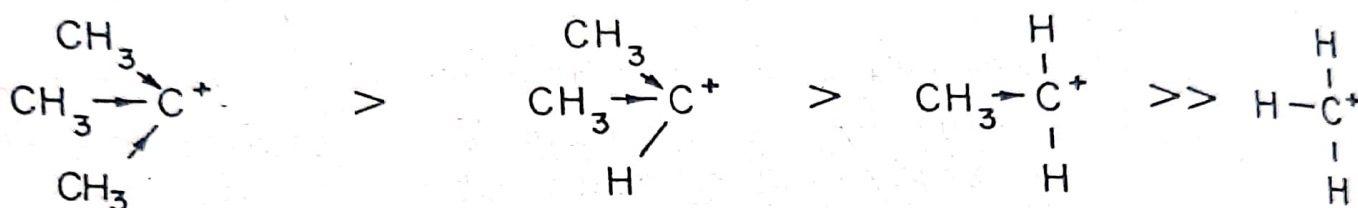


This explains the well-known order of stability of carbocations (C^+ species) which is:



The arrows on the bonds show the direction of the I effect. Clearly the carbocation which has three +I, CH_3 groups attached to it will be much more stable than CH_3^+ which has none. The ions

m/z 57 ($(\text{CH}_3)_3\text{C}^+$) and 43 ($(\text{CH}_3)_2\text{CH}^+$) are usually intense in the spectra of compounds containing these end-groups, while m/z 29 (CH_3CH_2^+) and 15 (CH_3^+) are weak.

There are two useful rules to remember about I effects. Firstly, atoms which lie to the left of carbon in the Periodic Table (or groups consisting largely of such atoms) are $+I$; those which lie to the right of carbon (or groups consisting largely of such atoms) are $-I$. The $-I$ groups *destabilise* positive ions. The second is that $\pm I$ effects only operate *at the most* over two bonds, the effect falls off rapidly with distance down a carbon chain.

The second way a neighbouring group can help to stabilise a positive centre is by conjugation with it through multiple bonds. Where conjugation (alternate single and double or triple bonds) exists, this is a powerful effect and far outweighs the inductive effect. It is called the *mesomeric* (M) effect. You may have met it before under the name resonance. Resonance *is* involved in explaining how the $\pm M$ effect works but the $\pm M$ effect itself defines how a group will behave when attached to a conjugated system. *If the system is positively charged, a $+M$ group will stabilise it by helping to spread (delocalise) that charge.*

Fig. 8.2a presents a range of organic groups classified according to their I and M effects. There is no need to try to memorise all these, they are for reference when needed. You will see how they work in the examples which follow. Before you look at these, there is one point of difficulty which should be clear from Fig. 8.2a(ii).

(i) Inductive Effects of Groups ($\pm I$)

-I Groups			+I Groups
-NO ₂	-CHO	-RC=CR ₂	-CH ₃
-C≡N	-COR	-C≡CH	-CH ₂ R
-COOH	-F	-C≡CR	-CHR ₂
-COOR	-Cl	-SO ₂ OH	-CR ₃
-OH	-Br	-SH	
-OR	-I	-SR	
C ₆ H ₅	-CH=CH ₂	-NH ₂	

-I groups are better electron attractors than H-

+I groups are poorer electrons attractors than H-

(ii) Mesomeric Effects of Groups ($\pm M$)

+M, -I Groups		-M, -I Groups		+M, +I Groups
-F	-SH	-NO ₂	-CONH ₂	-CH ₃
-Cl	-SR	-C≡N	-SO ₂ R	-CH ₂ R
-Br	-NH ₂	-CHO	-CF ₃	-CHR ₂
-I	-NHR	-COR	-CCl ₃	-CR ₃
-OH	-NR ₂	-COOH		
-OR	-NHCOR	-COOR		
-OCOR	-C ₆ H ₅			
-CH=CH ₂	-CH=CR ₂			

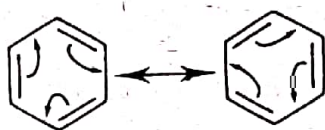
+M and +I groups supply electron density to conjugated systems

-I and -M groups withdraw electron density from conjugated systems

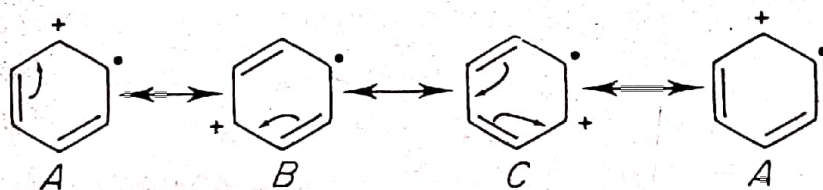
+M, -I groups usually work to *stabilise* a positive ion. The reason is that the +M effect operates through the more weakly held π electrons in the double bonds of the ion. These are more readily distorted and the effect is transmitted over any number of conjugated bonds, unlike the I effect which is short range. Now for some examples.

