Studies in Mass Spectrometry. XXXI.[1] A Comparison of Reaction Rates in Common Ions Generated *via* Fragmentation and Direct Ionization

Dudley H. Williams, R. Graham Cooks, and Ian Howe

Contribution from the University Chemical Laboratory, Cambridge, England.
Received March 28, 1968

Abstract: A brief discussion concerning the effect of different internal energies of common precursor ions on the further breakdown pattern is presented. The relative rates of decomposition of some common ions, generated *via* fragmentation and direct ionization, are compared. If the neutral particle eliminated in the fragmentation reaction is small (*e.g.*, CO or CO_2), the excess threshold energy ($\sim$1–2 eV) in the ions produced *via* fragmentation results in a greater mean rate of decomposition for such ions in the cases studied. However, the excess threshold energy present in $C_6H_6O\cdot^+$ ion generated *via* loss of ethylene from phenetole is more than offset by the vibrational energy lost to neutral ethylene in the case of those ions which have sufficient internal energy to undergo the further reaction $C_6H_6O\cdot^+ \longrightarrow C_5H_6\cdot^+ + CO$.

There are, in mass spectrometry, well-documented methods used for the determination of structures of organic ions in the gas phase. Methods using deuterium labeling and appearance potential measurements have been employed for some time as aids to ion structure elucidation and even to determination of fragmentation pathways.[2] Comparison methods employing similarities of breakdown patterns have also been used. For example, if a substance decomposes from its molecular ion *via* loss of a neutral fragment to a positive ion A^+, and the further breakdown pattern of A^+ so formed is "identical" or "similar" to that of A^+ generated by direct ionization, it has in the past been common practice to conclude that A^+ ions generated by the two methods have the same structure.[3,4] While it is true that similar or "identical" breakdown patterns strongly implicate a common structure, it is not conversely true that common structure should necessitate identical breakdown pattern, independent of the energy of the fragmenting species. It is an immediate consequence of the assumption of equilibrium reaction kinetics that the kinetic behavior of an excited molecule of definite structure should be a function *only* of its internal energy,[5] and if two ions of identical structure are formed by different routes with different mean internal energies, then the ion of higher energy will have a breakdown pattern consistent with a faster mean rate of fragmentation.[6] So if one is able to implement conditions where one ion would definitely be expected to have higher energy than another of identical structure, then the breakdown pattern of the higher energy ion should correlate with a faster rate of decay. It is the object of this paper to make such correlations. Common ions produced both by direct ionization and by fragmentation are used to provide suitable models.

Discussion

In order to compare reaction rates in common ions, we have generated a number of ions both by direct ionization and *via* fragmentation. The processes studied are summarized by eq 1–5; the further decompositions of the common ions which have been used as a measure of their relative reaction rates are also indicated. In the absence of any evidence to the contrary, we *assume* that only common ions are generated by the two methods. However, we wish to emphasize that in view of the strong evidence that at least a portion of the $C_4H_4O\cdot^+$ ions from 2-pyrone (**1**) or 4-pyrone (**2**) do not have the same structure as the $C_4H_4O\cdot^+$ ions obtained by ionization of furan (**3**),[7] this assumption may not be completely justified. Yet, in all cases, the generation of a considerable fraction of common ions is strongly supported by the close correspondence in shapes of common "metastable peaks;" the matching of "metastable peaks" is typified by the logarithmic transfer 70-eV spectra of methyl phenyl carbonate (**8**) and anisole (**9**) reproduced by Brown and Djerassi.[8] The 70-eV mass spectra of various pairs (with the exception of **4** and **5**, which have previously been reproduced)[9] are given in Figures 1 and 2.

Before dealing with these specific instances, we consider the general case of the sequence $M^+ \rightarrow (X^+ + N) \rightarrow A^+$, where X^+ is also produced by direct ionization of X. We can use eq 6 and 7 at the threshold for appearance of X^+.[10] The symbols I.P. and A.P. represent ionization and appearance potentials, respectively. If ΔH_f corresponds to the formation of X^+ in the ground ionized state by direct ionization, then X^+ formed by the fragmentation route must possess at the threshold at least that energy or more; *i.e.*, $E =$

---

[1] XXX: I. Howe and D. H. Williams, *J. Am. Chem. Soc.*, 90, 5461 (1968).

