**The E<sub>1</sub>cb Mechanism**

Elimination reactions we have discussed involve the loss of a proton and a leaving group from adjacent (vicinal) carbons. When the two groups depart simultaneously, we call the process $E_2$ – a bimolecular concerted elimination – and when the leaving group departs first to form a carbocation, followed by rapid loss of the proton, we call the process $E_1$ – unimolecular elimination.

However, it is also conceivable that an elimination reaction could proceed by first removing the proton to form a carbanion, followed by slow loss of the leaving group. This type of mechanism is called $E_{1cb}$ – unimolecular elimination via the conjugate base.

**Carbanions**

Carbanions are generally very reactive species because most of them are *very strong* Brønsted bases. Recall that to a first approximation we can use the pKa of a Brønsted acid as a guide to the stability of its conjugate base. The pKa of a simple aliphatic C-H bond is approximately 50. This high pKa value essentially means that C-H bonds of this kind are not acidic at all, in the usual sense.

Given the weak acidity of typical C-H bonds, it is clear that most organic compounds will not undergo elimination by an E1cb pathway. In fact, this is a key reason for the concerted nature of the $E_2$ reaction – removal of a proton from a typical sp<sup>3</sup> carbon is only energetically possible if it is linked to the simultaneous expulsion of a good leaving group.

The $E_{1cb}$ mechanism is only observed when there is at least one good electron-withdrawing group (EWG) adjacent to the C-H bond to be cleaved. The effect of an electron-withdrawing group is to increase the Brønsted acidity of adjacent C-H bonds, or in other words, to stabilize their conjugate bases. Some typical EWGs and the approximate pKa values for their adjacent protons are shown in the table. As you can see, the C-H bond next to a nitro group is quite acidic – more acidic than water at any rate. The other compounds are weaker acids but ketones and nitriles can be deprotonated using bases like sodium methoxide (CH<sub>3</sub>O<sup>-</sup>Na<sup>+</sup>).'
Sulfones require stronger bases like sodium hydride (NaH) used in aprotic solvents, but this is not difficult to achieve in the laboratory.

**A specific example of an E1cb reaction**

The clearest examples of E1cb reactions involve compounds containing very acidic C-H bonds and rather poor leaving groups. This makes the deprotonation as easy as possible, and also slows down the loss of the leaving group. One such reaction is shown below, in which a cyanide anion acts as the leaving group. The pKa of HCN (the conjugate acid of cyanide) is 9.2, which means that cyanide anion is a moderately weak leaving group. Notice how the two cyano groups stabilize the conjugate base although only one resonance structure is shown.

Another example of an E1cb elimination is:

In this process, methoxide is the leaving group. With a pKa for methanol of approximately 15.2 (roughly the same as that of water) the methoxide group is a poor leaving group in general, rather like the hydroxide ion. However, we can see in this case that if hydroxide deprotonates the ketone, the resulting anion (called an enolate) can expel methoxide and the similarity between the base and the leaving group means that there will not be a significant energetic difference due to the anions.

If you click on the link below you can see some 3-D structures and animations of an E1cb reaction very similar to the one shown above.