quinone complexes (Figure 6A) or as oxidized dithiolene complexes (Figure 6B).

Perhaps a better interpretation of the reduction properties, however, is one that places the added electrons in a ligand π^* MO of b_{1u} symmetry (Figure 7). The bathochromic shift of the M → L ($b_{3g} \rightarrow L\pi^*$) transition in the electronic spectra of the adducts and the energy of this transition relative to that of the d–d transition[52] suggest that, in the adducts, the ligand π^* MO of b_{1u} symmetry is of lower energy than the d_{xy} metal orbital. The per cent metal character of the b_{1u} MO cannot be ascertained, although the reduction properties of the adducts and the stability of the reduction products clearly depend[55] on the type of metal atom bonded to the α-diketone portion of the coordinated dithiooxalate ligand and to a lesser extent on the environment about this atom.

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[52] From the Δ_0 reported by Carlin and Canziani[53] for Co(Dto)$_3^{3-}$ the energy of the Δ_1 transition for the Ni(Dto)$_2^{2-}$ is calculated to occur at 17,700 cm^{-1}. A shoulder found at 17,700 cm^{-1} in the spectrum of Ni(Dto)$_2^{2-}$ has been assigned[49] to the Δ_1 transition. In agreement with the stronger M–S bonding in the adducts is the fact that, in the adducts, larger values of Δ_0 are generally observed.[54]

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[55] With $TiCl_4$ or $SnCl_2$ the dithiooxalate complexes form adducts which undergo ill-defined irreversible reductions.

Application of Collisional Activation Spectra to the Elucidation of Organic Ion Structures[1,2]

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Abstract: The relative abundances of most product ions resulting from collisional decomposition of a gaseous ion are shown to depend only on the ion's structure, and not on its internal energy. The structure of an ion can be characterized by matching its collisional activation (CA) spectrum with that of a known reference ion; $C_2H_5O^+$, $C_3H_6O^+$, $C_7H_8^+$, and $C_{13}H_9^+$ ions are used as examples. The resemblance of ion decomposition pathways of CA spectra to those of conventional mass spectra makes possible the interpretation of CA spectra to provide structural information of unknown ions.

The structure characterization of gaseous positive ions has been the subject of an increasing number of studies involving ion–molecule[3] and unimolecular-ion reactions.[4,5] Definitive structural information is often difficult to obtain; reactivity behavior studies can be subject to unpredictable effects of ion internal energy and usually require isotopic labeling, and thermochemical energy requirements must be interpreted with caution. The importance of ion structures for both fundamental studies of ion reactions and determination of unknown molecular structures would make valuable a simple, direct method for ion structure identification and characterization. This paper describes the use of collisional activation (CA) spectra[6] in such applications.

Increasing the pressure in a field-free drift region of a mass spectrometer causes ion–neutral collisions in which some of the ion's kinetic energy is converted into internal energy. The resulting ion decomposition products (the "CA spectrum")[6] can be studied using the same techniques developed for unimolecular metastable ion decompositions.[4b,7] CA spectra, like metastable ion (MI) spectra,[4b] appear to add on "extra dimension" of information to a normal electron-impact (EI) mass spectrum in that a CA spectrum can be obtained for each product ion of an EI spectrum,

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[1] Metastable Ion Characteristics. XXIV. Part XXIII: D. J. McAdoo, P. F. Bente III, F. W. McLafferty, M. L. Gross, and C. Lifshitz, *Org. Mass Spectrom.*, in press.

[2] (a) John Simon Guggenheim Memorial Foundation Fellow, 1972; (b) taken in part from the Cornell University Ph.D. Theses of R. K., 1971, and S.-C. T., 1972; (c) visiting scientist on leave from Toray Industries, Kamakura, Japan. (d) We are grateful to the National Institutes of Health (GM 16609) and the Army Research Office (D-31-124-G1117) for generous support of this work.

[3] (a) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971); (b) G. Eadon, J. Diekman, and C. Djerassi, *J. Amer. Chem. Soc.*, **92**, 6205 (1970); (c) J. L. Beauchamp and R. C. Dunbar, *ibid.*, **92**, 1477 (1970); (d) D. J. McAdoo, P. F. Bente III, and F. W. McLafferty, *ibid.*, **94**, 2027 (1972).

