The $Si^+$–$CH_2$ and $Si^+$–CH bond energies are 104 ± 3 and 100 ± 7 kcal/mol, respectively. It is surprising that these bonds are no stronger than $D°(Si^+–CH_3)$, although this is certainly consistent with the notion that silicon does not readily make $\pi$ bonds with carbon. One rationale for why no apparent $\pi$ bond is formed in the $SiCH_2^+$ and $SiCH^+$ molecules is that $Si^+$ has a valence electron configuration of $3s^23p^1$. Thus, formation of a single bond to $Si^+$ can occur readily with the lone p electron, while formation of a double bond requires disruption of the fully occupied $3s^2$ orbital. This means that it may be more appropriate to compare $D°(Si^+–CH_2)$ and $D°(Si^+–CH)$ with $D°(HSi^+–CH_3) = 65 \pm 4$ kcal/mol. This comparison implies that $\pi$ bonds of ~35 kcal/mol may be formed in these molecules. This is in reasonable agreement with the $\pi$ bond energy in $H_2Si{=}CH_2$ of 34 ± 4 kcal/mol calculated by Shin et al.[32] and that in $H_3CSi{=}CH_2$ of 39 ± 5 kcal/mol estimated by Walsh.[45]

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# AM1 Studies of E2 Reactions. 1. Mechanism and Leaving Group Effects

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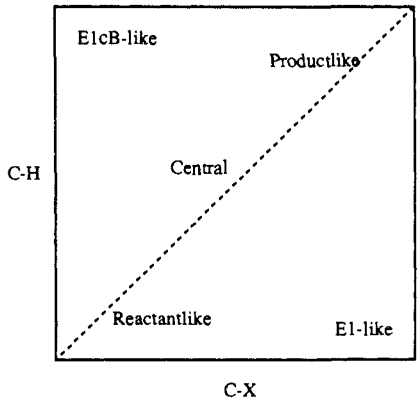
**Abstract:** The mechanisms of bimolecular gas-phase elimination (E2) reactions have been studied, by use of the AM1 model. Calculations are carried out for E2 reactions between a base (B) and a molecule H-CHR-CHS-X, where B is methoxide anion and X is a neutral leaving group (Cl, Br, I, $NO_2$, $OCOCF_3$), and where B is a neutral base (ammonia) and X is an 'onium ion [$^+OH_2$, $^+OHCH_3$, $^+OC_2H_6$, $^+SH_2$, $^+SH(CH_3)$, $^+NH_3$]. The results are compared with experiment, and earlier calculations and interpretations.

Bimolecular base-induced elimination reactions, classed as E2 by Ingold,[1] represent one of the most important and most thoroughly documented classes of organic reactions. Here we will be concerned with the most common reactions of this kind, involving the 1,2-elimination of HX from adjacent carbon atoms of an organic compound; viz.

$$B + H{-}CHR{-}CHS{-}X \rightarrow BH^+ + RCH{=}CHS + X^- \quad (1)$$

where B is a base and R and S are substituents or hydrogen. Extensive mechanistic studies of such reactions have been reported, both in solution[2,3] and in the gas phase.[4-12]

**Chart I.** Variable Transition State of Elimination



Reactions of this kind involve a combination of two basic processes; removal of a hydrogen atom $\beta$ to X by the base, and ionization of C–X. These may take place in a single kinetic step (E2 mechanism) or in two distinct steps, the first step usually being rate determining. In an E1cB elimination, deprotonation occurs

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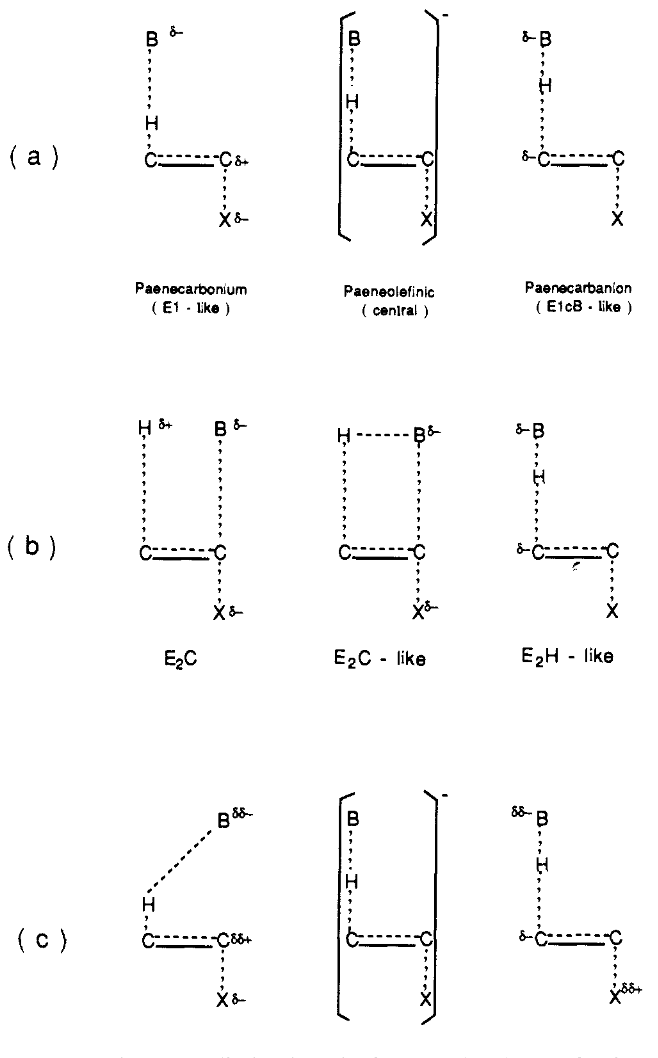
**Chart II.** Geometries of the E2 Transition States



first, while in an E1 elimination, the first step involves ionization of the leaving group. Thus, the first step in an E1 reaction is the same as that in a corresponding $S_N1$ reaction, the intermediate cation either losing a proton to form an olefin (E1) or combining with a nucleophile ($S_N1$).