[2] For examples of the application of such methods to the spectra of alkylbenzenes, see H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 10, and references cited therein.

[3] For a summary of references using such arguments, see P. Brown and M. M. Green, *J. Org. Chem.*, 32, 1681 (1967).

[4] In no case does the comparison of two such spectra appear to lead rigidly to the conclusion of complete identity (in terms of relative abundances of *all* ions (parent, daughter, and metastable) and shapes of *all* "metastable peaks").

[5] H. M. Frey, *Trans. Faraday Soc.*, 56, 51 (1960).

[6] See, for example, M. L. Gross and F. W. McLafferty, *Chem. Commun.*, 254 (1968).

[7] W. T. Pike and F. W. McLafferty, *J. Am. Chem. Soc.*, 89, 5954 (1967); W. H. Pirkle and M. Dines, *ibid.*, 90, 2318 (1968).

[8] P. Brown and C. Djerassi, *ibid.*, 89, 2711 (1967).

[9] D. H. Williams, S. W. Tam, and R. G. Cooks, *ibid.*, 90, 2150 (1968).

[10] It has been pointed out by a referee that there might aso be an excess energy term, $E > 0$ on the right-hand side of eq 6, as one normally obtains vertical, not adiabatic, ionization by electron impact. The statement that X^+ generally has excess energy at the A.P. is still correct.

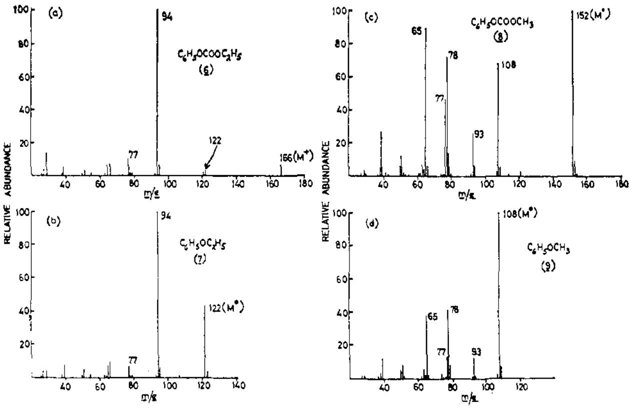
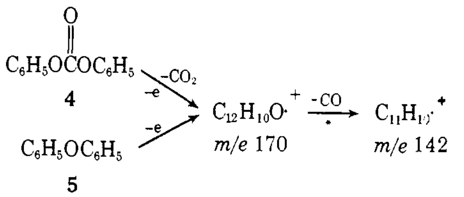
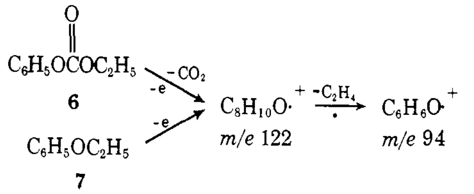


Figure 1. Mass spectra (70 eV) of (a) ethyl phenyl carbonate (**6**), (b) phenetole (**7**), (c) methyl phenyl carbonate (**8**), and (d) anisole (**9**).

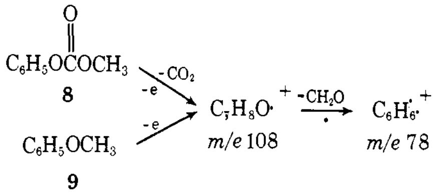
0, or is positive, the latter situation meaning that X⁺ is produced with excess energy at its appearance potential. This excess energy could take a number of forms. First, it could take the form of electronic excitation energy if X⁺ is initially produced on a potential energy surface above the ground ionized state. Unless the excited electronic state is an "isolated" one, it is probable that this electronic energy will be converted (reversibly) to vibrational energy of the ground ionized state *via* crossing of potential energy surfaces.[11] Second, it may immediately take the form of vibrational energy of the ground ionized state, in which case it is probably meaningful to equate the excess energy E with the energy of activation for the back-reaction in the equation $M^+ \rightleftharpoons X^+ + N$. Third, it is also possible for E to be converted to translational energy, in which case X⁺ and N will fly apart with a change in velocity from that of M⁺ before fission took place. Fourth, N may be formed in an electronically, or vibrationally, excited state. The translational energy released gives rise to