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[7] T. Wachs, P. F. Bente III, and F. W. McLafferty, *Int. J. Mass Spectrom. Ion Phys.*, **9**, 333 (1972).

as well as for the molecular ion. In contrast to MI spectra, however, changes in precursor ion internal energy cause relatively little change in CA spectra, especially for product ions requiring higher activation energy.[6] Such ions are usually negligible in MI spectra, so that CA spectra in general contain many more peaks. CA spectra can now be measured easily and accurately with a double-focusing mass spectrometer in which a mass-analyzed ion beam enters the collision region and the products are energy analyzed, the reverse of the usual order of analyzers.[7]

Experimental Section

For the data of Tables I–III, the reversed geometry Hitachi RMU-7 described previously[7] was used with an ion accelerating potential of 3.8 kV, ionizing electrons of 70 eV and 100 μA, and sample reservoir and ion source temperatures of 150–200° (220° for 5α-pregnan-20β-ol-3-one). The other data reported were measured with a conventional Hitachi RMU-7 using the Barber-Elliott-Major defocusing technique as described previously. Most of the measurements of Tables I–III were also made separately with this earlier technique. The magnetic field is adjusted to pass only the desired precursor ion mass; its unimolecular metastable decomposition products (the MI spectrum) are scanned by reducing the electrostatic analyzer (ESA) potential from its normal value to zero while recording the resulting ion current at the collector. The pressure in the field-free drift region between the magnet and the ESA is then increased with helium until the precursor ion intensity is reduced to 10% of its original value,[6c] and the ion product abundances (the CA spectrum) are determined in the same manner in a second ESA scan. The contributions from MI products are subtracted from these values to obtain the CA spectrum. In this work the MI abundances were corrected for mass discrimination in ion scattering as described previously,[6c] although omission of this correction would not have affected the conclusions appreciably. Corrections were also made for isobaric precursor ions. For example, in generating the $C_7H_8\cdot^+$ precursor ions from either toluene or cycloheptatriene approximately 10% of the *m/e* 92 ions are $C_6{}^{13}CH_7^+$; the contributions of these to the CA spectrum of $C_7H_8\cdot^+$ were determined from the CA spectrum of $C_7H_7^+$. The values reported represent the average of at least two determinations.

Samples. 2-Hexanone-*1,1,1,3,3-d*$_5$ was the gift of Dr. J. Tou and L. B. Westover, The Dow Chemical Co., Midland, Mich. 1,2,3,5-Tetra-*O*-methyl-β-D-ribofuranose was prepared by treatment of the corresponding sugar with NaH–dimethyl sulfoxide–CH_3I.[8] All other compounds were obtained commercially, checked for purity by mass spectrometry, and purified by gas chromatography where necessary.

Results and Discussion

The relative abundances of the peaks in a CA spectrum arising from the lowest energy processes can be dependent on the precursor ion's internal energy as well as on its structure.[6c] To facilitate comparison of CA spectra, these peaks are omitted from the total ion abundance used to determine the relative abundance values. The lowest energy processes usually can be identified by their low appearance potentials or because they give abundant peaks in the MI spectrum. It is conceivable that a particular low energy process will not give an abundant peak in the MI (or even the EI) spectrum because precursor ions of the proper internal energy are not formed.[6c] However, it should be possible to establish unequivocally the energy-independent CA reference spectrum of an ion by comparing the CA spectra of the ion formed from a variety of precursor molecules.

$C_2H_5O^+$ Ions. A number of studies have been made on the isomeric $C_2H_5O^+$ ions; a–e (see Table I) are possible structures.[3b,5] The definitive study of Beauchamp and Dunbar[3c] using ion cyclotron resonance spectroscopy showed that b is the lowest energy form. MI spectra indicate that ions of incipient structures b, d, and e isomerize during or immediately after formation to a common structure, probably b.[5b] This appears to be true also of ion c; the reactions of protonated ethylene oxide with 2-propanol were found to be identical with those of b with one exception which was thought to be due to a difference in ion energy.[3c]

The CA spectra of $C_2H_5O^+$ ions from a wide variety of precursors, Table I, completely support these conclusions, indicating that only two stable structures, presumably a and b, are formed. All of the compounds which are expected to yield $CH_3O^+{=}CH_2$ (a) by either direct cleavage or rearrangement[4a] (these are the first four compounds of Table I) give $C_2H_5O^+$ ions whose CA spectra are identical within experimental error. In the same way, the CA spectrum of protonated acetaldehyde matches the spectra from $C_2H_5O^+$ ions of compounds which should yield $CH_3CH{=}^+OH$ (see the next nine entries in Table I). In both of these cases even the product ions whose abundance could vary with precursor ion internal energy (*m/e* 29 and 19 for a and b, respectively) show good reproducibility.

