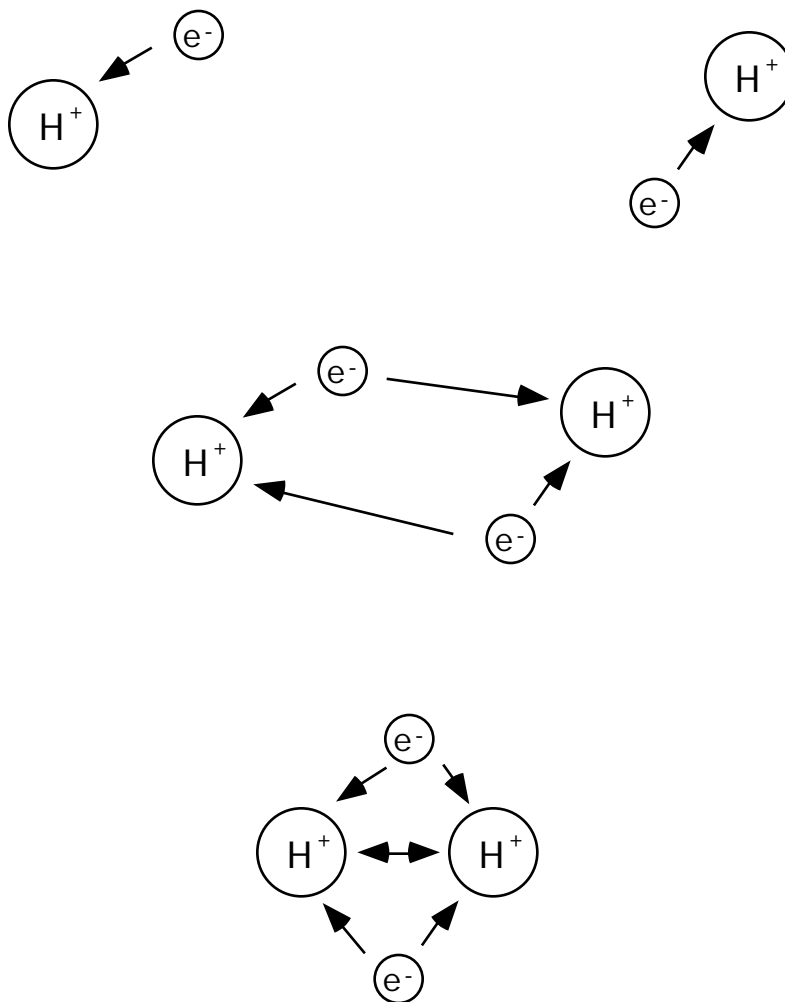


## Covalent bonds

Since electrons are negatively charged, they are attracted to the nucleus because it is positively charged. If two atoms get close enough together then the electrons of each atom will be attracted to