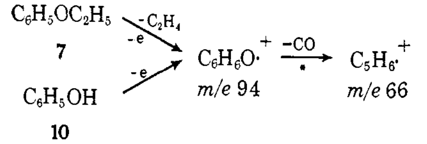
$$C_6H_5O\overset{O}{\overset{\|}{C}}OC_6H_5\ (\mathbf{4}) \xrightarrow[-e]{-CO_2},\quad C_6H_5OC_6H_5\ (\mathbf{5}) \xrightarrow{-e}\ \underset{m/e\ 170}{C_{12}H_{10}O\cdot^{+}} \xrightarrow[\bullet]{-CO} \underset{m/e\ 142}{C_{11}H_{10}\cdot^{+}} \quad (1)$$



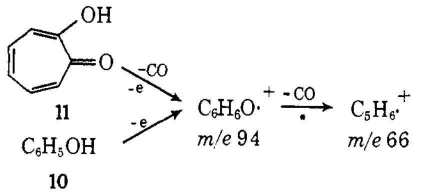
$$C_6H_5O\overset{O}{\overset{\|}{C}}OC_2H_5\ (\mathbf{6}) \xrightarrow[-e]{-CO_2},\quad C_6H_5OC_2H_5\ (\mathbf{7}) \xrightarrow{-e}\ \underset{m/e\ 122}{C_8H_{10}O\cdot^{+}} \xrightarrow[\bullet]{-C_2H_4} \underset{m/e\ 94}{C_6H_6O\cdot^{+}} \quad (2)$$



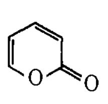
$$C_6H_5O\overset{O}{\overset{\|}{C}}OCH_3\ (\mathbf{8}) \xrightarrow[-e]{-CO_2},\quad C_6H_5OCH_3\ (\mathbf{9}) \xrightarrow{-e}\ \underset{m/e\ 108}{C_7H_8O\cdot^{+}} \xrightarrow[\bullet]{-CH_2O} \underset{m/e\ 78}{C_6H_6\cdot^{+}} \quad (3)$$



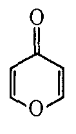
$$C_6H_5OC_2H_5\ (\mathbf{7}) \xrightarrow[-e]{-C_2H_4},\quad C_6H_5OH\ (\mathbf{10}) \xrightarrow{-e}\ \underset{m/e\ 94}{C_6H_6O\cdot^{+}} \xrightarrow[\bullet]{-CO} \underset{m/e\ 66}{C_5H_6\cdot^{+}} \quad (4)$$



$$\mathbf{11} \xrightarrow[-e]{-CO},\quad C_6H_5OH\ (\mathbf{10}) \xrightarrow{-e}\ \underset{m/e\ 94}{C_6H_6O\cdot^{+}} \xrightarrow[\bullet]{-CO} \underset{m/e\ 66}{C_5H_6\cdot^{+}} \quad (5)$$



1



2

3

$$\Delta H_f(X) + \text{I.P.}(X) = \Delta H_f(X^+) \quad (6)$$

$$\Delta H_f(M) + \text{A.P.}(X^+) - \Delta H_f(N) = \Delta H_f(X^+) + E \quad (7)$$