An E2 elimination may be not merely concerted but synchronous, deprotonation and ionization of the leaving group having taken place to comparable extents in the corresponding transition state (TS). This, however, is not essential. There could in principle be a continuous range of E2 reactions that are concerted but not synchronous, varying from ones with transition states (TSs) where ionization of C–X has barely begun, to ones where deprotonation has hardly started, i.e., from E1cB-like to E1-like. While there has been argument in the past concerning the synchronicity of elimination reactions, there now seems to be a consensus[13] that their transition states do seem to show a continuous variation from one extreme to the other [variable transition state (VTS) mechanism]. However, controversy still exists concerning the geometries of the TSs. See Chart I.

Cram[14] and Bunnett[15] concluded that the reactions involve linear proton transfer from carbon to the base (E2H), the transition from E1-like to E1cB-like reactions thus involving steady changes in the lengths of the BH, HC, CC, and CX bonds in the TS; see Chart IIa.

On the other hand Parker, Winstein, et al.[16] assumed that the E1-like eliminations and the corresponding $S_N1$ reactions take place by a "merged" ($E_2C$) mechanism, via a common intermediate in which the attacking base is poised between the $\alpha$-carbon and the $\beta$-hydrogen. The transition to E1cB-like mechanisms involves a progressive decrease in the importance of the loose covalent interaction with the $\alpha$-carbon ($E_2H$); see Chart IIb.

McLennan[17] suggested a mechanism of intermediate type (Chart IIc) where the interaction between the base and the $\alpha$-carbon, while very weak, is nevertheless sufficient to lead to nonlinear proton transfer, at least in reactions near the E1 limit.

While each of these three divergent theories can account for most of the available experimental data, each also fails in certain cases. In particular, problems arise[18,19] in the case of reactions of weak bases with substrates containing a good leaving group attached to a secondary or tertiary carbon atom, the $\beta$-hydrogen not being activated by an electron-withdrawing substituent.

Problems concerning the timing of bond making and bond breaking during a reaction are notoriously difficult to solve by experiment. This is an area where theoretical calculations should in principle be particularly useful. However, while the mechanisms of $S_N2$ reactions have been extensively studied by both semiempirical[20] and ab initio[21] procedures, and while a number of E2 reactions have been studied experimentally in the gas phase,[4-12] few theoretical calculations have been reported[22,23] and only one by a currently acceptable theoretical procedure.

The exception was a study by Yamabe,[23] using the 3-21G+ ab initio model, of some simple E2 reactions that have been studied in the gas phase, namely, those of fluoride and chloride ions with ethyl fluoride or chloride:

$$X^- + H_3C—CH_2X \rightarrow X—H + H_2C═CH_2 + X^- \qquad (2)$$

These were predicted to be concerted, the C–H and C–halogen bonds having both been weakened to comparable extents in the TS. However, these reactions can hardly be regarded as good models for typical E2 processes in solution, solvent effects being exceptionally large for reactions involving fluoride or chloride ions.

We therefore decided to carry out an extensive survey of elimination reactions, using the AM1 model.[24] Here we report our results for some basic E2 reactions, involving different leaving groups.

## Procedure

The calculations were carried out using the standard AM1[24] procedure, as implemented in the AMPAC program.[25] Geometries of stable species were calculated by minimizing the energy with respect to all

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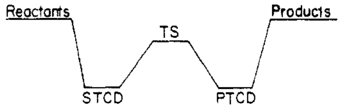

**Figure 1.** Form of the reaction path for an E2 elimination.

geometrical variables, without making any assumptions, using the Davidon–Fletcher–Powell (DFP)[26] algorithm incorporated in AMPAC. TSs were located approximately by the reaction coordinate method[27] or by either of two other methods recently developed here,[28,29] refined by minimizing the norm of the gradients, following McIver and Komornicki.[30] All stationary points were characterized by calculating force constants.[30] The force constants were also used to calculate molecular vibration frequencies and hence molecular entropies and enthalpies of activation.[31] Options for all these procedures are included in AMPAC.

In view of comments by a reviewer, it should be noted that AM1 gives good results for anions,[32] provided that the negative charge is not localized on a single atom.[32] Even methoxide ion is reproduced satisfactorily. The situation is different from that in ab initio studies of anions where diffuse orbitals have to be included in the basis set.

## Results and Discussion

Elimination reactions can be divided into four groups, depending on the nature of the base (B) and leaving group (X) in eq 1. The base can be either anionic (e.g., $MeO^-$) or neutral (e.g., $NH_3$), while the leaving group can be either neutral (e.g., Cl) or cationic (e.g., $OH_2^+$).

