The Relative Rates of Fragmentation of Benzoyl Ions generated upon Electron Impact from Different Precursors

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WE have recently generated ions X^+, both by direct ionisation of X, and also *via* the sequence $M^+ \rightarrow X^+ + N$ (where N is a stable neutral particle, CO or CO_2, possessing only 1 or 4 degrees of internal freedom).[1] In all cases, X^+ was produced with excess energy (usually 1—2·5 ev) at the threshold when generated by the fragmentation route (relative to the direct ionisation step $X \rightarrow X^+$). This excess energy caused a faster rate of a subsequent reaction $X^+ \xrightarrow{m^*} A^+$, relative to the rate observed for the same reaction when X^+ was produced by direct ionisation of X.[1] The faster rate of decomposition in the presence of threshold excess energy was measured in terms of decreased $[X^+]/[A^+]$, $[X^+]/[m^*]$, and/or $[m^*]/[A^+]$ ratios. Since the threshold excess energy manifests itself as a higher apparent heat of formation for X^+ formed by the fragment route, this work establishes a correlation between apparent heat of formation of X^+ and its further rate of fragmentation.[2]

However, McLafferty and Pike[3] have already shown for a reaction sequence $M^+ \rightarrow X^+(+N) \xrightarrow{m^*} A^+$, that $[X^+]/[m^*]$ increases regularly with increasing degrees of vibrational freedom in M^+ (as the size of M^+ is increased by increments of $-CH_2-$ in a homologous series, while X^+ is maintained as a common ion). Here is shown the importance of this "degrees of freedom effect" relative to threshold excess energy (E_t) in determining the rate of the $X^+ \xrightarrow{m^*} A^+$ reaction.

The relative importance of the "degrees-of-freedom effect" and E_t can be examined in specific instances by the generation of X^+ with different apparent heats of formation from M^+ ions containing varying numbers of vibrational degrees of freedom. This has been done for benzoyl ions ($PhC \equiv O^+$, *m/e* 105), which are generated from compounds (I)—(V) and then undergo the reaction $PhCO^+ \xrightarrow{m^*} C_6H_5^+$ (*m/e* 77); the data are summarised in Table 1.

At 70ev, the $[m/e\ 105]/[m^*]$ ratio increases with increasing size of the neutral particle in the $M^+ \rightarrow PhCO^+ + N$ reaction. As M^+ ions with sufficient energy to undergo the further $PhCO^+ \rightarrow C_6H_5^+$ reaction pass over the transition state for the $M^+ \rightarrow PhCO^+ + N$ step, they must possess internal energy E_v considerably in excess of that required to reach the transition state in question, because the appearance potential of

TABLE 1[a]

Compound	ΔH_f[b] PhCO+	Degrees of freedom (%) in N[c]	70 ev[d]		17 ev	
			$\frac{[m/e\ 105]}{[m^*]}$	$\frac{[m/e\ 105]}{[m/e\ 77]}$	$\frac{[m/e\ 105]}{[m/e\ 77]}$	$\frac{[m/e\ 105]}{[m/e\ 77]}$
PhCHO (I)	200	0	574	1·15	15·5	11·9
PhCOMe (II)	186	15	658	1·54	22·0	18·5
PhCOPh (III)	220	45	901	2·26	171	147
$PhCO_2Ph$ (IV)	201	48	1000	3·25	143	135
PhCO·COPh (V)	197	50	1136	3·08	104	111

[a] Focussing controls, beam energy, and source temperature were held constant for a given set of ion abundance data for (I)—(V). The ratios have no absolute physical significance, but the internal consistency is reproducible; this reproducibility is exemplified by the two sets of 17 ev data obtained on different days. [b] In kcal./mole, taken from ref. 5; some values are adjusted in view of more recent thermochemical data. [c] (D.F. in N)/(D.F. in N + D.F. in $PhCO^+$); D.F. = vibrational degrees of freedom. [d] Although the [m/e 105][m/e 77] ratios are given for 70 ev spectra, they need not be kinetically reliable, since, for example, $PhCOPh^{+\cdot} \rightarrow C_6H_5^{+\cdot}$ occurs in one step at 70 ev, but not at 17 ev;[4] [m/e 105/][m^*] is the most reliable parameter at 70 ev.