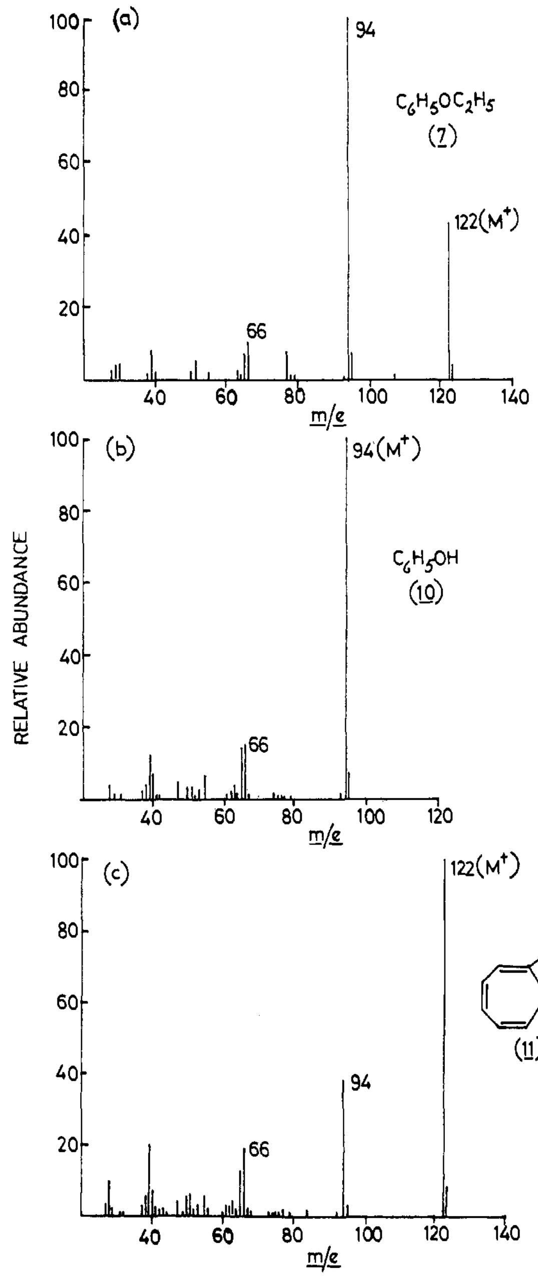


Figure 2. Mass spectra (70 eV) of (a) phenetole (**7**), (b) phenol (**10**), and (c) tropolone (**11**).

---

[11] H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Natl. Acad. Sci. U. S.*, 38, 667 (1952).

"flat-topped metastable peaks;"[12–14] although this translational energy release has been equated to the energy of activation for the back-reaction,[15–17] there would appear to be little experimental or theoretical knowledge as to how the energy released after passing over the transition state (for the $M^+ \rightarrow X^+ + N$ reaction) will be partitioned between internal and translational energy. For our purposes, we note that if X^+ is produced with excess vibrational energy from M^+ (this situation should not be uncommon if N is a particularly stable neutral particle), and this excess vibrational energy is not all converted into kinetic energy (measured from the width of the appropriate "metastable peak"), then a greater fraction of X^+ should decompose on the time scale of the mass spectrometer when generated from M^+ than when generated by ionization of X.[18]

Before the above generalization is tested, an important difference between threshold behavior and behavior at higher energies must be considered. At the threshold, the only excess energy available to X^+ produced *via* fragmentation is that corresponding to E in eq 7. It will be seen subsequently that the excess energies available for the processes under consideration (eq 1–5) are insufficient to produce the neutral molecules ($N = CO_2$, C_2H_4, or CO) in excited states. Hence N can only carry off vibrational energy. If it is assumed that the excess energy is available as vibrational energy, and that it is partitioned in the ratio of the number of internal degrees of freedom of X^+ and N (ignoring fluctuation effects),[19] then it is obvious that only a small fraction of the excess energy will be given to CO_2, C_2H_4, or CO at the threshold, and this can be neglected. However, at the internal energies at which the further decomposition of X^+ can be observed, all those M^+ ions which decompose in the sequence $M^+ \rightarrow X^+ \rightarrow A^+$ must have internal energies corresponding at least to the appearance potential of A^+. If the appearance potential of A^+ is relatively high (compared to that of X^+), then all M^+ ions which eventually become A^+ ions must have internal energies considerably in excess of that needed to attain the transition state of the $M^+ \rightarrow X^+$ reaction. Should the $M^+ \rightarrow X^+$ reaction be occurring in these ions of high internal energy from the same electronic state as for the ions of low internal energy, then vibrational energy greatly in excess of E (eq 7) may now be available for partition between X^+ and N. To illustrate the potential importance of this effect, a hypothetical but plausible example may be considered. Suppose the high-energy M^+ ions possess internal energy of 3 eV in excess of that required to reach the transition state for the $M^+ \rightarrow X^+$ reaction. If the excess energy term at the threshold is 1 eV, as calculated from eq 6 and 7, then in the case where all the excess energy is available as vibrational energy and the ratio of internal degrees of freedom in X^+ and N is 3:1, on the basis of equipartition the excess energy carried off by N will be 1 eV on the average. Therefore, in X^+ ions generated from highly excited M^+ ions, the energy removed by N may be equal to, or exceed, that gained due to the energy of activation for the back reaction of the $M^+ \rightarrow X^+ + N$ process.