Reactions where the base and leaving group carry opposite charges, and where the products are therefore neutral, are extremely exothermic in the gas phase, and the corresponding TSs differ little from the reactants. Conversely, eliminations involving neutral reactants, and hence ionic products, are excessively endothermic in the gas phase, and the corresponding TSs differ little from the products. The gas-phase reactions therefore bear little relation to the corresponding reactions in solution where the effects of charge destruction, or charge separation, are countered by the very large heats of solvation of the ions. Since calculations refer to reactions of isolated molecules, corresponding to reactions in the gas phase, whereas chemists are concerned primarily with reactions in solution, studies of these two types of elimination would serve little purpose. We therefore confined our attention to reactions of anionic bases with neutral substrates, and of neutral bases with cationic substrates.

Our initial calculations were concerned with reactions of simple ethyl derivatives (R = S = H in eq 1), the object being to establish the general mechanisms of elimination for the two kinds of systems indicated above and the effect of variations in the leaving groups.

**A. Reactions of Methoxide Ion with Monosubstituted Ethanes.** We first studied the reactions of methoxide ion with chloroethane (**1a**), bromoethane (**1b**), iodoethane (**1c**), nitroethane (**1d**), and (trifluoroacetoxy)ethane (**1e**). In each case the reactants combined exothermically to form an electrostatic (charge–dipole; CD) complex (STCD), separated from the final product by an activation barrier and a second CD complex (PTCD) formed from the products; see Figure 1. Here, and subsequently, the structures shown were computer drawn from the calculated geometries. Figure 2 shows the geometries and formal atomic charges calculated for the free reactants, while Figure 3 provides similar information for the STCD complexes and the TSs for the overall reactions. The STCD complexes are the same as those involved as intermediates in analogous $S_N2$ reactions where methoxide replaces the leaving group instead of abstracting hydrogen.[20] Their geometries indicate that the methoxy anion is hydrogen bonded to both carbon atoms. Similar structures have been reported[23] from ab initio calculations. The O–H–C bond angle in each TS (Figure 2) was close to 180°, implying linear transfer of hydrogen as advocated by Bunnett.[15]

$CH_3CH_2X$

1 a, X = Cl
b, X = Br
c, X = I
d, X = $NO_2$
e, $F_3CCOO$

$CH_3OH\cdots CH_2CH_2X$

2

$CH_3CH_2Y$

3 a, Y = $H_2O^+$
b, Y = $MeHO^+$
c, Y = $Me_2O^+$
d, Y = $H_2S^+$
e, Y = $MeHS^+$
f, Y = $H_3N^+$

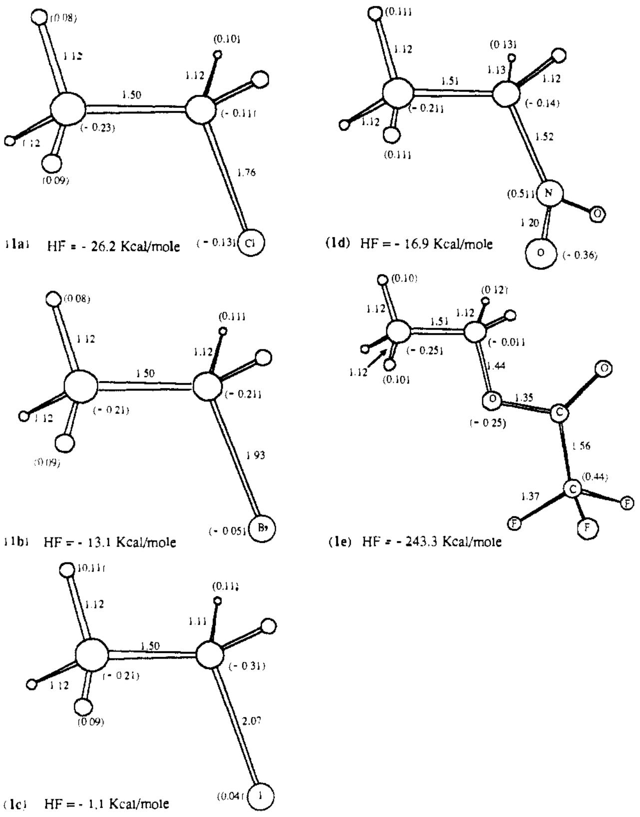

**Figure 2.** Bond lengths (Å) and distribution of formal charges (e) in monosubstituted ethanes.

**Table I.** Heats of Formation of Stationary Points on the MERPs for Reactions of Methoxide Ion with Alkyl Halides

| leaving group | heat of formation, kcal/mol | | | | |
|---|---|---|---|---|---|
| | reactant | STCD[a] | TS[b] | PTCD[c] | product |
| **1a** Cl | -64.7 | -74.8 | -68.6 | -84.2 | -78.2 |
| **1b** Br | -51.6 | -61.5 | -56.6 | -76.2 | -61.0 |
| **1c** I | -39.6 | -49.1 | -44.0 | -56.5 | -42.8 |
| **1d** $NO_2$ | -55.4 | -73.3 | -70.0 | -121.9 | -109.2 |
| **1e** $OCOCF_3$ | -281.6 | -296.9 | -291.5 | -338.6 | -327.8 |

[a] CD complex formed by reactants. [b] Transition state. [c] CD complex formed by products.

