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An Approach to the Interpretation of the Mass Spectra of Aliphatic Acids

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Synopsis. A method of comparing the sum of the total energies of fragment molecules has been applied to the interpretation of simple cleavage and rearrangement reactions in electron-impact mass spectrometry for the straight chain aliphatic acids.

The quasi-equilibrium theory has been successful in explaining the mass spectra of saturated hydrocarbons.[1] This theory is based on the hypothesis that the active molecular ion is first formed and the energy is distributed throughout the ion. The molecular ion subsequently decomposes when the ion is in the proper configuration and possesses a sufficient amount of vibrational energy. As long as the quasi-equilibrium theory holds in mass spectra, a comparison of the sum of the total energies of the fragments will be able to predict fragmentation. Ichikawa and Ogata used the method to predict the most probable course of bond-scission by comparing the sum of the total energies of the fragments thus produced.[2]

In this paper, the method has been applied to formic, acetic, propionic, and butyric acids. Mass spectrometric studies of those carboxylic acids have been conducted by several investigators, and the fragment ions studied using isotopic labelled compounds and the detection of metastable ion peaks.[3] The total energies of the fragment molecules have been calculated by the CNDO/2 method, the parameters of which were the same as in the paper of Pople and Segal.[4] The total energy may vary with the structure but it is difficult to know the structure of the radical and ionic species. The possible configurational changes were considered to take place to those appropriate forms (*e.g.*, $sp^3 \rightarrow sp^2$), in the cationic and radical molecules and the most stable energy adopted after calculation of the probable configurations. In the present calculation, the following bond lengths (Å) have been assumed: $C(sp^3)–C(sp^3)$, 1.54; $C(sp^3)–C(sp,sp^2)$, 1.50; $C(sp^2)–C(sp)$, 1.45; C=C, 1.35; C–O, 1.32; C=O, 1.25; C≡O, 1.15; C–H, 1.09; O–H, 0.96. Bond angles have been taken to be 109°28′(sp^3); 120°(sp^2); 110°(<COH).

Results and Discussion

The total energies of the molecules, cations and radicals (eV) obtained by the CNDO/2 method are listed in Table 1. Combinations of the fragments listed in Table 1 would give a variety of fragmentation processes. From the point of view of energy comparison, the decomposition reactions appeared to occur more in the production of two fragments than in three fragments. Therefore, only the processes producing two fragments have been discussed here. The difference in energy between molecules and cations indicate the ionization potentials (IP). The IP values obtained were a little greater than that reported in the literature. The CNDO/2 method is not well suited for the estimation of the total energy, but this method proved sufficiently useful for the elucidation of mass spectra. A comparison of the sum of the total energies of the fragments produced and the relative intensities of the peaks are shown in Table 2 where the peak height of the most abundant species has been set at 100. The breakdown patterns of the mass spectra have been classified into simple

TABLE 1. TOTAL ENERGIES OF MOLECULES AND FRAGMENTS (eV)

Compound	Molecule	Ion	Fragment	Radical	Ion
HCOOH	−1232.9	−1220.8	CH_3	−248.1	−235.9
CH_3COOH	−1473.0	−1462.1	C_2H_5	−490.2	−480.7
C_2H_5COOH	−1712.3	−1701.1	C_3H_7	−729.4	−720.7
C_3H_7COOH	−1951.6	−1941.2	HCO	−704.3	−694.1
CO	−681.7	−664.4	CH_3CO	−944.7	−936.6
CO_2	−1187.5	−1173.1	C_2H_5CO	−1185.0	−1176.2
H_2O	−540.5	−525.2	C_3H_7CO	a)	−1415.6
CH_4	−275.2	−256.2	OH	−516.5	−498.9
C_2H_6	−514.5	−498.6	COOH	−1207.3	−1197.8
C_3H_8	−753.7	−738.8	HCOO	−1209.1	−1192.2
CH_3OH	−776.9	−763.8	CH_2COOH	−1449.3	−1436.7
C_2H_5OH	−1016.1	−1003.3	CH_2CH_2COOH	−1687.6	−1679.1
C_3H_7OH	−1255.3	a)	$CH_2=COH$	−944.6	−934.1
$CH_2=CH_2$	−469.1	−454.5			
$CH_3CH=CH_2$	−709.1	−696.0			
$CH_2C=(OH)_2$	−1473.4	−1461.8			
CH_2CO	−922.6	−911.4			
CH_2CH_2CO	−1157.1	−1150.3			

a) The calculation does not show convergence by the SCF method.