If X^+, generated by either method of initial preparation, undergoes further decomposition to A^+ when beam energies in excess of the threshold values are used, then the relative fractions of ions having the energy to undergo the reaction $X^+ \rightarrow A^+$ (which represents the *over-all* rate of removal of X^+ to A^+) can be expressed in terms of $[X^+]/[A^+]$ or $[X^+]/[m^*]$. The former suffers from the disadvantage that A^+ may be produced by more than one pathway, and that the fractions of A^+ ions, produced by the two methods, with sufficient energy to decompose further may vary slightly. Consequently, this parameter will be most meaningful when evaluated from low-voltage spectra. The parameter $[X^+]/[m^*]$ does not suffer from either of the above disadvantages. However, it must be remembered that because of the different electronic levels and Franck–Condon factors involved in the excitation reactions $M \rightarrow M^+$ and $X \rightarrow X^+$, the energy *distributions* ($f(E)$ *vs.* E; see ref 1) in X^+ generated by the two methods will probably differ somewhat. Hence, the intensities of the "metastable peaks," $[m^*]$, may be influenced by different fractions of the X^+ ions in the two cases which give rise to decompositions in the relatively narrow log $k \simeq 5$–6 range. This effect can operate in the absence of excess energy (E), and therefore $[X^+]/[m^*]$ will be a function of both differing $f(E)$'s and the excess energy term. The effect of differing $f(E)$'s on the $[X^+]/[A^+]$ parameter (which reflects a wide spread of internal energies) is probably relatively small in many cases. A third parameter, $[A^+]/[m^*]$, is of course not independent of the other two, but might show the most consistent trends if it were a common situation for different methods of initial preparation to produce ions which were not all of the same structure. Under these circumstances, if only the common ions X^+ decomposed to A^+, the parameter $[A^+]/[m^*]$ has the advantage that we do not need the term X^+, which we can no longer reliably measure. In view of the above effects, we have determined $[X^+]/[A^+]$, $[X^+]/[m^*]$, and $[A^+]/[m^*]$.

The foregoing discussion emphasizes the problem of obtaining reliable parameters to express increased "reaction rates." The situation is perhaps best summarized by stating that if two different methods of initial preparation produce ions X^+ with similar energy distributions prior to the introduction of excess vibrational energy, then if only common X^+ ions are produced in the same electronic state, $[A^+]/[m^*]$ will probably be greater for the X^+ ions produced with excess internal energy, while $[X^+]/[A^+]$ and $[X^+]/[m^*]$ will probably be smaller for such ions.

The appropriate heats of formation, ionization, and appearance potentials, and excess energies for ethyl phenyl carbonate (**6**), phenetole (**7**), methyl phenyl carbonate (**8**), anisole (**9**), phenol (**10**), and tropolone (**11**), are given in Table I. Data for diphenyl carbonate

---

(12) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Z. Naturforsch.*, 20a, 180 (1965).

(13) T. W. Shannon, F. W. McLafferty, and C. R. McKinney, *Chem. Commun.*, 478 (1966).

(14) J. H. Beynon and A. E. Fontaine, *Z. Naturforsch.*, 22a, 334 (1967).

(15) F. W. McLafferty and W. T. Pike, *J. Am. Chem. Soc.*, **89**, 5951 (1967).

(16) M. M. Bursey and F. W. McLafferty, *ibid.*, 88, 5023 (1966).

(17) J. H. Beynon, A. E. Fontaine, and G. R. Lester, *J. Mass Spec. Ion Phys*,, **1**, 1 (1968).

(18) A correlation between rates of decomposition of ions and their apparent heats of formation has previously been reported: K. R. Jennings and J. H. Futrell, *J. Chem. Phys.*, **44**, 4315 (1966); see also R. G. Cooks and D. H. Williams, *Chem. Commun.*, 627 (1968).

(19) H. M. Rosenstock and M. Krauss in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 1.