In two cases (**1b** and **1c**) the reaction led first to the carbanion that would be the intermediate in an E1cB reaction, hydrogen bonded to methanol. The structures and heats of formation of these species are shown in Figure 4. The methanol was clearly responsible for their stability because the free carbanions were predicted to dissociate without activation to ethylene and $Br^-$ or $I^-$. Schleyer and Kos[33] and Yamabe[23] have reported similar instability in the case of the fluoroethyl (**2**; X = F) and chloroethyl (**2b**) anions. It is indeed possible that the predicted stabilities of **2b** and **2c** are spurious because the activation energies calculated for their dissociation were very small. It is clear in any case that

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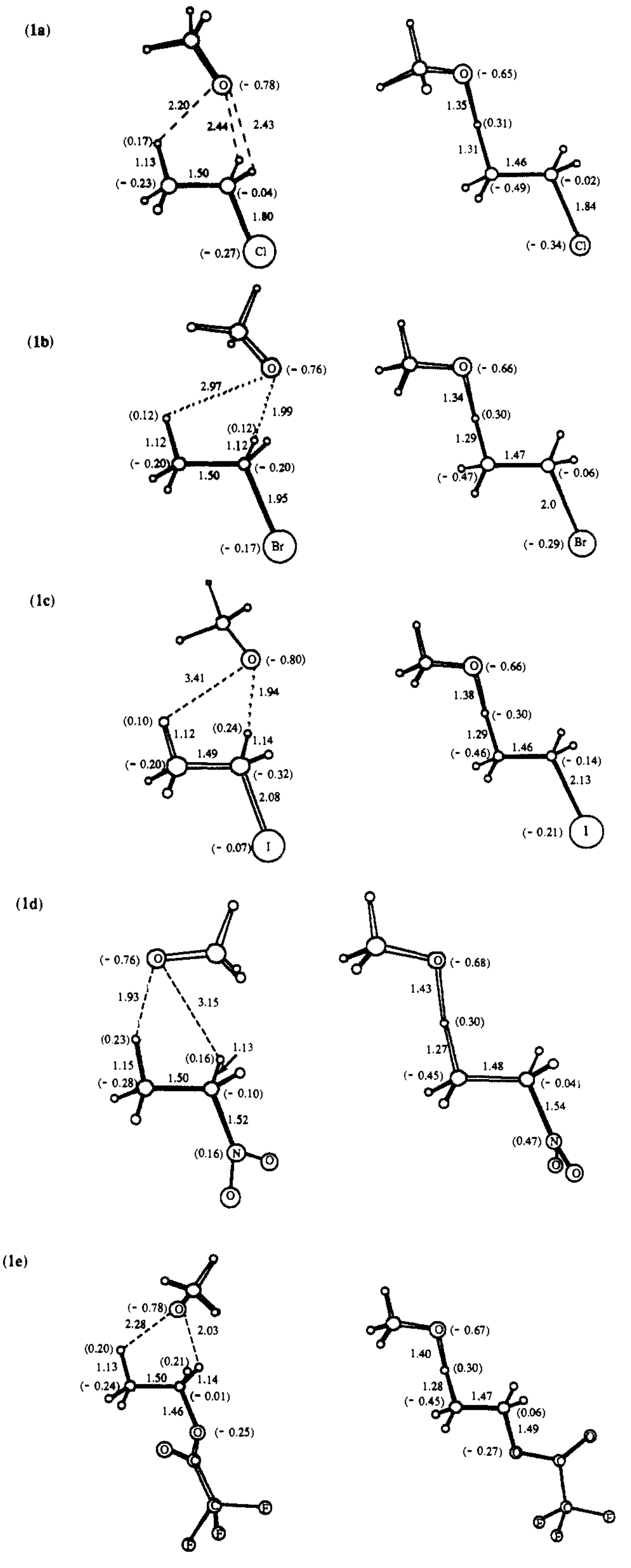

**Figure 3.** Bond lengths (Å) and charge distributions (e) in the initial CD complexes (STCD) and transition states (TS) for E2 reactions of ethane derivatives with methoxide ion.

they play no direct mechanistic role; the anionic intermediate occurs after the TS.

Table I shows the heats of formation (kcal/mol) calculated for the various stationary points in each minimum energy reaction path (MERP), while Table II compares activation energies, starting from the STCD complex, and relevant properties of the TSs.

If the marginal intermediates from **1b** and **1c** are disregarded, all these reactions are of E2 type, in agreement with experiment[11]

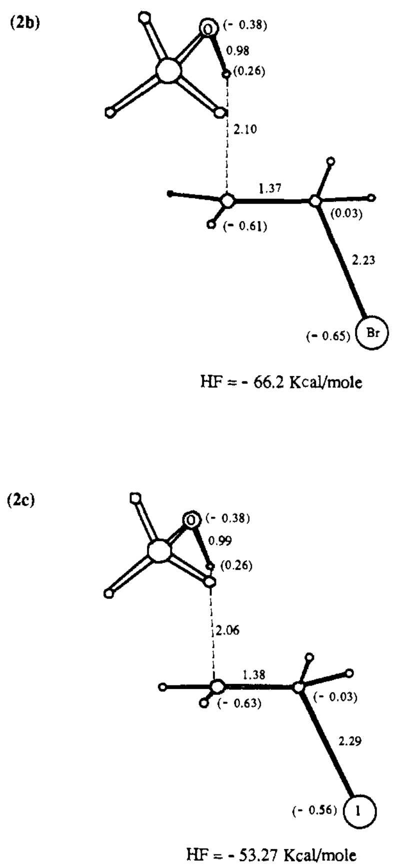

**Figure 4.** Bond lengths (Å) and charge distributions (e) in intermediates formed in the E2 reactions of ethyl bromide or ethyl iodide with methoxide ion.

