THE E2 REACTION

This section discusses base-promoted $\beta$-elimination, which is a second important reaction of alkyl halides. An example of such a reaction is the elimination of the elements of HBr from tert-butyl bromide:

$$\text{H}_3\text{C}\text{Br} + \text{Na}^+ \text{C}_2\text{H}_5\text{O}^- \rightarrow \text{H}_2\text{C}=\text{C}\text{Br} + \text{C}_2\text{H}_5\text{OH} + \text{Na}^+ \text{Br}^- \quad (9.32)$$

Recall from Sec. 9.1B that this type of elimination is a dominant reaction of tertiary alkyl halides in the presence of a strong base, and it competes with the $S_N2$ reaction in the case of secondary and primary alkyl halides.

A. Rate Law and Mechanism of the E2 Reaction

Base-promoted $\beta$-elimination reactions typically follow a rate law that is second order overall and first order in each reactant:

$$\text{rate} = k[(\text{CH}_3)_3\text{C}=\text{Br}][\text{C}_2\text{H}_5\text{O}^-] \quad (9.33)$$

A mechanism consistent with this rate law is the following:

This type of mechanism, involving concerted removal of a $\beta$-proton by a base and loss of a halide ion, is called an **E2 mechanism**. Reactions that occur by the E2 mechanism are called **E2 reactions**. The meaning of the “nickname” E2 is as follows:

Remember that **bimolecular** means that two molecules are involved in the rate-limiting step of the reaction. In this case, the two molecules are the base and the alkyl halide.

B. Why the E2 Reaction Is Concerted

The curved-arrow notation for the E2 mechanism in Eq. 9.34 is worth some attention. The simplest electron-pair displacement reactions we’ve encountered have involved the donation of an electron pair from a Lewis base (acting as either a Brønsted base or a nucleophile) to an electrophile and loss of a leaving group, and the process is fully described by two curved arrows. However, the E2 reaction involves three curved arrows. In the E2 reaction, the base acts as a Brønsted base to remove the $\beta$-proton, and the halide acts as a leaving group. How do we analyze the middle curved arrow? This arrow shows that the $\beta$-carbon acts *simultaneously* as a leaving group and a nucleophile that reacts at the $\alpha$-carbon. That is, the electron pair that departs from the $\beta$-hydrogen is donated to the $\alpha$-carbon to expel the bromide ion.
Let’s separate this concerted mechanism into two *fictional* but more conventional two-curved-arrow steps. This will help us to understand why the reaction is concerted. Suppose that in the first step of the elimination the base abstracts a proton to give a *carbon anion* as the product. In this step, the β-carbon acts as a leaving group. Then, in the second step, the electron pair of the carbon anion acts as a nucleophile by reacting at the α-carbon, displacing bromide ion:

We can calculate the approximate equilibrium constant for the first step (Eq. 9.36a) using the method of Sec. 3.4E. The $pK_a$ of the β-proton should be a little less than the $pK_a$ of an alkane—perhaps about 50. As we learned in Sec. 8.6A, the $pK_a$ of ethanol is 15.9. The equilibrium constant for the first step is then $10^{15.9 - 50}$ or about $10^{-34}$. The corresponding standard free-energy change is about 194 kJ mol$^{-1}$. This means that if the reaction were to occur by this stepwise mechanism, the standard free energy of activation for the first step of this reaction would be at least 194 kJ mol$^{-1}$, because this is the amount of energy required to form the carbon–anion intermediate. The rate of such a reaction is unimaginably small: the reaction would take approximately $10^{15}$ years at room temperature! In other words, the elimination would not occur. In fact, typical E2 reactions occur in minutes to a few hours and have standard free energies of activation typically in the 85–95 kJ mol$^{-1}$ range.

The concerted mechanism, then, avoids the formation of a very unstable, strongly basic, carbon–anion intermediate. The concerted mechanism brings about a net transfer of electrons from the oxygen of ethoxide to bromine to form the much weaker base bromide ion. And that is why the middle curved arrow doesn’t “pause” at carbon as an electron pair and “hang around” before it reacts at the α-carbon.