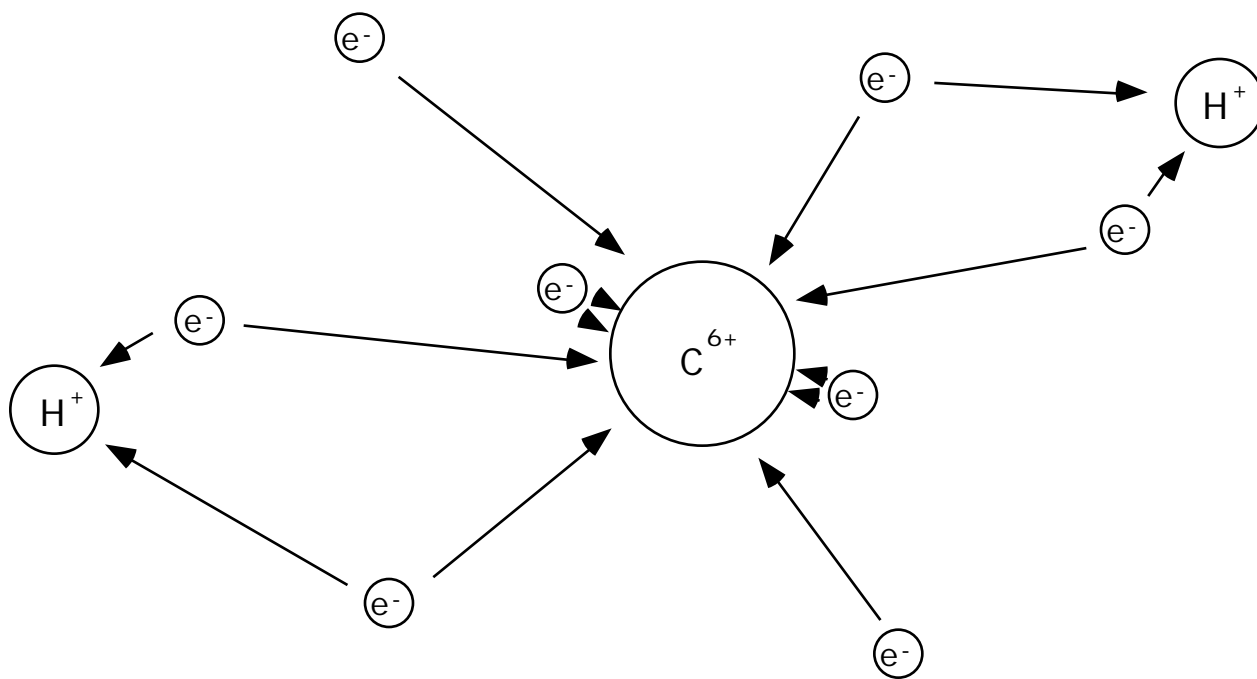
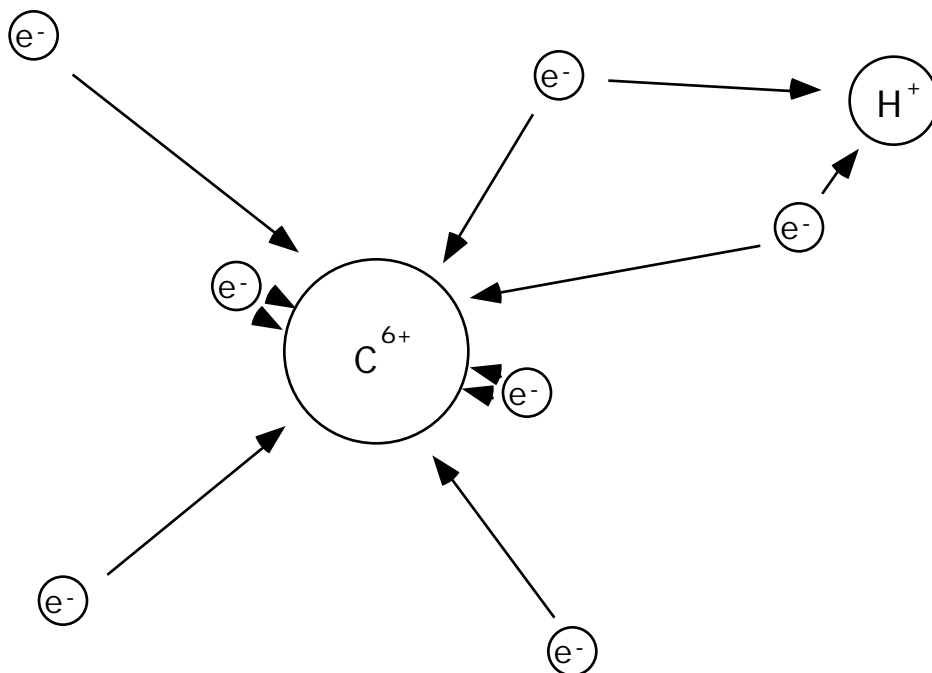
both nuclei.

single sided arrows represent attraction. Double sided arrows represent repulsion.