**Table II.** Bond Lengths and Formal Charges in the Transition States, and Activation Energies, for E2 Reactions of $CH_3O^-$ with $CH_3CH_2X$

| | bond length, Å | | formal charge | | | |
|---|---|---|---|---|---|---|
| X | $C_1$—H | C=C | on $C_1$ | on $C_2$ | $\Delta H^*$, kcal/mol | mechanism |
| **1a** Cl | 1.31 | 1.46 | −0.49 | 0.02 | 6.2 | E2/E1cB |
| **1b** Br | 1.29 | 1.47 | −0.47 | −0.06 | 4.9 | E2/E1cB |
| **1c** I | 1.29 | 1.46 | −0.46 | −0.14 | 5.1 | E2/E1cB |
| **1d** $NO_2$ | 1.27 | 1.48 | −0.45 | −0.04 | 3.3 | E2 |
| **1e** $OCOCF_3$ | 1.28 | 1.47 | −0.45 | −0.06 | 5.4 | E2 |

and calculation[23] for a number of analogous systems. Examination of Figure 3 shows that both deprotonation and C–X ionization have taken place to a significant extent in each TS. However, while the migrating hydrogen atom is in each case roughly equidistant between oxygen and carbon and while the charge on oxygen and on halogen in each TS differs greatly from that in the CD complex or product, the C–X bond distance in each TS is only marginally greater than in the CD complex. The reactions thus approximate E1cB processes, deprotonation having proceeded to a much greater extent in each TS than ionization of the leaving group. The leaving group played the role of stabilizing the $\beta$ carbanion.

The reactions of methoxide ion with **1a–e** may therefore be described as being of E2/E1cB type. As Table I shows, all are predicted to take place without activation in the gas phase, the reactants being higher in energy than the subsequent parts of the corresponding potential energy (PE) surfaces. This conclusion is in agreement with studies[4–13,23] of elimination in the gas phase. A similar situation has been predicted[21–23] and observed[34] in $S_N2$

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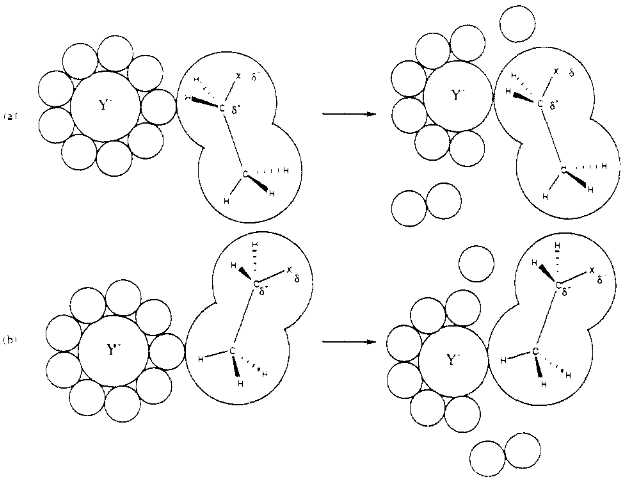
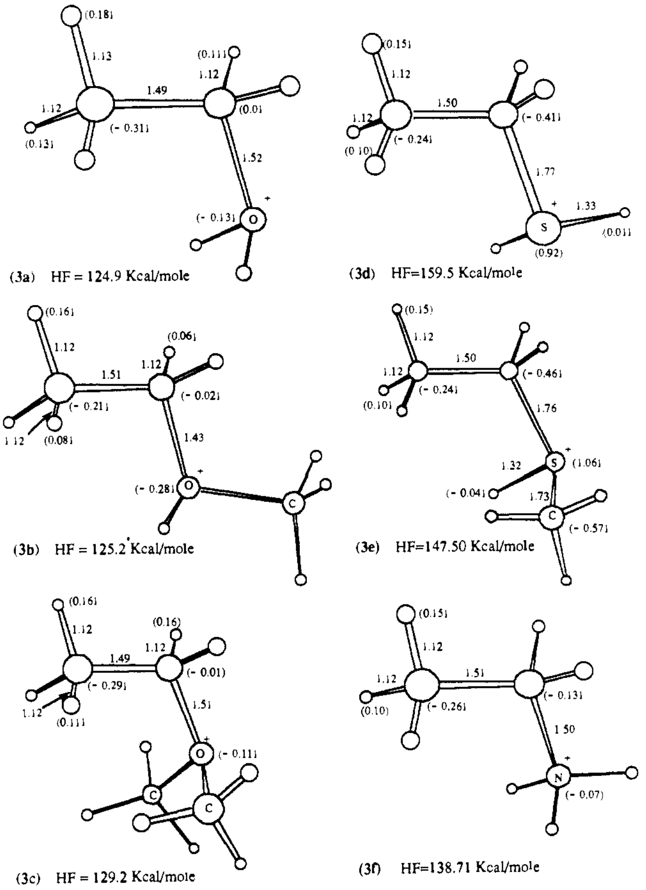


**Figure 5.** Solvent effects in the E2 and SN2 reactions.



(3a) HF = 124.9 Kcal/mole (3d) HF=159.5 Kcal/mole

(3b) HF = 125.2 Kcal/mole (3e) HF=147.50 Kcal/mole

(3c) HF = 129.2 Kcal/mole (3f) HF=138.71 Kcal/mole

**Figure 6.** Bond lengths (Å) and atomic charges (e) calculated for 'onium ions.

reactions, where the heat of reaction for forming of the initial CD complex is in many cases greater than the subsequent activation barrier.