8.2.1. Benzene and its Molecular Ion

Benzene has two Kekule resonance forms:

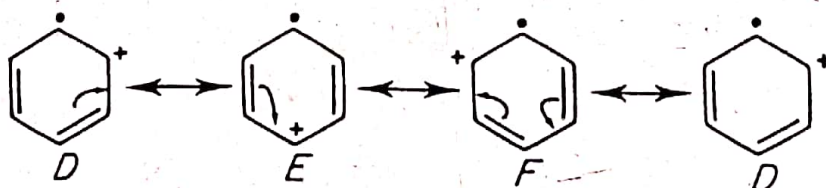


Notice how they are converted by movements of two π electrons as shown by the 'curly' arrows. The benzene molecular ion is formed by loss of a π electron, giving A:



Having reached ion C by resonance *via* B we can only return to A, as shown. Thus there appear to be three resonance forms of the benzene M^+ ion.

However, we could just as easily have formed A by placing the positive charge on the other carbon atom of the ionised double bond eg



so every possible resonance form of the benzene molecular ion can be derived from A and D. We can now see why the molecular ions of

Open Learning

aromatic hydrocarbons are so very intense and also why they tend to fragment, when they do, by loss of $\text{HC}\equiv\text{CH}$ units (Fig. 8.2b). They have a large number of resonance forms and contain