Table I. Data for the Calculation of Excess Energies[a]

Compound	ΔH_f-(X), kcal	I.P.-(X), eV	ΔH_f-(X^+), kcal	ΔH_f-(M), kcal	A.P.-(X^+), eV	ΔH_f-(N), kcal	E, kcal
6				-124^b	10.0	-94^c	+25
7	-25.5^d	8.6	175				
8				-118^b	10.3	-94^c	+34
9	-18.5^d	8.6	179				
7				-25.5^d	11.3	$+12.5^c$	+39
10	-23.0^e	9.0^f	184				
11				-37^g	10.8	-26^c	+54
10	-23.0^e	9.0^f	184				

[a] Symbols as defined in eq 6 and 7; the estimated error in E is ±10 kcal. [b] Estimated by the method of group equivalents, in conjunction with the value for diphenyl carbonate (ref 18). [c] See ref 18. [d] J. D. Cox, *Tetrahedron*, **18,** 1337 (1962). [e] R. J. L. Andon, D. P. Biddisçombe, J. D. Cox, R. Handley, D. Harrop, E. F. G. Herrington, and J. F. Martin, *J. Chem. Soc.*, 5246 (1960). [f] R. W. Kiser, "Tables of Ionization Potentials," U. S. Atomic Energy Commission, 1960. [g] W. N. Hubbard, C. Katz, G. B. Guthrie, and G. Waddington, *J. Am. Chem. Soc.*, **74,** 4456 (1952).

Table II. Relative Abundances $[C_{12}H_{10}O\cdot^+]/[C_{11}H_{10}\cdot^+]$, $[C_{12}H_{10}O\cdot^+]/[m^*]$, and $[C_{11}H_{10}\cdot^+]/[m^*]$ at Various Electron Voltages for $C_{12}H_{10}O\cdot^+$ Produced by Ionization and Fragmentation of Diphenyl Carbonate (**4**) and by Ionization of Diphenyl Ether (**5**)[a]

eV	$[C_{12}H_{10}O\cdot^+]/[C_{11}H_{10}\cdot^+]$	$[C_{12}H_{10}O\cdot^+]/[m^*] \times 10^{-2}$	$[C_{11}H_{10}\cdot^+]/[m^*] \times 10^{-3}$	
50	1.56	0.79	5.1	From **4**
25	1.80	0.93	5.1	
20	2.0	0.96	4.8	
18	2.4	1.00	4.2	
16	3.0	1.14	3.8	
14	4.2	1.39	3.3	
50	9.1	3.4	3.7	From **5**
25	9.6	3.6	3.7	
20	11.1	3.8	3.4	
18	13.7	4.7	3.4	
16	19.6	6.1	3.1	
14	34	8.0	2.4	

[a] The comparisons presented in Tables II–V are made by running the spectra consecutively, without changing any of the focusing controls. The beam energy is uncorrected. The ratios have no absolute significance and are dependent upon a number of instrumental parameters (*e.g.*, source, focusing controls), but self-consistent data are always obtained when the samples are run under identical conditions.

Table III. Relative Abundances $[C_8H_{10}O\cdot^+]/[C_6H_6O\cdot^+]$, $[C_8H_{10}O\cdot^+]/[m^*]$, and $[C_6H_6O\cdot^+]/[m^*]$ at Various Electron Voltages for $C_8H_{10}O\cdot^+$ Produced by Ionization and Fragmentation of Ethyl Phenyl Carbonate (**6**) and by Ionization of Phenetole (**7**)

eV	$[C_8H_{10}O\cdot^+]/[C_6H_6O\cdot^+]$	$[C_8H_{10}O\cdot^+]/[m^*] \times 10^{-2}$	$[C_6H_6O\cdot^+]/[m^*] \times 10^{-3}$	
50	0.029	0.75	2.5	From **6**
25	0.033	0.75	2.3	
20	0.040	0.60	1.5	
18	0.038	0.50	1.3	
16	0.055	0.60	1.1	
14	0.075	0.60	0.8	
50	0.48	4.3	0.90	From **7**
25	0.57	4.0	0.70	
20	0.72	3.9	0.54	
18	0.91	4.0	0.44	
16	1.3	3.9	0.30	
14	2.3	3.9	0.17	