Table 2. The sum of the total energies of the produced fragments (eV)

		Fragmentation	
HCOOH		$HCO^{+}+OH\cdot=-1210.6$	vs
		$HCO\cdot+OH^{+}=-1203.2$	
	R	$H_2O^{\dagger}+CO=-1206.9$	w
	R	$H_2O+CO^{\dagger}=-1204.9$	
CH_3COOH		$CH_3CO^{+}+OH\cdot=-1453.1$	vs
		$CH_3\cdot+COOH^{+}=-1445.9$	vs
		$CH_3CO\cdot+OH^{+}=-1443.6$	
		$CH_3^{+}+COOH\cdot=-1443.2$	m
	R	$CH_2CO^{\dagger}+H_2O=-1451.9$	w
	R	$CH_4+CO_2^{\dagger}=-1448.3$	
	R	$CH_2CO+H_2O^{\dagger}=-1447.8$	
	R	$CH_3OH^{\dagger}+CO=-1445.5$	
	R	$CH_4^{\dagger}+CO_2=-1443.7$	
C_2H_5COOH		$CH_3CH_2CO^{+}+OH\cdot=-1692.7$	w
		$CH_3CH_2^{+}+COOH\cdot=-1688.0$	s
		$CH_3CH_2\cdot+COOH^{+}=-1688.0$	m
		$CH_3^{+}+CH_2COOH\cdot=-1685.2$	
		$CH_3\cdot+CH_2COOH^{+}=-1684.8$	
		$CH_3CH_2CO\cdot+OH^{+}=-1683.9$	
	R	$CH_2{=}CH_2+HCOOH^{\dagger}=-1689.9$	
	R	$CH_3CH_2+CO_2^{\dagger}=-1687.6$	
	R	$CH_2{=}CH_2^{\dagger}+HCOOH=-1687.4$	vs
	R	$CH_3CH_3^{\dagger}+CO_2=-1686.1$	
C_3H_7COOH		$CH_3CH_2CH_2CO^{+}+OH\cdot=-1932.1$	
		$CH_3CH_2^{+}+CH_2COOH\cdot=-1930.0$	w
		$CH_3CH_2CH_2^{+}+COOH\cdot=-1928.0$	w
		$CH_3CH_2CH_2\cdot+COOH^{+}=-1927.2$	w
		$CH_3\cdot+CH_2CH_2COOH^{+}=-1927.2$	m
		$CH_3CH_2\cdot+CH_2COOH^{+}=-1926.9$	
	R	$CH_3COOH^{\dagger}+CH_2{=}CH_2=-1931.2$	
	R	$CH_2{=}C(OH)_2^{\dagger}+C_2H_4=-1930.9$	vs
	R	$CH_3CH{=}CH_2+HCOOH^{\dagger}=-1929.9$	
	R	$CH_3CH{=}CH_2^{\dagger}+HCOOH=-1928.9$	m
	R	$CH_2{=}C(OH)_2+C_2H_4^{\dagger}=-1927.9$	
$C_2H_5CO^{+}$		$CH_3CH_2^{+}+CO=-1162.4$	s
		$CH_3\cdot+CH_2CO^{\dagger}=-1159.5$	
		$CH_3^{+}+CH_2CO=-1158.5$	
	R	$CH_2{=}CH_2+HCO^{+}=-1163.2$	s
	R	$CH_2{=}CH_2^{\dagger}+HCO\cdot=-1158.8$	vs
$C_3H_7CO^{+}$		$CH_3CH_2^{+}+CH_2CO=-1403.3$	w
		$CH_3CH_2CH_2^{+}+CO=-1402.4$	w
		$CH_3CH_2\cdot+CH_2CO^{\dagger}=-1401.6$	
		$CH_3\cdot+\cdot CH_2CH_2CO^{+}=-1398.4$	
	R	$CH_2{=}CH_2+CH_2{=}COH^{+}=-1403.2$	w
	R	$CH_3CH{=}CH_2+HCO^{+}=-1403.2$	w
	R	$CH_3CH{=}CH_2^{\dagger}+HCO\cdot=-1400.3$	m
	R	$CH_2{=}CH_2^{\dagger}+CH_2{=}COH\cdot=-1399.1$	m