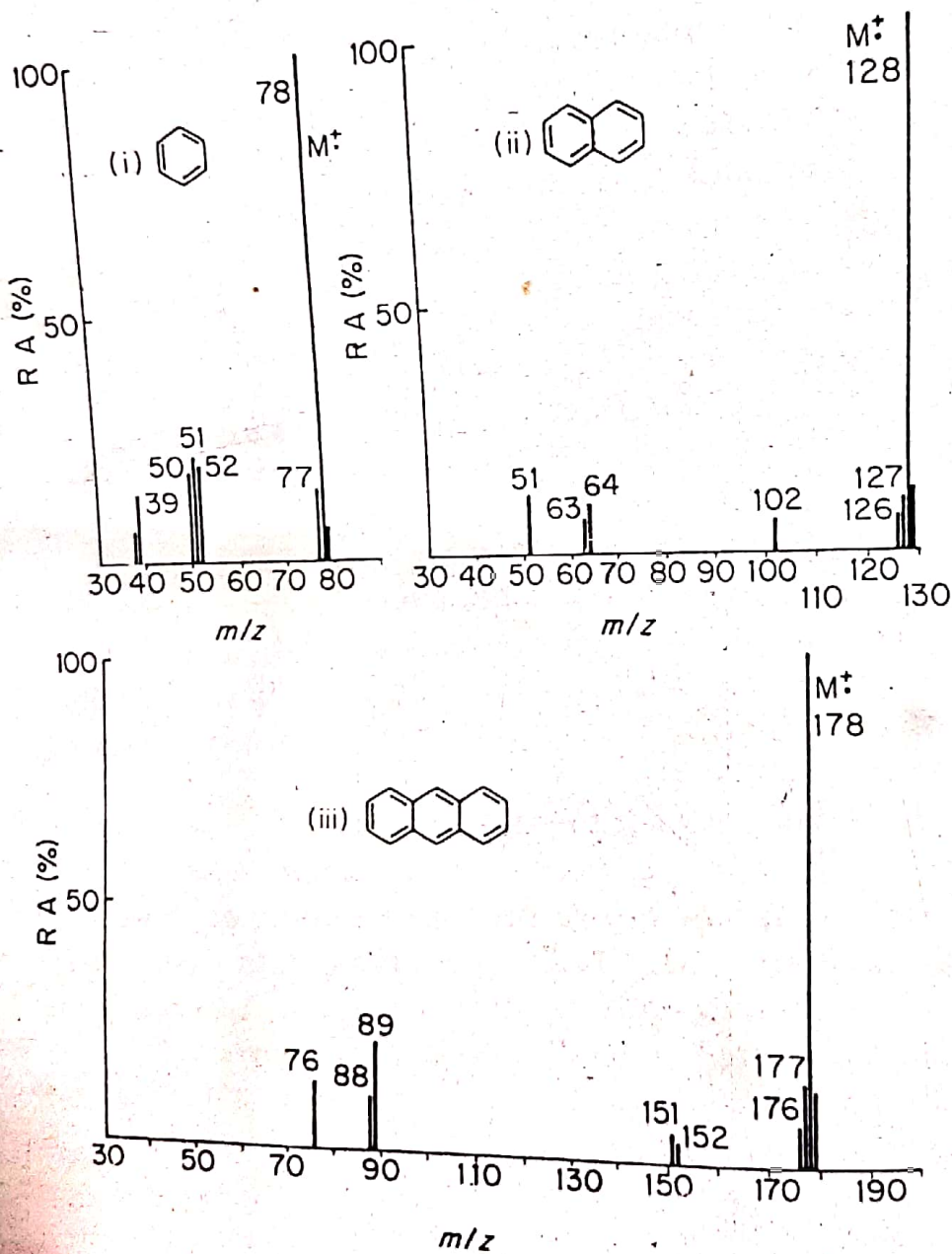
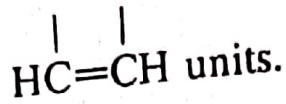
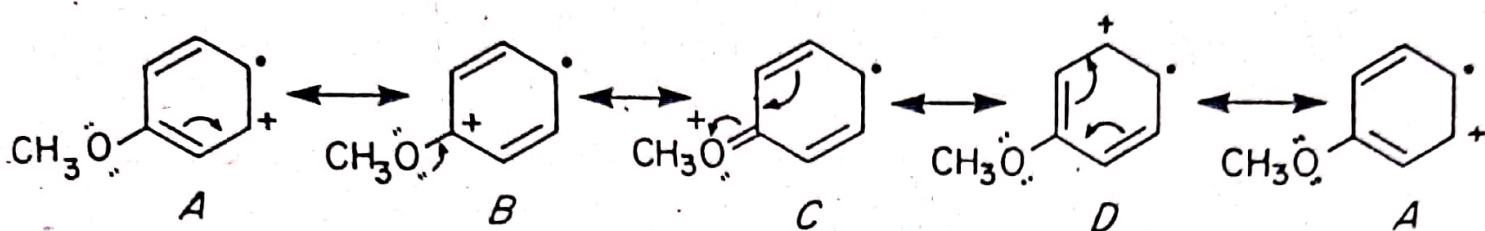


Fig. 8.2b. Mass spectra of benzene (i), naphthalene (ii) and anthracene (iii)

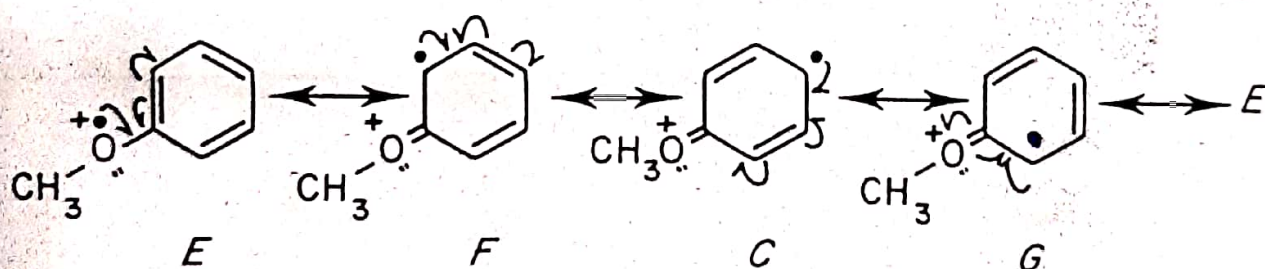
8.2.2. Methoxybenzene (Anisole)

This could be ionised on the benzene ring, or on the oxygen, but as we shall see, this is not important. We start with the electron lost from the π system, giving:



Ions A and B are similar to those formed from benzene in Section 8.2.1 but C is a key ion. It is formed by the use of one of the two lone pairs of p-electrons on the oxygen atom. This is how the oxygen atom exerts its +M effect to help stabilise the methoxybenzene molecular ion.