$C_6H_5^+$ is 3·2—5·4 ev greater than that of $PhCO^+$ in the compounds (I)—(V).[5] There is considerable evidence[5,6] that benzoyl ions are produced in their ground state upon electron impact and therefore it is reasonable to suppose that the total excess energy $E_t + E_v$ (for a given internal energy sufficient to produce $C_6H_5^+$ ions), is largely available for partition between $PhCO^+$ and N as vibrational energy. On the assumption that this partition is in proportion to their relative numbers of vibrational degrees of freedom (this assumption ignores fluctuation effects[7]), then a greater fraction of $E_t + E_v$ will be carried off with increasing size of N. Therefore, for example, the mean rate of decomposition of benzoyl ions generated from acetophenone (II) is greater than that of benzoyl ions produced from phenyl benzoate (IV) despite the fact that $PhCO^+$ ions from the latter compound possess roughly 15 kcal. more internal energy at the threshold. Phenyl benzoate molecular ions which are going to decompose to $C_6H_5^+$ must possess (as a minimum) 5·4 ev [5] of excess energy in the transition state for the $PhCO_2Ph^{+\cdot} \rightarrow PhCO^+ + \cdot OPh$ reaction. Fluctuation effects[7] permit in principle the possibility that none of this excess energy be imparted to the phenoxy-radical, but on average the phenoxy-radical can carry off 48% of the total excess energy (including E_t). This energy loss to the phenoxy-radical more than offsets the threshold excess energy of $PhCO^+$ from phenyl benzoate (IV). In 17 ev spectra, the mean value of E_v will be less, but E_t is of course unchanged. However, it is evident (Table 1), that the mean rate of decomposition of benzoyl ions is still much faster when their generation involves the elimination of small neutral particles (H· and Me·) as opposed to larger species from (III)—(V).† If the methods of initial preparation of X^+ are those summarised by equations (1) and (2), then a correlation between apparent heat of formation of X^+ and its further rate of decomposition will usually require the elimination of a very small neutral particle (*e.g.* CO) in the generation of the common ions. If the methods of initial preparation of X^+ are those summarised by equations (3) and (4), then a correlation between apparent heat of formation of X^+ and its further rate of decomposition will demand the elimination of neutral particles (N_1 and N_2) of similar size. Both ΔH_f and degrees of freedom effects may be invoked to rationalise the results of Jennings and Futrell.[2]

$$M^+ \rightarrow X^+ + N \xrightarrow{m^*} A^+ \tag{1}$$

$$X \rightarrow X^+ \xrightarrow{m^*} A^+ \tag{2}$$

$$M_1^{+\cdot} \rightarrow X^+ + N^1 \xrightarrow{m^*} A^+ \tag{3}$$

$$M_2^{+\cdot} \rightarrow X^+ + N^2 \xrightarrow{m^*} A^+ \tag{4}$$

Parameters representing the rates of fragmentation of benzoyl ions found from some alkyl phenyl ketones [PhCOR, (VI)—(XI)] are given in Table 2. In these cases, the heats of formation of the benzoyl ions are not known but it is improbable that there are any marked variations. As expected, there is a correlation between further rate of fragmentation of the benzoyl ion and the

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† The lack of a precise correlation between [m/e 105]/[m/e 77] and a combination of ΔH_f and degrees of freedom effects for (I)—(V) at 17 ev may well be due to different energy distributions in ionized (III)—(V). In addition, ΔH_f for $PhCO^+$ from benzophenone assumes the loss of a phenyl radical and may not be a reliable value.

TABLE 2

Compound (R)	Degrees of freedom (%) in N^{a}	$[m/e\ 105]/[m/e\ 77]$		
		70 ev	16 ev	14 ev
Me (VI)	15	1·54	10·9	59
Et (VII)	31	2·74	20·8	135
Pr^{n} (VIII)	42	3·03	32·3	200
Pr^{i} (IX)	42	3·85	37·0	263
Bu^{n} (X)	50	3·03	35·7	286
Bu^{i} (XI)	50	3·64	45·5	357

[a] As defined in Table 1.

amount of excess vibrational energy which can be carried off by the neutral alkyl radical [*cf.* data for (VI), (VII), (VIII), and (X)]. The slower rates of fragmentation of the benzoyl ion which are produced in the presence of branching in the alkyl group [*cf.* data for (VII) and (IX), or (X) and (XI)] are contrary to earlier observations on chain branching effects.[3] We can currently offer no secure interpretation of such effects.

(*Received, April 8th,* **1968**; *Com.* 431.)

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[2] For a similar conclusion for tropylium ions, see K. R. Jennings and J. H. Futrell, *J. Chem. Phys.*, 1966, **44**, 4315.

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[6] (a) M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1966, **88**, 529; see also (b) M. L. Gross and F. W. McLafferty, *Chem. Comm.*, 1968, 254.

[7] H. M. Rosenstock and M. Krauss in "Mass Spectrometry of Organic Ions", ed., F. W. McLafferty, Academic Press, New York, ch. 1.