Carrion and Dewar[20] pointed out that a polar solvent should more or less cancel the difference in free energy between the separated reactants and the CD complex. Association of an alkyl halide with a nucleophilic anion to form a CD complex involves replacement of a solvent molecule in the solvation shell of the anion by the alkyl halide; see Figure 5. Since the number of individual particles remains unchanged, there will be no significant change in the translational and rotational contributions to the entropy of the system. Since alkyl halides have large dipole moments, the heat of association of the halide with the anion will not be much less than that for the molecule of solvent it displaces. Furthermore, since the entropy should be more negative the more tightly the solvent or halide molecule is bound to the anion, any difference between the enthalpies of association of solvent or reactant with the anion will be countered by an opposing change in entropy. The free energy of association to form the CD complex in solution should therefore be small. The activation parameters measured in solution should correspond to those calculated for a reaction starting from the CD complex. The effect of the solvent should be confined to the small difference in solvation energy between the CD complex and the TS, the latter having a greater dispersal of charge. Studies[20] of numerous $S_N2$ reactions support this conclusion, which is also consistent with a detailed theoretical study by Jorgensen[35] of solvent effects in the $S_N2$ reaction between chloride ion and methyl chloride in water. Similar considerations should apply equally to E2 reactions.

An alternative possibility is that association of the reactants to form the CD complex may itself require activation, due to the need to desolvate the anion before the other reactant can approach. Dewar and Storch[36] suggested that the activation barriers for anionic substitution at carbonyl carbon in solution are of this type [*desolvation barrier* (DSB) reactions]. However, it seems unlikely that this can be the case here because the observed substituent effects (see following paper) imply that extensive changes in bonding have taken place in the corresponding TSs.

The ease of ionization of ethyl halides in the gas phase increases in the order Cl < Br < I. In a synchronous E2 reaction, where the bond to halogen has been greatly weakened in the TS, the rate should tend to increase with ease of ionization of the halogen and this order is indeed observed in the condensed-phase reactions of **1a–c** with anions in polar solvents.[37] However, according to our calculations, the corresponding gas-phase reactions are *not* synchronous. Comparison of Figures 2 and 3 shows only marginal increases in the C–halogen bond length on passing from the reactant to the TS. The TS is indeed similar to that expected for a E1cB reaction, as indicated by the classification of these reactions as being of E2/E1cB type, and ethyl chloride (**1a**) is predicted to be the least reactive of the three halides in the gas phase. In solution, where ions are stabilized by solvation, the reactions are likely to be more nearly synchronous. These conclusions are further supported by the results for **1d** and **1e**, both of which are predicted to be highly reactive. While nitro and trifluoroacetoxy are poor leaving groups, both are highly polar. The lengths of the C=C bond and the breaking C—H bond, in the TSs (Table II), provide further confirmation that these reactions are of E2/E1cB type. Thus the length of the CH bond decreases with decreasing activation energy, as would be expected if deprotonation were the main rate-determining factor, while the C=C bond lengths vary very little, as would be expected if little change in bonding has taken place at the α-carbon atom.

The geometries calculated for the TSs (Figure 3) indicate trans (anti) attack by the base. Trans elimination is well-known to be favored in solution and the same has recently been shown to be true for an elimination in the gas phase.[9] Attempts to study cis (syn) or gauche elimination failed, indicating that no independent TS for such processes exists in these simple systems. This conclusion is not altogether certain because ready rotation about the C-C bond made it difficult to maintain other than trans conformations. The stereochemistry of elimination is discussed in detail in a later paper of this series, on the basis of studies of molecules where rotation is inhibited.

**B. Reactions of Ammonia with Monosubstituted Cationic Ethanes.** The second series of reactions studied involved reactions of a neutral base (ammonia) with cationic compounds:

$$H_3N + CH_3CH_2{-}X^+ \rightarrow H_4N^+ + H_2C{=}CH_2 + X \quad (3)$$

The ions studied included three ethyloxonium ions (**3a–c**), two

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(35) (a) Chandrasekhar, J.; Smith, S. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 154. (b) Chandrasekhar, J.; Jorgensen, W. L. *Ibid.* **1985**, *107*, 2974.

(36) Dewar, M. J. S.; Storch, D. M. *J. Chem. Soc., Chem. Commun.* **1985**, *2*, 94.

(37) Marshall, D. R.; Thomas, P. J.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1898.

**Table III.** Heats of Formation of Stationary Points on the MERPs for Reactions of Ammonia with Ethyl 'Onium Ions

| leaving group | heat of formation, kcal/mol | | | | |
|---|---|---|---|---|---|
| | reactant | STCD | TS | PTCD | product |
| **3a** $OH_2^+$ | 117.6 | 109.3 | 118.0 | 88.5 | 107.8 |
| **3b** $OHCH_3^+$ | 117.8 | 110.3 | 120.8 | 90.6 | 110.0 |
| **3c** $O(CH_3)_2^+$ | 121.9 | 114.5 | 126.3 | 94.6 | 113.9 |
| **3d** $SH_2^+$ | 152.2 | 140.1 | 160.2 | 149.9 | 168.3 |
| **3e** $SH(CH_3)^+$ | 140.2 | 128.4 | 153.0 | 143.3 | 162.7 |
| **3f** $NH_3^+$ | 131.4 | 115.4 | 161.1 | 137.3 | 159.8 |

ethylsulfonium ions (**3d** and **3e**), and an ammonium ion (**3f**). Figure 6 shows the bond lengths and charge distributions calculated for the parent ions and Figure 7 those calculated for the initially formed CD complexes and TSs. The heats of formation calculated for the various stationary points are listed in Table III, while Table IV shows activation energies calculated for reactions starting from the intermediate CD complexes together with relevant properties of the TSs.