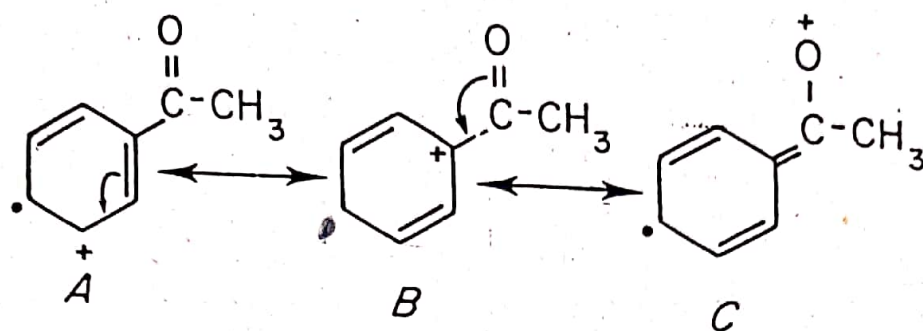
It is also possible that the molecular ion is formed by loss of one of these relatively easily ionised oxygen p-electrons, giving:



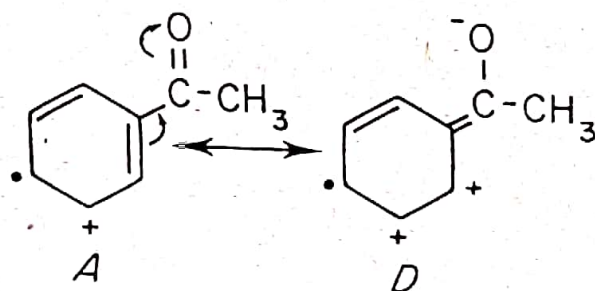
Ion C is formed in this sequence too! This shows that it does not matter where the initial loss of the electron occurs. All the possible forms of M^+ are interconverted by resonance. This result is quite general for the +M groups in Fig. 8.2a (ii).

8.2.3. 1-Phenylethanone (Acetophenone) $C_6H_5COCH_3$

1-Phenylethanone could be ionised on the benzene ring, or the carbonyl group. Let's start with the benzene ring:

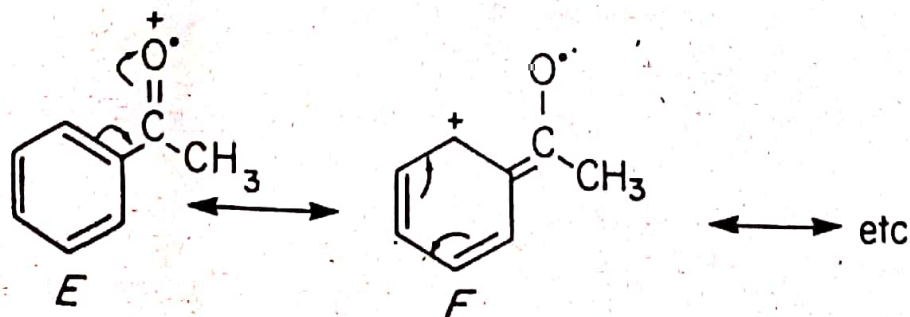


It would appear we can form C by using the π -electrons of the carbonyl group, which are conjugated with the benzene ring. Thus A would be more stabilised. But wait a minute. Isn't oxygen more electron attracting than carbon? It would be more likely to attract the electrons of the benzene ring itself, like this:



In D, you can see that two positive charges form on adjacent carbon atoms, a highly unstable arrangement. We can conclude that $-M$ groups, such as those in Fig. 8.2a (ii) will destabilise molecular ions like A.

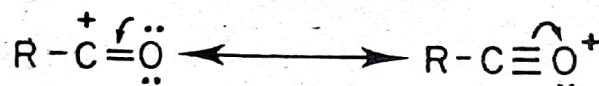
Ionisation in 1-phenylethanone could also take place on the carbonyl oxygen atoms to give E:



E can be stabilised by the $+M$ effect of the phenyl group as shown, so it is far more likely the M^+ of this type of compound will exist as E-type ions with the positive charge occurring on the $-M$ group.