In later sections of this text, we’ll learn about β-eliminations that *do* involve carbon–anion intermediates. As we might expect, these reactions can take place only if the carbon anion is stabilized in some way. To say that the carbon anion is more stable is to say that the β-proton is much more acidic. Hence, the stepwise β-elimination mechanism will be observed only with compounds in which the β-proton is unusually acidic.
PROBLEMS

9.16 The following hydroxide-catalyzed β-elimination takes place by a carbon–anion stepwise mechanism. Show the carbon–anion intermediate and explain its stability. Think in terms of a polar effect (Sec. 3.6C). Recalling also that resonance structures imply heightened stability (Sec. 1.4), draw a resonance structure for his anion as well.

\[
\begin{align*}
\text{HO} & \xrightarrow{\text{H}_2\text{O}} \text{CH}_2-\text{CH}_2-C≡\text{CH}_3 + \text{HO}^- \\
\end{align*}
\]

9.17 We can conceive of a stepwise version of the S\textsubscript{N}2 reaction consisting of a Lewis acid–base dissociation followed by a Lewis acid–base association. (Nuc\textsuperscript{−} = a nucleophile.)

(a) Why should the stepwise process be slower than the concerted process?
(b) For what type of alkyl halide is the stepwise process likely to be observed?

C. Leaving-Group Effects on the E2 Reaction

In the mechanism of the E2 reaction, the role of the leaving halide is much the same as it is in the S\textsubscript{N}2 reaction: Its bond to carbon breaks and it takes on an additional electron pair to become a halide ion. Consequently, it should not be surprising to find that the rates of S\textsubscript{N}2 and E2 reactions are affected in similar ways by changing the halide leaving group:

Relative rates of E2 reactions:

\[
R\text{Cl} < R\text{Br} < R\text{I} \tag{9.37}
\]

As in the S\textsubscript{N}2 reaction, the reactivity difference between alkyl bromides and iodides is not great. Alkyl bromides are usually used in the laboratory for E2 reactions as the best compromise of reactivity and expense, and, when possible, the less expensive alkyl chlorides are used in large-scale reactions.

D. Deuterium Isotope Effects in the E2 Reaction

The mechanism in Eq. 9.34 implies that a proton is removed in the transition state of the E2 reaction. This aspect of the mechanism can be tested in an interesting way. When a hydrogen is transferred in the rate-limiting step of a reaction, a compound in which that hydrogen is replaced by its isotope deuterium will react more slowly in the same reaction. This effect of isotopic substitution on reaction rates is called a primary deuterium isotope effect. For example, suppose the rate constant for the following E2 reaction of 2-phenyl-1-bromoethane is \(k_\text{H}\), and the rate constant for the reaction of its β-deuterium analog is \(k_\text{D}\):

\[
\begin{align*}
\text{Ph} \xrightarrow{\text{C}_2\text{H}_3\text{OH}} \text{CH}_2-\text{CH}_2-\text{Br} + \text{C}_2\text{H}_5\text{O}^- & \quad \text{rate constant } k_\text{H} \\
\text{Ph} \xrightarrow{\text{C}_2\text{H}_3\text{OH}} \text{CD}_2-\text{CH}_2-\text{Br} + \text{C}_2\text{H}_5\text{O}^- & \quad \text{rate constant } k_\text{D}
\end{align*}
\]

The primary deuterium isotope effect is the ratio of the rates for the two reactions—that is, \(k_\text{H}/k_\text{D}\); typically such isotope effects are in the range 2.5–8. For example, \(k_\text{H}/k_\text{D}\) for the reactions in Eq. 9.38 is 7.1. The observation of a primary isotope effect of this magnitude shows that the bond to a β-hydrogen is broken in the rate-limiting step of this reaction.