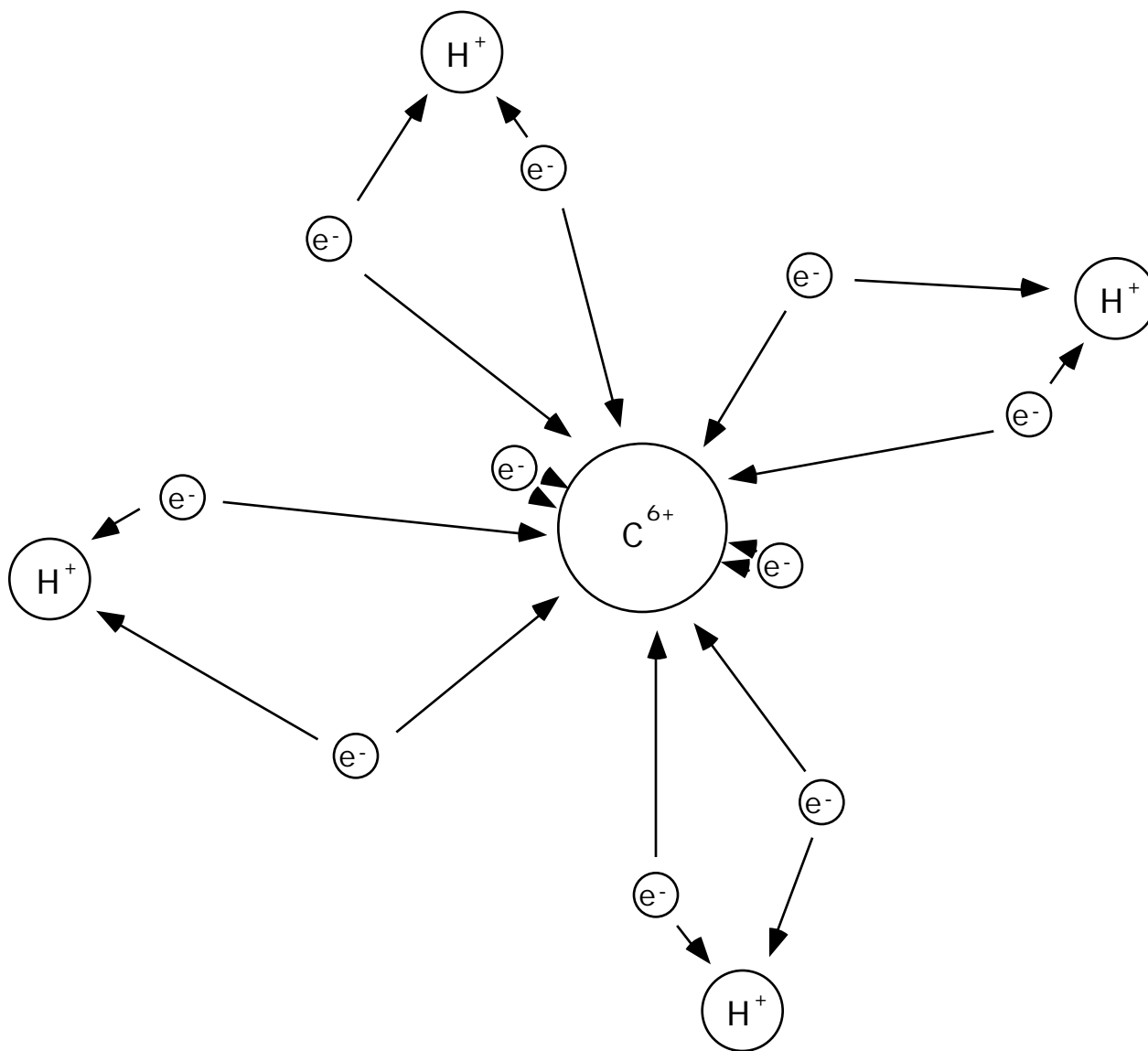
If the atoms get too close then the nuclei will repel each other.