The agreement between the CA spectrum of $C_2H_5O^+$ from protonated ethylene oxide and the spectra of b ions shows that ions formed as c which reach the field free drift region (lifetime $\sim 10^{-5}$ sec) will have isomerized to structure b. The higher abundance of the *m/e* 19 peak formed by the lowest energy process indicates that these $C_2H_5O^+$ ions differ in their distribution of internal energy values. This is supported by the MI spectral abundances, and is in keeping with the explanation of the difference in ion–molecule reactivity.[3c]

Isomerization of the ions presumably formed in the higher energy structures d and e also appears to be complete before the ions undergo collision; the six precursors C_2H_5O–Y and $HOCH_2CH_2$–Y yield $C_2H_5O^+$ ions whose CA spectra match those of b. The *m/e* 19 abundances and MI spectra indicate that the internal energies of these ions vary widely, however. Note that the *m/e* 19 abundance of 1,3-propanediol is five times that of the average for the first nine compounds giving b ions in Table I. Failure to recognize the possibility of this variation for the low-energy product, as well as the low sensitivity of the measurements, led us to conclude in a preliminary report[6b] that part of the $C_2H_5O^+$ ions from 1-alkanols did not have structure b.

All of the spectral data of Table I were also taken using ionizing electron energies of 17 eV, which reduced the absolute abundances by 80 or 90%. The relative abundances in these CA spectra for ions initially formed as a (except *m/e* 29) and b (except *m/e* 19) were identical with those using higher energy electrons. The 17-eV CA spectra gave no evidence that ions formed initially with structures c, d, or e had isomerized any less completely to b, despite their lower average internal energy. The only appreciable effect of this change on these CA spectra was to reduce the *m/e* 29 abundance for a and *m/e* 19 for b, as expected. In general, the use of low voltage electrons also caused a substantial reduction in the absolute abundances of the MI spectral peaks.

Inclusion of the C_2H_5O moiety in a large molecule,

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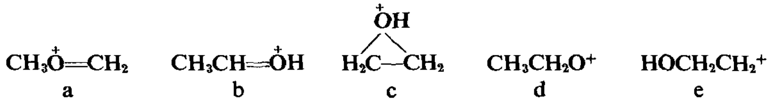
(8) D. W. Thomas, *Biochem. Biophys. Res. Commun.*, 33, 483 (1968).

Table I. CA and MI Spectra of $C_2H_5O^+$ Ions



$CH_3\overset{+}{O}{=}CH_2$ (a), $CH_3CH{=}\overset{+}{O}H$ (b), $CH_3CH_2O^+$ (d), $HOCH_2CH_2^+$ (e)