As Figure 7 shows, the TSs for the reactions of the 'onium ions (**3**) with ammonia differ from those for the reactions of the neutral ethane derivatives (**1**) with methoxide ion. In **3**, breaking of the CH and CX bonds has progressed to comparable extents in the TSs, implying that the reactions are more or less synchronous. Also, both bond changes have progressed further in the case of the TSs for reactions of the 'onium ions (**3**). In the case of **3f**, the forming NH bond is indeed shorter than the breaking CH bond.

The difference in mechanism between these reactions and those involving neutral leaving groups is easily understood. Since ammonia is a weak base, deprotonation by ammonia must be much harder than deprotonation by methoxide ion. Equally, since 'onium groups are far more easily heterolysed than neutral ones, breaking the bond to a cationic leaving group should be much easier than breaking the bond to a neutral one. Thus, while deprotonation is the rate-determining factor in cases where the leaving group is neutral and the base anionic, ionization of the leaving group plays a much larger role in cases where the base is neutral and the leaving group is cationic.

Since the effect of the leaving group on the rate of deprotonation depends on an electrostatic interaction and since the positively charged leaving groups should exert similar field effects, the ease of deprotonation should not change dramatically along the series **3a**–**e**. The rate should therefore be determined mainly by the lability of the leaving group. Thus, since alkyl substituents stabilize 'onium ions and so reduce their tendency to solvolyse, reactivity should decrease along the series **3a** > **3b** > **3c**, and **3e** should be less reactive than **3d**. Furthermore, since sulfonium ions are much more stable than 'onium ions, and ammonium ions than sulfonium ions, **3f** should be much less reactive than **3d** or **3e**, and the latter much less reactive than **3a**–**c**. Our results (Table III) follow these predictions.

Another notable difference between the two types of elimination is reflected by their stereochemistry. While the reactions of methoxide ion with neutral substrates are predicted to involve trans elimination and while this is also the preferred route in the case of the 'onium ions (**3**), we were able to locate alternative TSs corresponding to syn elimination in the case of the latter. The geometry is shown in Figure 8 and the corresponding activation energy in Table V. This difference can be attributed to electrostatic attraction between the ammonia and the 'onium ion, due to the fact that little positive charge has yet accumulated on ammonia. The calculated activation energies for syn elimination are, however, much greater than those for trans. This conclusion is in agreement with recent experimental studies of gas-phase base-induced eliminations.[12]

## Comparison with Reactions in Solution

The conclusions reached here differ significantly from those expected on the basis of current theory or derived from studies of elimination reactions in solution. Thus, the rate of elimination

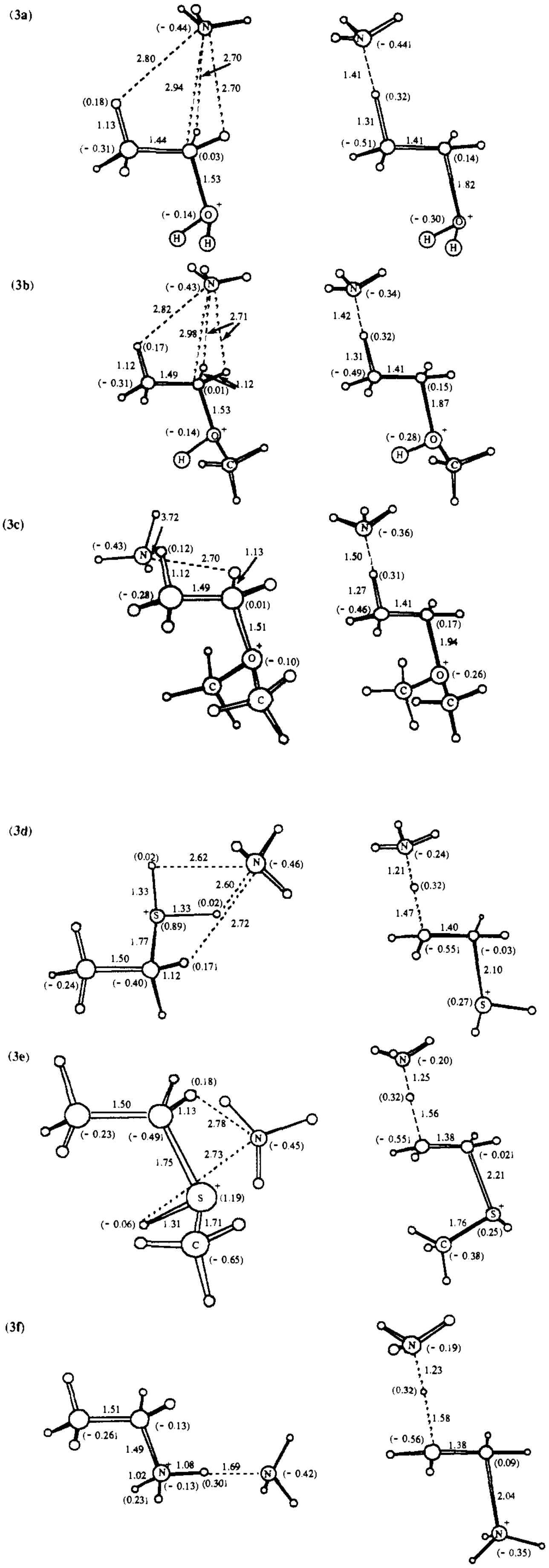

**Figure 7.** Bond lengths (Å) and atomic charges (e) in the initial CD complexes (STCD) and transition states (TS) for trans E2 elimination reactions of 'onium ions with ammonia.