The theoretical basis for the primary isotope effect lies in the comparative strengths of C—H and C—D bonds. In the starting material, the bond to the heavier isotope D is slightly
stronger (and thus requires more energy to break; Sec. 5.6E) than the bond to the lighter isotope H. However, in the transition states for both reactions, the bond from H or D to carbon is partly broken, and the bond from H or D to the attacking group is partly formed. To a crude approximation, the isotope undergoing transfer is not bonded to anything—it is “in flight.” Because there is no bond, there is no bond-energy difference between the two isotopes in the transition state. Therefore, the compound with the C—D bond starts out at a lower energy than the compound with the C—H bond and requires more energy to achieve the transition state (Fig. 9.8). In other words, the energy barrier, or free energy of activation, for the compound with the C—D bond is greater; as a result, its rate of reaction is smaller.

A primary deuterium isotope effect is observed only when the hydrogen that is transferred in the rate-determining step is substituted by deuterium. Substitution of other hydrogens with deuterium usually has little or no effect on the rate of the reaction.

**Figure 9.8** The source of the primary deuterium isotope effect is the stronger carbon-deuterium bond. (The difference between the bond energies of the C—H and C—D bonds is greatly exaggerated for purposes of illustration.)

**PROBLEMS**

9.18 In each of the following series, arrange the compounds in order of increasing reactivity in the E2 reaction with Na⁺ C₂H₅O⁻.

(a) CH₃ CH₃ 
H₃C—C—Br D₃C—C—Cl H₃C—C—Cl
CH₃ CD₃ CD₃ CH₃ 
A B C

(b) CH₃ CH₃ 
H₃C—C—F H₃C—C—I
CH₃ CH₃ 
A B
9.19 (a) The rate-limiting step in the hydration of styrene (Ph—CH=CH₂) is the initial transfer of the proton from H₂O⁺ to the alkene (Sec. 4.9B). How would you expect the rate of the reaction to change if the reaction were run in D₂O/D₃O⁺ instead of H₂O/H₃O⁺? Would the product be the same?
(b) How would the rate of styrene hydration in H₂O/H₃O⁺ differ from that of an isotopically substituted styrene Ph—CH=CD₂? Explain.

E. Stereochemistry of the E2 Reaction

When an E2 reaction occurs, the tetrahedral α- and β-carbons become trigonal when the β-proton is removed and the halide leaves. The R-groups on these two carbons move into a common plane that also contains the alkene carbons. This motion is shown in Fig. 9.9.

The stereochemistry of the E2 reaction uses this plane as a frame of reference. The E2 reaction can occur in two stereochemically distinct ways, illustrated as follows for the elimination of the elements of H⁻—X from a general alkyl halide:

\[
\text{syn: base: } \quad \text{anti: base: } \quad + \text{base—H + } X^- \quad + \text{base—H + } X^- \quad (9.39a)
\]

(The elimination shown in Fig. 9.9 is anti.) In a syn-elimination, the dihedral angle between the C—H and C—X bonds is 0°; that is, the H and X groups leave from the same side of the reference plane. In an anti-elimination, the dihedral angle between the C—H and C—X bonds is 180°; that is, the H and X groups leave from opposite sides of the reference plane. Only syn- and anti-eliminations are possible because only these geometries result in the planar alkene geometry that is required for π-orbital overlap. Recall from Sec. 7.9A that the terms syn and anti were used in discussing the stereochemistry of additions to double bonds. Notice that syn-elimination is conceptually the reverse of a syn-addition, and anti-elimination is conceptually the reverse of an anti-addition.