R indicates rearrangement breakdown. vs, s, m, and w indicate relative intensities as follows: vs; 100—76, s; 75—51, m; 50—26, w; 25—10.

cleavage and rearrangement reactions, the rearrangement processes being denoted by the letter R.

In the mass spectrum of HCOOH, the peak at *m/e* 29 (HCO^{+}) was predicted as a simple fragment ion. The ion *m/e*=45, as shown in Table 1, $COOH^{+}$ was calculated to be more stable than $HCOO^{+}$. Ono *et al.*, however, reported that $HCOO^{+}$ and $COOH^{+}$ occurred in equal abundance in the spectrum of HCOOH.3)

In the mass spectrum of CH_3COOH, the ions CH_3CO^{+} (*m/e*=43) and $COOH^{+}$ (*m/e*=45) were predicted to appear abundantly from simple cleavage, and $CH_2CO^{\dagger}$ (*m/e*=42) from rearrangement.

In the mass spectrum of C_2H_5COOH, the ions $C_2H_5CO^{+}$ (*m/e*=57), $C_2H_5^{+}$ (*m/e*=29), $COOH^{+}$ (*m/e*=45) were predicted to appear abundantly as simple fragment ions.

In the mass spectrum of C_3H_7COOH, the following ion peaks were considered as simple fragment ions: $C_3H_7CO^{+}$ (*m/e*=81), $C_2H_5^{+}$ (*m/e*=29), $C_3H_7^{+}$ (*m/e*=43), $COOH^{+}$ (*m/e*=45), $CH_2CH_2COOH^{+}$ (*m/e*=73). The ions $CH_3COOH^{\dagger}$ (*m/e*=60), $CH_2{=}C(OH)_2^{\dagger}$ (*m/e*=60) were considered as rearrangement ions. The peak at *m/e* 60 is known as the McLafferty rearrangement ion $CH_2{=}C(OH)_2^{\dagger}$. Levsen and Schwarz reported that there is no isomerization, or only minor isomerization of $CH_2{=}C(OH)_2^{\dagger}$ to $CH_3COOH^{\dagger}$.5)

The first process which straight chain aliphatic acids undergo upon electron-impact is the removal of one of the lone pair electron on the oxygen atom. The active molecular ions vibrate and bond-scission occurs statistically in terms of energy. In the mass spectra of the carboxylic acids, $R{-}C{\equiv}O^{+}$, is predicted to appear in appreciable amounts from simple cleavage. The peak heights of $C_2H_5CO^{+}$ from C_2H_5COOH and $C_3H_7CO^{+}$ from C_3H_7COOH were, however, not as high as expected. Concerning the $C_2H_5CO^{+}$ and $C_3H_7CO^{+}$ ions, the secondary decomposition processes were examined by comparing the sum of the total energies of the fragment molecules, the results of which are shown in Table 2. The probable fragment ions $C_2H_5^{+}$, HCO^{+} (*m/e*=29) from $C_2H_5CO^{+}$ and $C_2H_5^{+}$ (*m/e*=29), $CH_2{=}COH^{+}$ (*m/e*=43) from $C_3H_7CO^{+}$ were found respectively in the mass spectrum. It is suggested that the $C_2H_5CO^{+}$, $C_3H_7CO^{+}$ ions may be unstable, decomposing immediately.

The main peaks in the electron-impact mass spectra are concordant with the results for simple cleavage, but not so good for the rearrangement reactions. The configurational structure may play an important role in the occurrence of rearrangement ions.

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