**Table IV.** Bond Lengths and Formal Charges in the Transition States, and Activation Energies, for Anti Elimination (E2) Reactions of Ammonia with Ethyl 'Onium Ions ($CH_3CH_2X$)

| | bond length, Å | | | formal charge | | | | |
|---|---|---|---|---|---|---|---|---|
| X | $C_1$—H | $C_2$—X | C=C | on $C_1$ | on $C_2$ | on X | $\Delta H^*$, kcal/mol | mechanism |
| **3a** $OH_2^+$ | 1.82 | 1.31 | 1.41 | −0.51 | 0.14 | −0.30 | 8.7 | E2 |
| **3b** $OH(CH_3)^+$ | 1.87 | 1.31 | 1.41 | −0.49 | 0.15 | −0.28 | 10.5 | E2 |
| **3c** $O(CH_3)_2^+$ | 1.94 | 1.27 | 1.41 | −0.46 | 0.17 | −0.26 | 11.8 | E2 |
| **3d** $SH_2^+$ | 1.47 | 2.10 | 1.40 | −0.54 | −0.03 | 0.26 | 20.1 | E2/E1 |
| **3e** $SH(CH_3)^+$ | 1.56 | 2.22 | 1.38 | −0.55 | −0.02 | 0.26 | 24.6 | E2/E1 |
| **3f** $NH_3^+$ | 1.14 | 2.04 | 1.38 | −0.56 | 0.09 | −0.35 | 45.7 | E1 |

**Table V.** Bond Lengths and Formal Charges in the Transition State, and Activation Energy, for Syn Elimination (E2) Reaction of Ammonia with Ethyl 'Onium Ion ($CH_3CH_2O(CH_3)_2^+$)

| leaving group | heat of formation, kcal/mol | | | | | $\Delta H^*$, kcal/mol |
|---|---|---|---|---|---|---|
| | reactant | STCD | TS | PTCD | product | |
| $O(CH_3)_2^+$ | 121.9 | 114.0 | 127.6 | 88.1 | 113.9 | 13.6 |

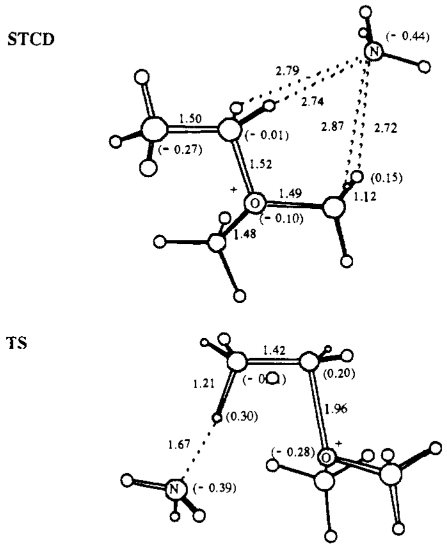

Figure 8. Bond lengths (Å) and charge distributions (e) calculated for the initial CD complexes (STCD) and transition states (TS) for cis E2 elimination reaction of 'onium ion with ammonia.

from an 'onium ion is usually thought to depend primarily on the ease of ionization of the $\beta$-hydrogen, which is increased by the field effect of the 'onium ion. Such a reaction would be of E2/E1 type. Conversely, eliminations from neutral substrates are thought to be not only more nearly synchronous but usually closer to the E2/E1cB extreme.

The differences can reasonably be attributed to solvent effects. Ionic dissociation of a neutral molecule is extremely endothermic in the gas phase but becomes much less so in solution, due to solvation of the resulting ions. Deprotonation of a neutral substrate by an anionic base is, on the other hand, relatively little affected by solvation because it involves no separation of charge. A polar solvent should therefore make an E2 reaction between an anionic base (e.g., $MeO^-$) and a neutral substrate tend toward the E1 extreme. Since reactions of this kind are predicted to be of E2/E1cB type in the gas phase, they should be more nearly synchronous in solution, as seems to be the case.

Conversely, in the case of an E2 reaction between a neutral base and an 'onium ion, solvation should have relatively little influence on ionization of the leaving group but should greatly accelerate deprotonation. Solvation should therefore make the mechanisms of reactions of this type tend toward the E1cB extreme. Thus, while reactions of this kind are predicted to be closer to the E1 extreme in the gas phase, it is not surprising that they are of E2/E1cB type in solution.

Solvent simulation studies of the kind recently reported by Jorgensen's group[35] would clearly be of much interest.

**Detailed Structures.** AMPAC archive files for all the species reported here and in the following paper are available from the author on a floppy disk (MS-DOS).

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**Registry No.** **1a**, 75-00-3; **1b**, 74-96-4; **1c**, 75-03-6; **1d**, 79-24-3; **1e**, 383-63-1; **3a**, 18639-79-7; **3b**, 17456-36-9; **3c**, 17009-83-5; **3d**, 18683-24-4; **3e**, 18683-25-5; **3f**, 16999-99-8; $MeO^-$, 3315-60-4; $NH_3$, 7664-41-7.