Investigation of the stereochemistry of an elimination reaction requires the α- and β-carbons to be stereocenters in both the starting alkyl halide and the product alkene. In such cases, it is found experimentally that most E2 reactions are stereoselective anti-eliminations, as in the following example.

\[
\text{C}_2\text{H}_5,\quad \text{C}_2\text{H}_5\quad + \quad \text{phenyls are cis}
\]

When the hydrogen and halogen are eliminated from a conformation in which they are anti, the phenyl groups (Ph) are on the same side of the molecule and therefore must end up in a cis relationship in the product alkene. A syn-elimination would give the other alkene stereoisomer:
Anti-elimination is preferred for three reasons. First, syn-elimination occurs through a transition state that has an eclipsed conformation, whereas anti-elimination occurs through a transition state that has a staggered conformation. Because eclipsed conformations are unstable, the transition state for syn-elimination is less stable than the transition state for anti-elimination. As a consequence, anti-elimination is faster. The second reason that anti-elimination is preferred is that the base and leaving group are on opposite sides of the molecule, out of each other’s way. In syn-elimination, they are on the same side of the molecule and can interfere sterically with each other. Finally, calculations of transition-state energies using molecular orbital theory show that anti-elimination is more favorable; the reasoning relates to the fact that an anti-elimination involves all-backside electron displacements, as in the $S_N2$ reaction.
9.20 Predict the products, including their stereochemistry, from the E2 reactions of the following diastereomers of stilbene dibromide with sodium ethoxide in ethanol. Assume that one equivalent of HBr is eliminated in each case.

(a) \((\pm)\text{-Ph} \text{--CH--CH--Ph}\)  
(b) meso-\(\text{Ph} \text{--CH--CH--Ph}\)

9.21 Draw the structure of the starting material that would undergo \(\text{anit}\)-elimination give the \(E\) isomer of the alkene product in the E2 reaction of Eq. 9.40.

F. Regioselectivity of the E2 Reaction

When an alkyl halide has more than one type of \(\beta\)-hydrogen, more than one alkene product can be formed (Sec. 9.1B).

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H} \\
\text{H} & \quad \beta\text{-hydrogens}
\end{align*}
\]

This section focuses on which of the possible products is preferred and why.

When simple alkoxide bases such as methoxide and ethoxide are used, the \textit{predominant product of an E2 reaction is usually the most stable alkene isomer}. Recall that the most stable alkene isomers are generally those with the most alkyl substituents at the carbons of the double bond (Sec. 4.5B). These isomers, then, are the ones formed in greatest amount.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C}((\text{CH}_3)_2\text{Br} & \quad \text{C}_2\text{H}_5\text{OH} \quad \text{C}_2\text{H}_5^+ \quad \text{k}^+ \\
& \quad \text{CH}_3\text{CH}==\text{C}((\text{CH}_3)_2 \quad \text{CH}_3\text{CH}==\text{C}((\text{CH}_3)_2 + \text{CH}_3\text{CH}==\text{CH}_2 \quad \text{(70\%)}
\end{align*}
\]

In this reaction, the alkene isomer formed in smaller amount would actually be favored on statistical grounds: six equivalent hydrogens can be lost from the alkyl halide to give this alkene, but only two can be lost to give the other alkene. In the absence of a structural effect on the product distribution, three times as much of the 1-alkene would have been formed. The fact that the other alkene is the major one shows that some other factor is operating.

The predominance of the more stable alkene isomer does \textit{not} result from equilibration of the alkenes themselves, because the alkene products are stable under the conditions of the reaction. Because the product mixture, once formed, does not change, the distribution of products must reflect the relative rates at which they are formed. Hence, we look for the explanation in transition-state theory.

The transition state for the E2 reaction can be visualized as a structure that lies somewhere between alkyl halide and alkene (plus the other species present). To the extent that the transition state resembles the alkene product, it is stabilized by the same factors that stabilize alkenes—and one such factor is alkyl substitution at the double bond. A reaction that can give two alkene products is really two reactions in competition, each with its own transition state. The reaction with the transition state of lower energy—the one with more alkyl substitution at the developing double bond—is the faster reaction. Hence, more product is formed through this transition state (Fig. 9.10)
When an alkyl halide has more than one type of \( \beta \)-hydrogen, a mixture of alkenes is generally formed in its E2 reaction, as Eq. 9.41 illustrates. The formation of a mixture means that the yield of the desired alkene isomer is reduced. Furthermore, because the alkenes in such mixtures are isomers of closely related structure, they generally have similar boiling points and are therefore difficult to separate. Consequently, the greatest use of the E2 elimination for the preparation of alkenes occurs when the alkyl halide has only one type of \( \beta \)-hydrogen, and only one alkene product is possible.