8.2.4. The Acyl Ion $R-\overset{+}{C}=O$

The acyl ion itself is $CH_3\overset{+}{C}=O$, m/z 43. Such ions are frequently found as intense fragments in the mass spectra of such compounds as aldehydes, ketones and esters. This must be due to some innate stability they have. In order to explain this we need to remember that oxygen has lone-pair electrons which can be used:



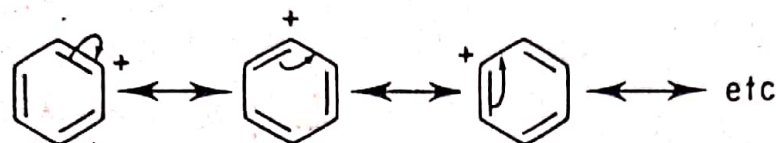
If R is a +I group, this will also help to stabilise the acyl ion.

8.2.5. The Phenyl Ion, $C_6H_5^+$, (m/z 77)

The phenyl ion is frequently found in the spectra of phenyl compounds and is usefully diagnostic, since few other compounds produce ions of m/z 77.

II Try writing resonance structures for the $C_6H_5^+$ ion.

You probably wrote:



or some such, showing that the positive charge is delocalised round the ring. Nine out of ten students would too! Unfortunately, it's wrong – you cannot delocalise the positive charge in $C_6H_5^+$ because the charge is *in the plane of the ring*. Fig. 8.2c attempts to show this, using phenylethanone as the source of the $C_6H_5^+$ ion.

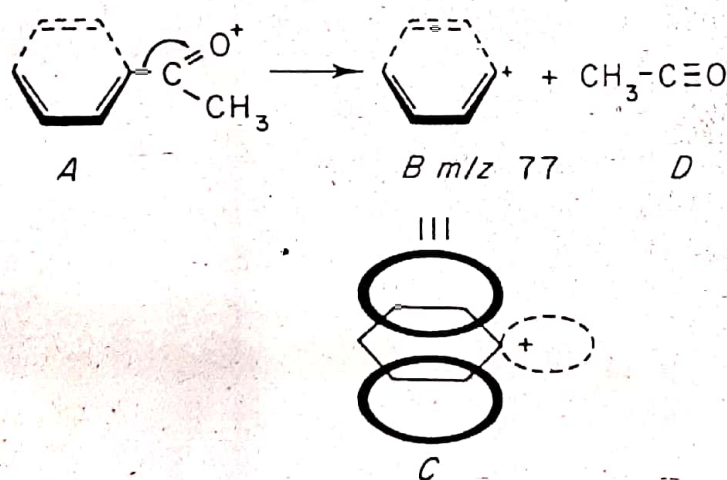


Fig. 8.2c. Formation and structure of $C_6H_5^+$

When the bond between the benzene ring and the acyl group breaks, the positive charge occupies the position left by the departing group, as shown in *B*, Fig. 8.2c. This is an empty sp^2 orbital, shown by dashed line in *C*, Fig. 8.2c. Electrons in the π orbitals of the benzene ring shown by the shaded regions cannot interact with this orbital, so the positive ion is *not* especially stabilised. Phenyl cations are still aromatic however, so are reasonably stable compared to alternative, non-aromatic ions which might be formed in the fragmentation of the M^+ ion.

Π Which do you think would be the most intense fragment ion line in the spectrum of phenylethanone, $C_6H_5^+$ or CH_3CO^+ ?

The spectrum of phenylethanone is shown in Fig. 8.2d. It clearly shows that $C_6H_5^+$ is more stable than CH_3CO^+ because the RA's are in the ratio 70 : 30 approximately. If you chose CH_3CO^+ because it has two resonance forms to help stabilise it (Section 8.2.4) and $C_6H_5^+$ has no resonance forms which delocalise the positive charge, you have to bear in mind that the benzene ring itself is highly stabilised. But you were thinking along the right lines to add up the number of resonance forms available to the ion – the more there are, the more stable it tends to be.