Table IV. Relative Abundances $[C_7H_8O\cdot^+]/[C_6H_6\cdot^+]$, $[C_7H_8O\cdot^+]/[m^*]$, and $[C_6H_6\cdot^+]/[m^*]$ at Various Electron Voltages for $C_7H_8O\cdot^+$ Produced by Ionization and Fragmentation of Methyl Phenyl Carbonate (**8**) and by Ionization of Anisole (**9**)

eV	$[C_7H_8O\cdot^+]/[C_6H_6\cdot^+]$	$[C_7H_8O\cdot^+]/[m^*] \times 10^{-2}$	$[C_6H_6\cdot^+]/[m^*] \times 10^{-2}$	
70	1.0	1.0	1.0	From **8**
20	1.4	1.2	0.86	
16	2.5	1.3	0.52	
14	6.2	1.5	0.24	
70	2.3	2.9	1.3	From **9**
20	4.2	5.0	1.2	
16	9.1	6.7	0.74	
14	25	9.1	0.36	

(**4**) and diphenyl ether (**5**) have previously been compared[20] and establish that $C_{12}H_{10}O\cdot^+$ is produced with 37 kcal of excess energy from the carbonate at its appearance potential.

It is evident that for the reactions summarized by eq 1-5, the ions produced *via* fragmentation are all formed with considerable excess energy at the threshold. Yet the "metastable peaks" for loss of CO_2 from diphenyl carbonate (**4**), ethyl phenyl carbonate (**6**), and methyl phenyl carbonate (**8**), and of C_2H_4 from phenetole (**7**) are narrow. That for loss of CO from tropolone (**11**) is broadened, and corresponds to the conversion of 0.2 eV of internal energy to translational energy. Thus the excess energy which is released as kinetic energy is negligible in these cases. These specific instances reinforce our earlier statement that at present it is impossible to know *a priori* how excess energy will be partitioned between internal energy and kinetic energy of the fragments. Therefore, a lack of substituent effects on "flat-topped metastable peaks" associated with loss of CO from molecular ions of 2-pyrones and coumarins cannot be regarded as giving reliable information as to the structures of the $M^+ - CO$ ions.[21]

The ratios $[X^+]/[A^+]$, $[X^+]/[m^*]$, and $[A^+]/[m^*]$ for the comparison summarized by eq 1 are given in Table II. It is evident that at any given beam energy the ratio $[C_{11}H_{10}\cdot^+]/[m^*]$ is greater in the diphenyl carbonate (**4**) spectrum, while the ratios $[C_{12}H_{10}O\cdot^+]/[C_{11}H_{10}\cdot^+]$ and $[C_{12}H_{10}O\cdot^+]/[m^*]$ are smaller in the spectrum of the carbonate. Thus the kinetic behavior is consistent with, but does not prove, the production of structurally identical $C_{12}H_{10}O\cdot^+$ ions (*m/e* 170) from **4** and **5**.

Table III gives the corresponding data for comparison of the kinetic behavior of the ion $C_8H_{10}O\cdot^+$ generated from phenetole (**7**) and generated by loss of CO_2 from the molecular ion of ethyl phenyl carbonate (**6**). The comparison for the M^+ ion from anisole (**9**) and the $M^+ - CO_2$ ion from methyl phenyl carbonate (**8**) is given in Table IV.

The data in Table III establish that at any given beam energy the ratio $[C_6H_6O\cdot^+]/[m^*]$ is greater in the ethyl phenyl carbonate (**6**) spectrum, while the ratios $[C_8H_{10}O\cdot^+]/[C_6H_6O\cdot^+]$ and $[C_8H_{10}O\cdot^+]/[m^*]$ are much smaller in the spectrum of the carbonate. Once more the kinetic behavior is consistent with the production of structurally identical $C_8H_{10}O\cdot^+$ (*m/e* 122 ions) from **6** and **7**. Although the excess energy (+34 kcal) present in $C_7H_8O\cdot^+$ (*m/e* 108) produced from methyl phenyl carbonate (**8**) at the threshold results in less

---

(20) P. Natalis and J. L. Franklin, *J. Phys. Chem.*, **69,** 2943 (1965).