\[ \text{Zaitsev’s Rule} \]

An elimination reaction that forms predominantly the most stable alkene isomers is sometimes called a Zaitsev elimination, after Alexander M. Zaitsev (1841–1910), a Russian chemist who observed this phenomenon in 1875. Just as the Markovnikov rule describes the regioselectivity of hydrogen halide addition to alkenes, the Zaitsev rule describes the regioselectivity of elimination reactions. And, like the Markovnikov rule, the Zaitsev rule is purely descriptive; it does not attempt to explain the reasons behind the observations.

When an alkyl halide has more than one type of \( \beta \)-hydrogen, a mixture of alkenes is generally formed in its E2 reaction, as Eq. 9.41 illustrates. The formation of a mixture means that the yield of the desired alkene isomer is reduced. Furthermore, because the alkenes in such mixtures are isomers of closely related structure, they generally have similar boiling points and are therefore difficult to separate. Consequently, the greatest use of the E2 elimination for the preparation of alkenes occurs when the alkyl halide has only one type of \( \beta \)-hydrogen, and only one alkene product is possible.

\[ \text{G. Competition between the E2 and S}_2\text{N} \text{ Reactions: A Closer Look} \]

Nucleophilic substitution reactions and base-promoted elimination reactions are competing processes (Sec 9.1C). In other words, whenever an \( S_2N \) reaction is carried out, there is the possibility that an E2 reaction can also occur (if the alkyl halide has \( \beta \)-hydrogens), and vice versa.
This competition is a matter of relative rates: The reaction pathway that occurs more rapidly is the one that predominates.

Two variables determine which reaction—the S\textsubscript{N}2 reaction or the E2 reaction—will be the major process observed in a given case: (1) the structure of the alkyl halide; and (2) the structure of the base.

The feature of an alkyl halide’s structure that determines the amount of elimination versus substitution is the number of alkyl substituents at both the α- and β-carbons. For the S\textsubscript{N}2 reaction to occur on an alkyl halide with α- or β-substituents, the nucleophile must “fight through” a thicket of hydrogen atoms on the substituents that impede its access to the α-carbon. The resulting van der Waals repulsions create an energy barrier to the S\textsubscript{N}2 reaction that decreases its rate. On the other hand, when the Lewis base acts as a Brønsted base to initiate the E2 reaction, it reacts with a β-proton that lies near the periphery of the molecule. Reaction at the β-proton is much less affected by steric repulsions than reaction at the α-carbon atom.

Another reason that alkyl substitution promotes the E2 reaction is that the standard free energy of the E2 transition state, like that of an alkene, is lowered by alkyl substitution (Sec. 9.5F). Consequently, the rate of the E2 reaction is increased by alkyl substitution. Two effects of alkyl substitution, then, favor the E2 reaction: the rate of the S\textsubscript{N}2 reaction is decreased, and the rate of the E2 reaction is increased.

These same effects can be seen not only in tertiary alkyl halides, but also in secondary and even primary alkyl halides. Notice in the following examples that the alkyl halides with more β alkyl substituents show a greater proportion of elimination.

Secondary alkyl halides:

\[
\begin{align*}
\text{β-carbons} & \quad \text{CH}_3 \\
\text{H}_3\text{C}—\text{CH}—\text{Br} + \text{C}_2\text{H}_5\text{O}^- & \rightarrow \quad \text{H}_2\text{C}==\text{CH}—\text{CH}_3 + \text{H}_3\text{C}—\text{CH}—\text{OC}_2\text{H}_5 \\
(\text{about 55% elimination}) & \quad (\text{about 45% substitution}) \\
\text{one β-substituent} & \quad \text{H}_3\text{C}—\text{CH}_2—\text{CH}—\text{Br} + \text{C}_2\text{H}_5\text{O}^- & \rightarrow \\
& \quad \text{H}_3\text{C}—\text{CH}==\text{CH}—\text{CH}_3 + \text{CH}_3—\text{CH}_2—\text{CH}==\text{CH}_2 + \text{H}_3\text{C}—\text{CH}_2—\text{CH}—\text{OC}_2\text{H}_5 \\
(82\% \text{ elimination}) & \quad (18\% \text{ substitution})
\end{align*}
\]
The structure of the base is the second variable that determines whether the E2 reaction or the $S_{N}2$ reaction is faster in a given case. First of all, a highly branched base, such as tert-butoxide, increases the proportion of elimination relative to substitution.

When a highly branched base reacts at the $\alpha$-carbon to give a substitution product, the alkyl branches of the base suffer van der Waals repulsions with the surrounding hydrogens in the alkyl halide molecule; these repulsions raise the energy of the transition state for substitution. When such a base reacts at a $\beta$-proton to give the elimination product, the base is further removed from the offending hydrogens in the alkyl halide, and van der Waals repulsions are less severe, as shown in Eq. 9.44. Consequently, the $S_{N}2$ reaction is retarded more than the E2 reaction by branching in the base, and elimination becomes the predominant reaction. In summary, with a highly branched base, a steric effect selectively retards the $S_{N}2$ reaction.

A further effect of base structure on the E2–$S_{N}2$ competition has to do with its Brønsted basicity versus its nucleophilicity. Recall from Sec. 9.4E that the nucleophilicity of a Lewis base affects the rate of its $S_{N}2$ reactions, whereas its Brønsted basicity affects the rate of its E2 reactions (because the base is reacting with a proton). Recall also that species with nucleophilic atoms from higher periods of the periodic table, such as iodide ion, are excellent nucleophiles even though they are relatively weak Brønsted bases. A greater fraction of $S_{N}2$ reaction is observed in the reactions of such nucleophiles. For example, the reaction of potassium iodide with isobutyl bromide in acetone gives mostly substitution product and little elimination, because iodide is an excellent nucleophile and a weak base:

$$\ce{CH(CH_3)_3CHBr + K^+I^- -> CH(CH_3)_3CHI + K^+Br^-(acetone)}$$ (9.48)
Contrast this reaction with that in Eq. 9.46c, in which sodium ethoxide reacts with the same alkyl halide. Ethoxide, a strong Brønsted base, gives a significant percentage of alkene and a smaller percentage of substitution product.

Let’s summarize the effects that govern the competition between the \( S_N^2 \) and E2 reactions.

1. **Structure of the alkyl halide:**
   a. Alkyl halides with greater numbers of alkyl substituents at the \( \alpha \)-carbon give greater amounts of elimination. Consequently, tertiary alkyl halides give more elimination than secondary alkyl halides, which give more than primary alkyl halides.
   b. Alkyl halides with greater numbers of alkyl substituents at the \( \beta \)-carbon give greater amounts of elimination.
   c. Alkyl halides that have no \( \beta \)-hydrogens cannot undergo \( \beta \)-elimination.

2. **Structure of the base:**
   a. In a comparison of alkoxide bases with similar strengths, tertiary alkoxide bases such as tert-butoxide give a greater fraction of elimination than primary alkoxide bases.
   b. Weaker bases that are good nucleophiles give a greater fraction of substitution.

The application of these ideas is illustrated in Study Problem 9.1.

**Study Problem 9.1**

Which alkyl halide and what conditions should be used to prepare the following alkene in good yield by an E2 elimination?