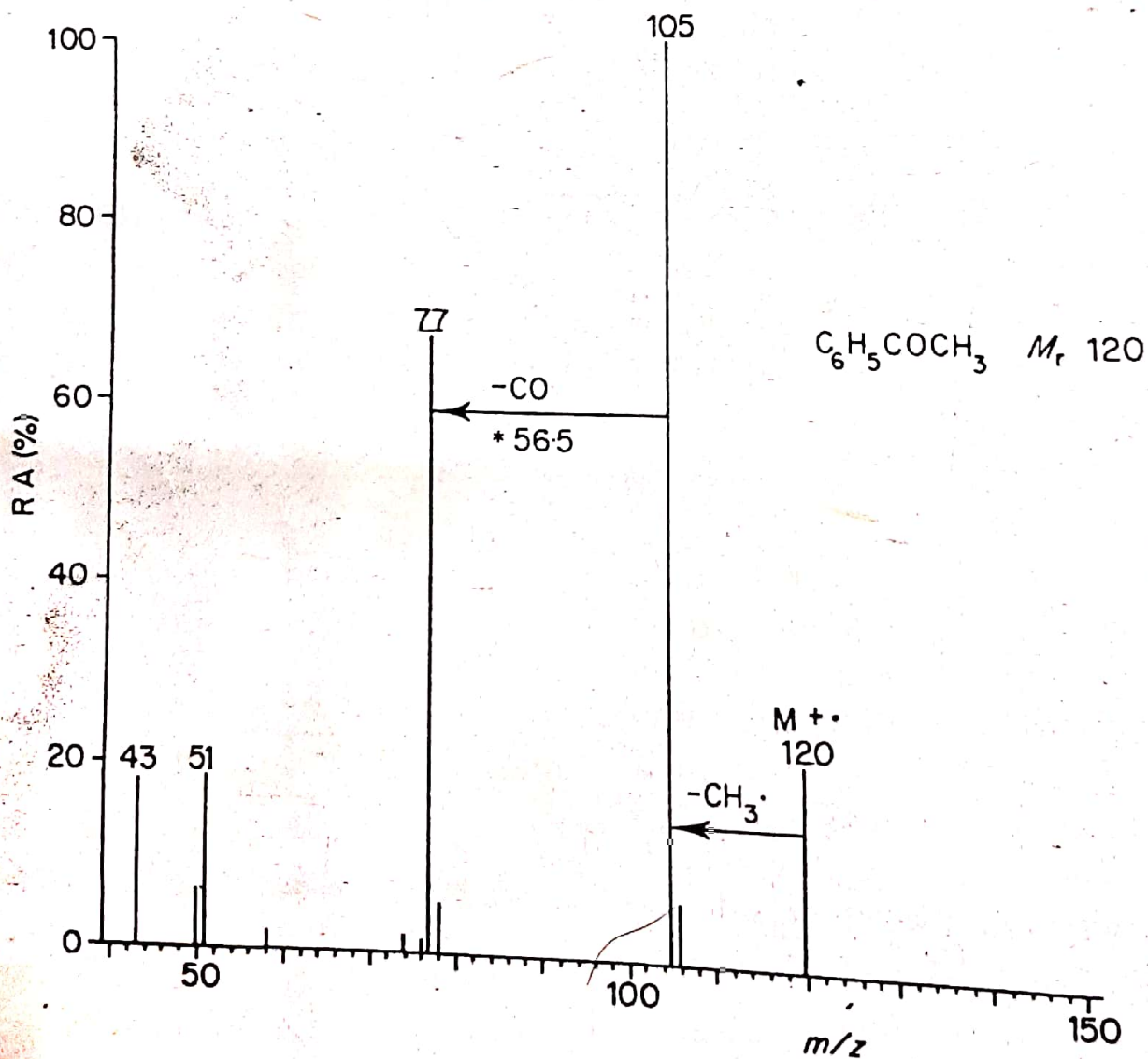
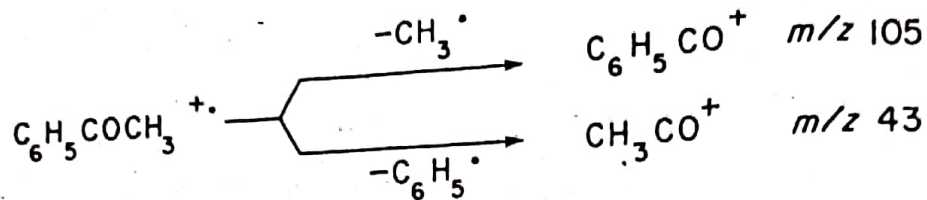


Fig. 8.2d. Mass spectrum of phenylethanone (acetophenone)

Fig. 8.2d shows the base peak at m/z 105. Clearly this is due to loss of a CH_3 group (15 amu.). There must be something specially stable about this ion for it to be so intense relative to the alternative CH_3CO^+ ion formed by loss of C_6H_5 .



In the next example we will consider why $\text{C}_6\text{H}_5\text{CO}^+$ is so preferred in the fragmentation of phenylethanone.