Because the electrons are attracted to both nuclei pulling the two atoms apart would require energy. So, the energy of two hydrogen atoms is lower when the two atoms are together than when the two atoms are apart; that is why they stay together.

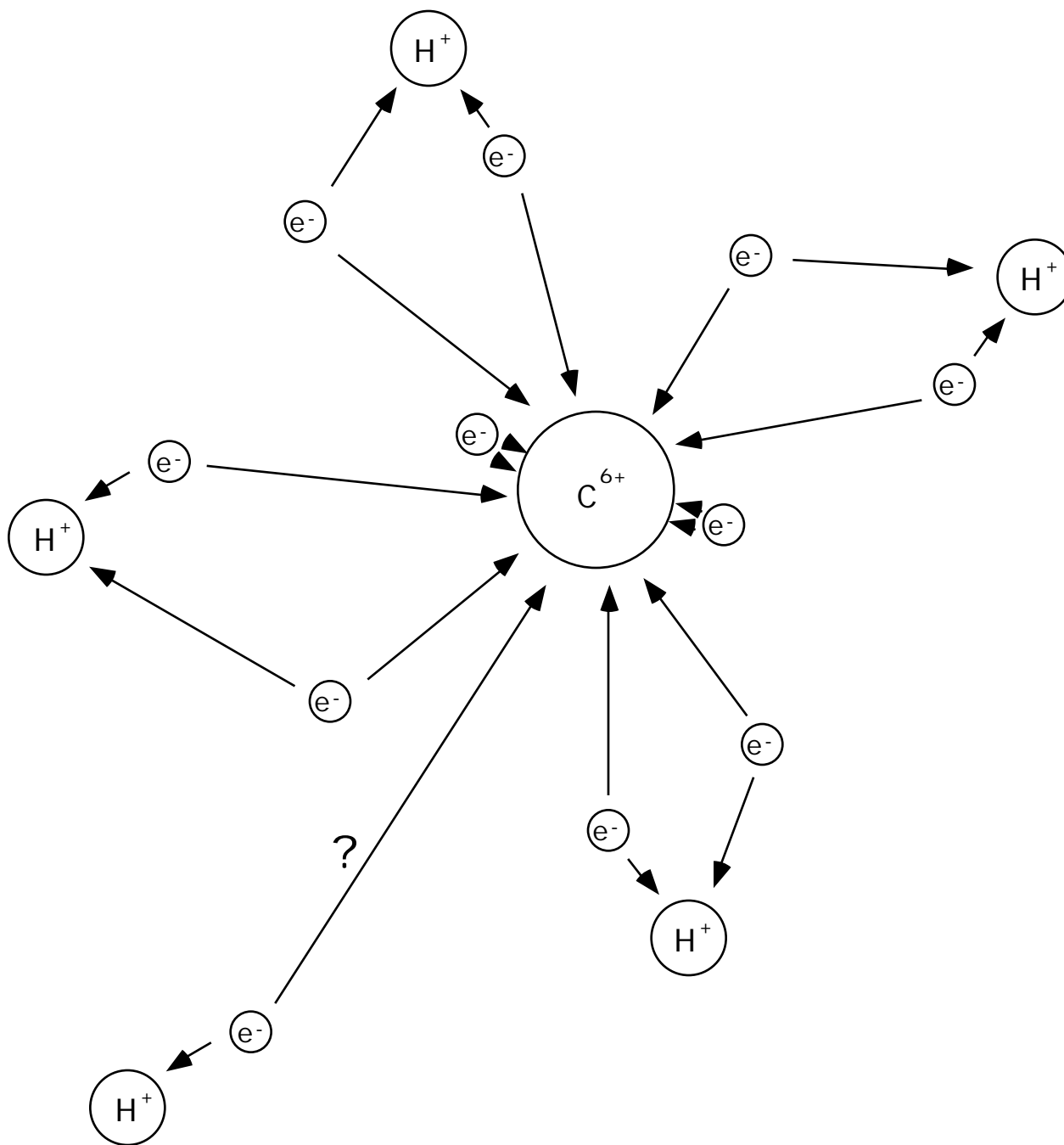
The same thing can be said for methane,  $\text{CH}_4$ . That is, if a carbon atom gets close to a hydrogen atom then the nuclei of each atom will attract the other atoms electrons.