![methylene cyclohexane](image)

**Solution** If this alkene is to be produced in an E2 reaction from an alkyl halide, the halide must be located at one of the two carbons that eventually become carbons of the double bond. This means that there are two choices for the starting alkyl halide:

A and B

The advantage of alkyl halide A is that, because it is tertiary, it poses no significant competition from the \( S_N^2 \) reaction. The disadvantage of this alkyl halide is that it contains more than one type of \( \beta \)-hydrogen, and, consequently, more than one alkene product could be formed:

\[
\begin{align*}
\text{A} & \quad \beta\text{-hydrogens (a)} \\
\text{B} & \quad \beta\text{-hydrogens (b)} \\
\text{A} & \quad \beta\text{-hydrogens (a)}
\end{align*}
\]

Product C is the more stable alkene because its double bond has three alkyl substituents; hence, if A is used as the starting material, a major amount of this undesired alkene will be formed. If alkyl...
halide $B$ is the starting material, then the desired product $D$ is the only possible product of \( \beta \)-elimination. Because this alkyl halide is primary, however, it is possible that some by-product derived from the \( S_n\)2 reaction will be formed. The way to minimize the \( S_n\)2 reaction is to use a tertiary alkoxide base such as tert-butoxide. In addition, the \( \beta \)-substitution in alkyl halide $B$ should also minimize the substitution reaction. Hence, a reasonable preparation of the desired alkene is the following:

\[
\begin{align*}
\text{CH}_3\text{Br} & \rightarrow K^+ (\text{CH}_3)_2\text{C}^--\text{O}^- \\
& \quad (\text{CH}_3)_3\text{C}^--\text{OH} \\
& \quad \text{CH}_2
\end{align*}
\]

(9.50)

---

**PROBLEMS**

9.22 What nucleophile or base and what type of solvent could be used for the conversion of isobutyl bromide into each of the following compounds?

(a) \((\text{CH}_3)_2\text{CHCH}_2\text{S}(\text{CH}_3)_2\)  
(b) \((\text{CH}_3)_2\text{CHCH}_2\text{SCH}_3\)  
(c) \((\text{CH}_3)_2\text{C}==\text{CH}_2\)

9.23 Arrange the following four alkyl halides in descending order with respect to the E2 elimination to \( S_n\)2 substitution product ratio expected in their reactions with sodium ethoxide in ethyl alcohol. Explain your answers.

\[
\begin{align*}
\text{CH}_3\text{I} & \quad (\text{CH}_3)_2\text{CHCH}_2==\text{Br} & (\text{CH}_3)_2\text{CH}_2\text{CH}_2==\text{Br} & (\text{CH}_3)_2\text{CHCHCH}==\text{Br} \\
A & \quad B & \quad C & \quad D \\
& \quad \text{CH}_3
\end{align*}
\]

9.24 Arrange the following three alkoxide bases in descending order with respect to the E2 elimination to \( S_n\)2 substitution product ratio expected when they react with isobutyl bromide. Explain your answers.

\[
\begin{align*}
(\text{CH}_3)_2\text{CH}==\text{O}^- & \quad \text{CH}_3\text{O}^- & \quad (\text{C}_2\text{H}_5)_3\text{C}==\text{O}^- \\
A & \quad B & \quad C
\end{align*}
\]

---

**H. Summary of the E2 Reaction**

The E2 reaction is a \( \beta \)-elimination reaction of alkyl halides that is promoted by strong bases. The following list summarizes the key points about this reaction:

1. The rates of E2 reactions are second order overall: first order in base and first order in the alkyl halide.
2. E2 reactions normally occur with anti stereochemistry.
3. The E2 reaction is faster with better leaving groups—that is, those that give the weakest bases as products.
4. The rates of E2 reactions show substantial primary deuterium isotope effects at the \( \beta \)-hydrogen atoms.
5. When an alkyl halide has more than one type of \( \beta \)-hydrogen, more than one alkene product can be formed; the most stable alkenes (the alkenes with the greatest numbers of alkyl substituents at their double bonds) are formed in greatest amount.
6. E2 reactions compete with \( S_n\)2 reactions. Elimination is favored by alkyl substitution in the alkyl halide at the \( \alpha \)- or \( \beta \)-carbon atoms, by alkyl substituents at the \( \alpha \)-carbon of the base, and by stronger bases.