8.2.6. The Benzoyl Ion, $\text{C}_6\text{H}_5\text{CO}^+$, m/z 105

This ion, like any carbonyl ion, could have two structures A and A' in Fig. 8.2e, which are then delocalised using the π electrons of the benzene ring to give B , C , D and E .

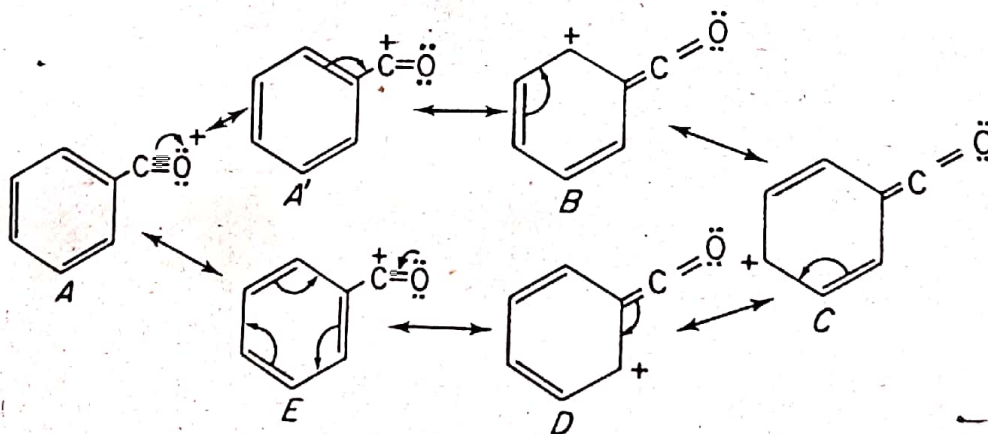
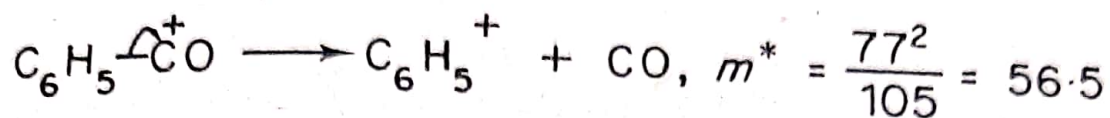


Fig. 8.2e. Resonance structures of the $\text{C}_6\text{H}_5\text{CO}^+$ ion

Thus $\text{C}_6\text{H}_5\text{CO}^+$ has six resonance forms to stabilise it. Here the phenyl group is acting as a +M group to stabilise the benzoyl ion and this explains why it is the base peak in the $\text{C}_6\text{H}_5\text{COCH}_3$ spectrum. An interesting feature of the spectrum is a metastable (m^*) ion at m/z 56.5 (not shown on Fig. 8.2d as it is too small) which shows that the benzoyl ion decomposes by loss of CO to give C_6H_5^+



This route to m/z 77 is not perhaps what you would have expected from Fig. 8.2c which implies direct cleavage of M^+ to give C_6H_5^+ and CH_3CO^+ . Remember though from Part 5 that we do not necessarily observe a m^* for *every* fragmentation process. Some m/z 77 could have formed directly from M^+ – there is no evidence that they did not!

This is a good example of how the existence of a stabilised ion influences the fragmentation pathways of a molecular ion. Most of the positive ion current is carried by the two stabilised ions, m/z 105 and 77 in the spectrum of phenylethanone.

8.2.7. Some Basic Rules about Resonance Structures

Now that you have seen some examples of mesomeric effects in action you might find it useful if we summarise the basic rules for writing down the resonance structures and qualitatively assessing their relative importance.

1. Resonance structures are interconvertible by one or a series of short electron shifts: electrons do not *jump* across space.
 2. Resonating structures must have the same number of electrons:
Thou shalt neither create nor destroy electrons!
 3. Resonance structures involving even numbers of electrons are more stable than those involving odd numbers of electrons.
 4. The more bonds that are involved in the resonance, the greater is the stability of the resulting structure eg benzene, resonance energy 144 kJ mol^{-1} , naphthalene 244 kJ mol^{-1} .
 5. The closer the stabilities of resonance structures, the greater is the degree of resonance and the lower the energy of the system eg the Kekulé forms of benzene which are equivalent.
 6. Resonance can only occur between structures that correspond to very nearly the same relative positions of *all* the atoms involved. Bond distances and angles should remain the same and be compatible with the overlap of the orbitals being used eg resonance cannot occur between *isomers* of structures.
-