(21) M. M. Bursey and L. R. Dusold, *Chem. Commun.*, 712 (1967).

abundant *m/e* 108 ions (relative to *m/e* 78, or relative to [m*] for the *m/e* 108 → 78 transition) from the carbonate (Table IV), the *m/e* 78 daughter ion is *more* abundant relative to [m*] in the spectrum of anisole (**9**). This latter situation indicates that the different distributions of *k* states[22] of $C_7H_8O\cdot^+$ (*m/e* 108) ions produced by the two methods results in a greater weighting of daughter ions relative to [*m/e* 108] when excess energy is present, but also leads to a slightly larger increase in [m*] relative to [*m/e* 78]. The kind of complication is by no means unexpected and emphasizes the difficulties inherent in a simple kinetic approach to mass spectrometry and, further, the advantage of measuring all the parameters listed in Tables II–V.

Table V. Relative Abundances $[C_6H_6O\cdot^+]/[C_5H_6\cdot^+]$, $[C_6H_6O\cdot^+]/[m^*]$, and $[C_5H_6\cdot^+]/[m^*]$ at Various Electron Voltages for $C_6H_6O\cdot^+$ Produced by Ionization and Fragmentation of Phenetole (**7**) and Tropolone (**11**) and by Ionization of Phenol (**10**)

eV	$[C_6H_6O\cdot^+]/[C_5H_6\cdot^+]$	$[C_6H_6O\cdot^+]/[m^*] \times 10^{-2}$	$[C_5H_6\cdot^+]/[m^*] \times 10^{-2}$	
70	10.0	7.3	0.73	From **7**
20	36	17.0	0.47	
16	~3500			
70	2.0	3.2	1.6	From **11**
20	3.7	5.6	1.5	
16	20	17.4	0.86	
70	6.8	6.0	0.89	From **10**
20	16	12.5	0.76	
16	110	56	0.51	

In Table V, the relevant data for a comparison of the kinetic behavior of $C_6H_6O\cdot^+$ (*m/e* 94) produced by three methods of initial preparation (eq 4 and 5) are given.

The comparison between tropolone (**11**) and phenol (**10**) accords perfectly with the simple prediction (it is calculated that $C_6H_6O\cdot^+$ (*m/e* 94) is produced with 54 kcal of excess energy at the threshold from tropolone (Table I)). However, *all* the ratios for the decomposition of the $M^+ - C_2H_4$ ion from phenetole (**7**) by further loss of CO are precisely the opposite in magnitude (relative to those for phenol (**10**)) in comparison with those expected from consideration of only the threshold excess energy (+39 kcal). In the reaction $C_6H_5OC_2H_5\cdot^+ \rightarrow C_6H_6O\cdot^+ + C_2H_4$, the neutral ethylene molecule will on the average carry off 27% of the excess vibrational energy in the transition state (assuming equipartition of energy and ignoring fluctuation effects),[19] plus 27% of the excess energy term at the threshold (39 kcal (≡1.7 eV), Table I). If we assume that the same electronic state is involved for ions undergoing this reaction at the threshold and for ions with excess energy in the transition state, then arbitrarily fixing the latter term at 4.3 eV, approximately 1.6 eV of vibrational energy will be carried off by neutral ethylene [(4.3 + 1.7) × 27%]. The average vibrational energy left in $C_6H_6O\cdot^+$ would therefore be 4.4 eV, which corresponds closely to the activation energy for loss of CO from $C_6H_6O\cdot^+$ produced by ionization of phenol. Hence, the ions produced by ionization of phenetole (**7**) which eventually contribute to the $[C_5H_6\cdot^+]$ or [m*] abundances of Table V will have lost on the average[19] *ca.* 1.6 eV or more of vibrational energy to neutral ethylene. This loss is therefore equal to or greater than the excess energy term at the threshold, and accounts in a semiquantitative manner for the reduction in $[C_5H_6\cdot^+]$ and [m*] intensities relative to $[C_6H_6O\cdot^+]$ when the data are compared with those for phenol (Table V). The neutral molecules CO and CO_2 are of course much less effective than C_2H_4 in carrying off vibrational energy.

Experimental Section

Mass spectra were measured on an AEI MS9 double-focusing mass spectrometer, operating with an accelerator potential of 8 kV and a source temperature of approximately 200°. All samples were either commercially available or synthesized in our laboratory, and purified by standard techniques. The samples were introduced into the mass spectrometer through a heated inlet system.

---

[22] See, for example, J. Hertel and Ch. Ottinger, *Z. Naturforsch.*, **22a**, 40 (1967).