Precursor molecule	Ion structure	$[C_2H_5O^+]$ EI[a]	CA product ion abundance,[a] m/e								MI product ion abundance,[b] m/e				
			14	15	19[a]	26	27	29[a]	42	43	19	27	29	42	43
$CH_3OCH_2CH_2OCH_3$	a	34	8	49	<2	<2	<4	190	12	31	<0.1	<0.1	7	<0.1	0.4
$CH_3OCH_2CH_2CN$	a	35	9	54	<0.5	<0.5	<1	170	11	27	<0.1	<0.1	12	<0.1	0.4
$CH_3OCH_2\overline{CH(CHOCH_3)_3O}$[c]	a	10	7	47	<2	<2	<3	160	11	36	<0.2	<0.2	12	0.3	3
$CH_3OCOOCH_3$	a[d]	22	9	54	<2	<2	<3	190	10	27	<0.2	<0.2	15	<0.2	<0.6
$CH_3CH{=}OH^+$[e]	b		1	3	5	3	9	13	16	56	7	1	0.9	1	3
$CH_3CH(OH)CH_3$	b	53	2	3	6	4	12	13	17	49	18	1	2	2	5
$CH_3CH(OH)$-*n*-$C_{15}H_{31}$	b	25	2	4	2	4	9	12	18	52	2	0.7	0.6	1	4
$CH_3CH(OH)CH(OH)CH_3$	b	47	2	3	4	3	11	12	15	55	10	2	1	1	5
$CH_3CH(OH)COCH_3$	b	33	1	3	6	3	11	11	17	54	12	2	1	0.5	3
$CH_3CH(OH)$-c-C_3H_5[f]	b	30	1	2	6	4	12	12	16	53	21	4	2	0.8	7
$CH_3CH(OH)$-pregnanone[g]	b	5	2	3	4	4	11	12	17	52	12	2	2	1	7
$(CH_3)_2CHOCH(CH_3)_2$	b[d]	39	1	3	3	4	10	12	18	53	2	0.7	0.6	2	5
$CH_3CH(OC_2H_5)_2$	b[d]	32	1	3	3	4	10	12	18	52	3	0.6	0.3	0.4	2
$\overline{CH_2CH_2{}^+O}H$[e]	b		1	2	9	2	14	11	13	56	81	20	10	3	33
$C_2H_5OC_2H_5$	b[d,h]	12	1	2	5	3	10	11	17	56	12	2	1	0.8	4
$(C_2H_5OCO)_2CH_2$	b[h]	3.3	1	2	4	4	11	13	16	53	13	4	2	2	11
$HOCH_2CH_2Br$	b[h]	74	1	3	5	3	11	12	15	54	7	3	2	0.9	7
$HOCH_2CH_2CH_3$	b[h]	2.0	1	2	13	3	15	14	13	52	79	7	8	1	10
$HOCH_2CH_2CH_2OH$	b[h]	4	1	2	21	4	15	11	13	55	60	8	4	0.8	9
$(HOCH_2CH_2)_2O$	b[h]	44	1	2	6	3	11	13	15	55	18	3	2	0.4	3
$(n\text{-}C_4H_9)_2CHOH$	b[d]	2.9	1	3	5	4	10	14	19	50	9	4	3	<2	9
$(n\text{-}C_4H_9)_2O$	a, b[i]	0.9	3	12	10	4	10	35	18	54	10	1	2	<0.5	4
$(n\text{-}C_5H_{11})_2O$	a, b[i]	1.0	4	13	5	3	10	46	16	54	5	1	4	0.7	5
$\overline{(CH_2)_4O}$	a, b[j]	2.2	8	38	0.9	0.5	2	120	11	40	0.3	0.1	1	0.2	0.6
$CH_3CH_2\overline{CHCH_2O}$	a, b[j]	0.9	7	36	6	2	7	110	13	37	3	<1	8	<1	3

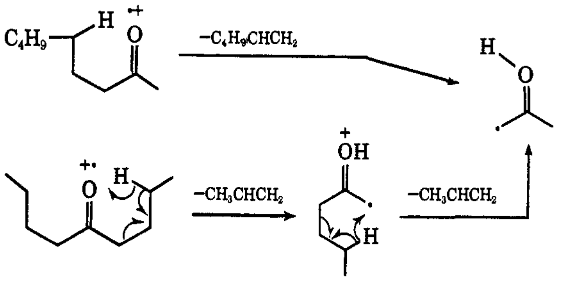
[a] Abundances relative to the total ion abundance = 100. CA: excluding *m/e* 29 for ions of structure a; excluding *m/e* 19 for ions of structure b; excluding both if both a and b are present. Peak at *m/e* 44 not measured; other peaks are of smaller abundance than those reported. EI: abundance of $C_2H_5O^+$ in electron ionization spectrum. [b] Abundances relative to the abundance of the $C_2H_5O^+$ precursor ion × 10^6. [c] 1,2,3,5-Tetra-*O*-methyl-β-D-ribofuranose. [d] Ion structure produced by rearrangement decompositions. [e] Formed by protonation at high sample pressures. [f] Methylcyclopropylcarbinol. [g] 5α-Pregnan-20β-ol-3-one. [h] Simple cleavage will give a less stable $C_2H_5O^+$ ion. [i] Data are consistent with approximately 20% a, 80% b. [j] Data are consistent with approximately 70% a, 30% b.

which should lower the average internal energy of the resulting $C_2H_5O^+$ ion through the "degree-of-freedom effect,"[1] also had no appreciable effect on the ion's CA spectrum, as can be seen from the data from 1,2,3,5-tetra-*O*-methyl-β-D-ribofuranose, 2-heptadecanol, and 5α-pregnan-20β-ol-3-one. If these were unknown molecules, the CA spectra of their $C_2H_5O^+$ ions would obviously be of help in elucidating their structures.

