to the products. The extent of charge development in the leaving group parallels the order of bond elongation: greatest for Cl, less for F, and least for N. Changes in the extent of C−H elongation vary much less with variation in the leaving group, and the same holds for changes in the charge at C2. One can conclude, again between comparable reactions, that the carbanion character of the transition structure runs in the order RCl < RF < $RNMe_3^+$.

There are also significant regularities in comparisons of anti vs syn elimination and of free vs ion-paired bases. For reaction between the ethyl halides and hydroxide ion, C−X elongation and the charge on X are greater in the anti than in the syn elimination. In all four cases the C−H is greater than the C−X elongation, but the charge development at C2 presents a more mixed picture. There is more charge development at C2 than at F for both syn and anti elimination from the fluoride, but less at C2 than at Cl for the anti elimination from the chloride and somewhat more for the syn. With both leaving groups there is more carbanion character in the syn elimination than in the anti.

The quaternary ammonium salt transition structures show more C−H bond extension and more charge development at C2 in the syn than in the anti eliminations. The effect is more pronounced in the reactions with LiOH than in those with hydroxide. Thus all of the transition structures from the quaternary ammonium salt possess high carbanion character which is greater for the syn than the anti eliminations and greater with LiOH than with hydroxide.

The consistent increase in positive charge (0.19−0.26) of the proton in transit cannot arise simply from the fact that it is being transferred to a more electronegative atom. The values of Δq(H) correlate only weakly with the extent of proton transfer as measured by Δr(CH) or Δr(OH), and the increase in charge for complete transfer to oxygen (0.27−0.33) is only a little greater than the range of values in the transition structures. Valence bond terminology is useful in rationalizing these facts.[39] In addition to the obvious contributors (reactant-like, product-like, carbanion-like, and carbocation-like), a significant contributor to the resonance hybrid of the transition structure must be a triple ion species such as **3**.

$$B^- \; H^+ \; {}^-CH_2\text{-}CH_2\text{-}X$$

3

An analogous structure ($R^- \; H^+ \; R^-$) has recently been shown by valence bond (VBSCF) calculations to be the single most important contributor to the resonance hybrid transition structure in the identity-reaction deprotonation of propene by allyl anion.[40] It is likely that such structures are a common feature in proton-transfer reactions.

Acknowledgment. This work was supported by NSF Grant CHE-9706242.

Supporting Information Available: Energies in hartrees and *Z*-matrixes for the optimized reactant complexes and elimination transition structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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