**C** will continue to attract electrons until four H's have taken position around the C atom.



If a fifth H atom comes by its electrons will not experience an attraction to the C nuclei. Why not?



Lets stop and count electrons around the carbon and think about where they are. With four H's present there are ten electrons around the C atom. Where are these ten electrons going to go?

First two fit into the *1s orbital*. The next two fit into the *2s orbital*. The last six can fit into the *2p orbitals*. (The electrons do not actually

go into the atomic orbitals, but this will demonstrate the point we want to make. In chapter 9 we will talk about where the electrons actually go.)

A fifth H comes along. Adding the fifth H to the molecule would increase the count of electrons around the C atom to eleven. Where would the eleventh electron go?  $3s$ , the eleventh electron would have to go into the next principal quantum level. The C nucleus simply does not have enough positive charge to effectively attract that eleventh electron, because (1) the electron is farther away, and (2) there are ten electrons shielding the eleventh electron; that is, the eleventh electron is not attracted because the cloud of negative charge between it and the positively charged nucleus. (This is the basis for the octet rule. A rule which is violated very often by the way.)

So, molecules are collections of atoms which are held together by the attraction of one nucleus to the electrons of another atom. This is not a convenient way to think of molecules.

We invented the **Bond**.

Four H atoms and one C atom are attracted to each others electrons. When all the atoms come together and form a mole  $\text{CH}_4$  1652 kJ is released. What holds the H atoms in place, the attraction of the C electrons to H, and the H's electrons to C; we say that there is a *bond* holding the C and the H atoms together. Since there are four bonds each bond contributes a certain amount of stability.

$$\frac{1652 \text{ kJ}}{4 \text{ bonds}} = 413 \text{ kJ per C-H bond}$$

In this manner we can estimate the bond energy for all sorts of different compounds.

A mole of gaseous  $\text{CH}_3\text{Cl}$  is 1578 kJ more stable than a mole of gaseous C, three moles of gaseous H's and one mole of gaseous Cl. Estimate the bond energy for  $\text{CH}_3\text{Cl}$ .

In  $\text{CH}_3\text{Cl}$  there are three C-H bonds, and one C-Cl bond.

$$1 \text{ C-Cl} + 3 \text{ C-H} = 1578 \text{ kJ}$$

$$1 \text{ C-Cl} + 3 (413 \text{ kJ}) = 1578 \text{ kJ}$$

$$1 \text{ C-Cl} + 1239 \text{ kJ} = 1578 \text{ kJ}$$

$$1 \text{ C-Cl} = 339 \text{ kJ}$$

We can estimate the energy of the C-Cl bond by assuming that all the C-H bonds of  $\text{CH}_3\text{Cl}$  are worth the same amount of energy. Does this mean that all C-H bonds are "worth" 413 kJ of energy?

No, looking at a few simple molecules will show that this is not true.

$\text{H}_3\text{C-H}$	435	$\text{H}_3\text{C-CH}_3$	368	$\text{H}_3\text{C-F}$	452
$\text{CH}_3\text{CH}_2\text{-H}$	410	$\text{H}_5\text{C}_2\text{-CH}_3$	356	$\text{H}_3\text{C-Cl}$	351
$\text{H}_2\text{C=CH-H}$	435	$(\text{CH}_3)_2\text{CH-CH}_3$	347	$\text{H}_3\text{C-Br}$	293
$\text{H}_2\text{C=CHCH}_2\text{-H}$	356	$\text{PjCH}_2\text{-CH}_3$	292	$\text{H}_3\text{C-I}$	234
$\text{PhCH}_2\text{-H}$	356	$\text{H}_5\text{C}_2\text{-C}_2\text{H}_5$	343	$\text{H}_3\text{C-OH}$	381
$\text{H}_2\text{N-H}$	431	$(\text{CH}_3)_2\text{CH-CH}(\text{CH}_3)_2$	326		
$\text{CH}_3\text{NH-H}$	385				
$\text{CH}_3\text{O-H}$	427	$\text{H}_2\text{C=CH}_2$	682		
		$\text{HC CH}$	962		