The last five examples of Table I illustrate the use of CA spectra to distinguish between structures a and b for $C_2H_5O^+$ ions from compounds whose ion decomposition pathways are less clearly understood. 5-Nonanol gives only the $CH_3CH{=}^+OH$ structure, as might be expected. The alkyl ethers give small, though significant, amounts of less stable[3c] $CH_3O^+{=}CH_2$ ion, while this represents the majority of the $C_2H_5O^+$ ions from the cyclic ethers. The proportion of a and b was not changed appreciably by using 17-eV electrons. Of the compounds which have been found to produce appreciable amounts of $CH_3O^+{=}CH_2$, dimethyl carbonate (which is known to yield this ion by rearrangement[4a]) is the only one that does not contain an ether oxygen; the converse is not true, however.

As noted previously,[5b] the unimolecular metastable decompositions actually are also quite characteristic of structures a and b. The *m/e* 29 peak from b can be distinguished on the basis of its flat-topped appearance. The value of [*m/e* 19]/[*m/e* 29] is approximately 10 for the MI spectra of most, although not all,[9] b ions, and <0.02 for a ions; for a particular ion structure the variations in this ratio arise from variations in precursor internal energy.[10] Note, however, that unimolecular decompositions give information only on ions of a very narrow range of internal energies; abundant isomeric ions could be present with insufficient energy to yield an observable MI spectrum. This should not be possible for CA spectra.

$C_3H_6O^+$ Ions. The first application of ion cyclotron resonance spectroscopy in ion structure determination[3b] resolved the question of the structure of the $C_3H_6O^+$ ions resulting from single and double hydrogen rearrangements of alkanones,[11] reaction 1. The CA spectra of Table II[12] also show that the decomposition with single H rearrangement of 2-pentanone and 2-nonanone ions yields the same $C_3H_6O\cdot^+$ isomer (presumably f) as the double H rearrangement of 5-nonanone, and that most of these ions must have a different structure than the molecular ion of acetone (g). The CA spectral similarities are consistent with the previous conclusion[11] that most of the low-energy decompositions of f involve an initial isomerization to g. Note the much higher tendency of f to undergo loss of $C_2H_3\cdot$ to yield *m/e* 31 (presumably $CH_2{=}^+OH$), consistent with the enolic structure.



(1)

Table II. CA Spectra of $C_3H_6O^+$ Ions[a]

m/e	Acetone	2-Pentanone	2-Nonanone	5-Nonanone
14	6	3	2	2
15	16	5	4	4
27	14	9	8	8
29	13	15	16	18
31	1	13	12	12
37	3	5	3	4
39	9	14	16	16
42	81	16	18	20
43	690	78	64	54
55	2	4	4	4
57	37	34	35	31

[a] Abundances relative to the total ion abundance = 100 excluding *m/e* 42 and 43.

$C_7H_8\cdot^+$ Ions. Hoffman and Bursey have recently reported that toluene molecular ions undergo a specific ion–molecule reaction not found with cycloheptatriene or norbornadiene ions, which led them to conclude that the toluene ions must retain their structural integrity for the time of $\sim 10^{-2}$ sec required for reaction in the ion cyclotron resonance (icr) spectrometer.[13] They contrast this behavior to the many reports[14] that most *decomposing* toluene molecular ions first isomerize to a cycloheptatriene or similar structure. EI and CA spectral data of deuterated toluenes showed that only 11 and 2%, respectively, of toluene $M\cdot^+$ ions which lose a hydrogen atom do not also undergo H–D scrambling; it was pointed out that the lower CA value could be due in part to isomerization occurring in the $\sim 10^{-5}$ sec required for the toluene ions to reach the collision region.[14c] Thus, if the threshold energy for isomerization of the toluene ion is below that for decomposition, a substantial part of the toluene ions reaching the icr reaction region could have isomerized; the observation of unique icr reactivity[13] only indicates that *part* of the ions do not have the cycloheptatriene or norbornadiene structures.