When discussing bond strength we usually refer to *bond dissociation energies*. The book uses the letter *D* for bond dissociation energies; I typically use all three letters *BDE* (other books also use BDE which is what I am used to. Some book use *BD*).

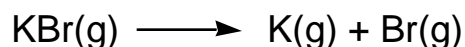
The BDE,  $H_D$ ,  $H_{BD}$ , or  $H_{BDE}$  is the amount of energy required to separate the two atoms involved in a bond.

Does the following reaction describe a BDE reaction; that is, is the BDE for KBr 20 kJ/mol?



**NO!** Putting KBr in water does not separate the two *atoms*; it separates the two *ions*.

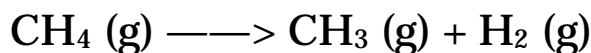
The reaction which describes the BDE for KBr is



So, the reaction which describes the BDE for  $\text{CH}_4$  is



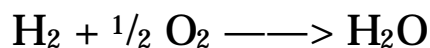
not



not



Now that we know what bond energies are, we can use them to calculate the  $H$ 's for reactions. Bond Energies can be used to estimate the amount of energy released or absorbed in a reaction.



1 mole of  $\text{H}_2$  bonds are broken which requires 432 kJ,  $\frac{1}{2}$  mol  $\text{O}_2$  bonds are broken 495, and 2 mol OH bonds are formed  $2 \times 467$ .

So,  $H = -2 \times 467 + 432 + \frac{1}{2}(495) = -255 \text{ kJ/mol}$

Back to CH bond energy. It is different in different compounds.

molecule	BDE C-H kJ/mole
CHBr <sub>3</sub>	380
CHCl <sub>3</sub>	380
CHF <sub>3</sub>	430
CH <sub>4</sub>	435

Why are the bond energies different for the same bond? Because they are not the same bond.

By putting an F on the C we change the C.

By putting an H on the C we change the C.

H and F are very different.



First ionization energies are different.

Nuclear charge is different.

Electron affinities are different

$H = -72 \text{ kJ/mol}$      $F = -322 \text{ kJ/mol}$ .

So, the C is different in each case.

So it would seem reasonable to say that an H would bond differently to a C that has an H on it as compared to a C that has an F on it.

So, it is not as simple as a bond is a bond. Bonds are effected by atoms that are not directly participating in the bond under discussion.



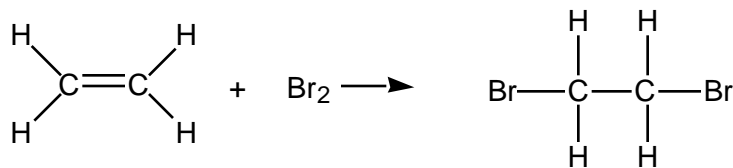
Which means that the model of an isolated bond between two atoms really is not the whole story; nonetheless, the bond is a very useful model.

Put in, add, energy to break react bonds and release energy, subtract, as product bonds form.



break 4 C–H bonds	4 x 413
break 2 O=O bonds	2 x 495
make 2 C=O bonds	-2 x 799
make 4 O–H bonds	<u>-4 x 467</u>
	<b>-824 kJ</b>

You do not have to make and break all the bonds, just the ones involved in the reaction.



break 1 C=C bond	614
break 1 Br–Br bond	193
make 1 C–C bond	-347
make 2 C–Br bonds	<u>-2 x 276</u>
	<b>-92 kJ</b>