The CA spectra of the $C_7H_8\cdot^+$ ions of toluene, cycloheptatriene, norbornadiene, *n*-butylbenzene, and 2-phenylethanol are compared in Table III; presumably rearrangement decomposition of the molecular ions of the latter two compounds initially forms $C_7H_8\cdot^+$ ions in the methylenecyclohexadiene structure. A wide variety of C_7H_8 isomeric molecules show very similar EI spectra; thus it is possible that these CA spectra could also be quite similar even if prior isomerization has not occurred. Reproducible differences can be identified in particular cases; peaks corresponding to the losses of CH_3 and CH_6 are substantially more abun-

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[9] The compounds which do not give this ratio were ones which were not examined in our earlier study[5b] of MI spectra of $C_2H_5O^+$ ions. In that study this ratio was found to vary by only ±15%; this case is thus another example of the possible pitfalls in utilizing MI spectral data for ion structure determination.[10]

[10] J. L. Occolowitz, *J. Amer. Chem. Soc.*, **91**, 5202 (1969); A. N. H. Yeo and D. H. Williams, *ibid.*, **93**, 395 (1971).

[11] F. W. McLafferty, D. J. McAdoo, J. S. Smith, and R. Kornfeld, *J. Amer. Chem. Soc.*, **93**, 3720 (1971).

[12] Acetone shows abundant peaks in its MI spectrum at *m/e* 42 and 43; the MI spectra of the $C_3H_6O\cdot^+$ ions from the other compounds only show such a peak at *m/e* 43.

[13] M. K. Hoffman and M. M. Bursey, *Tetrahedron Lett.*, 2539 (1971).

[14] (a) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963; (b) F. Meyer and A. G. Harrison, *J. Amer. Chem. Soc.*, **86**, 4757 (1964); (c) I. Howe and F. W. McLafferty, *ibid.*, **93**, 99 (1971).

Table III. Collisional Activation Spectra of $C_7H_8\cdot^+$ Ions

	Relative abundance[a]					
	Toluene		Cycloheptatriene,	Norbornadiene,	*n*-Butylbenzene,	2-Phenylethanol,
m/e[b]	70 eV	13 eV[c]	70 eV	70 eV	70 eV	70 eV
27	1.6	1.7	1.6	1.1	1.8	1.5
39	6.7	6.6	7.7	5.8	7.5	6.3
41	1.4	1.8	1.5	1.4	1.7	1.6
51	6.9	7.0	6.6	5.7	6.7	6.7
63	7.5	7.0	6.9	6.2	6.9	6.9
65	26	24	29	29	30	28
66	1.6	2.1	4	10.0	4	5.6
74	2.1	2.3	1.3	1.6	1.3	1.6
77	12.3	15.4	8.1	4.9	7.6	8.8
89	33	32	33	34	32	33
91	1060	630	1110	2000	970	1090

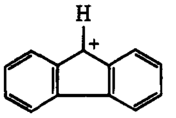
[a] Abundances relative to the total metastable ion intensity excluding *m/e* 91; reproducibility ±10%. This peak accounts for >90% of the total ions in the MI spectrum; *m/e* 90 and 91 have the lowest appearance potentials in the EI spectrum. In the MI spectra of toluene and cycloheptatriene [*m/e* 66]/[*m/e* 65] < 0.03; but this ratio = 2 for norbornadiene. [b] Poorly resolved peaks at *m/e* 26, 50, 75, 76, and 90 have been omitted. [c] On this electron energy scale the abundance of the toluene molecular ion at 9.5 eV was 1% relative to its abundance to 70 eV.

dant in the CA spectrum of toluene than in the others. An increased CH_3 loss is mechanistically consistent with the presence of the $C_6H_5CH_3$ structure. Lowering the electron energy to 13 eV increased $[(M - CH_3)^+]$ significantly (Table III); lowering it further to 11 eV gave an apparent additional increase of 3%, although this value is less than the experimental error. (No additional change was observable at 10 eV, but the sensitivity was very poor.) The estimated distribution of internal energy values, *P*(E), of toluene $M\cdot^+$ ions generated by 70-eV electrons[14c] indicates that most ions reaching the collision region, or the reaction region of the icr spectrometer, will have energies of 0.0–1.5 and 2.5–3.0 eV (ionization potential = 8.8 eV). Lowering the electron energy to 13 eV should eliminate most of these higher energy ions, suggesting that these are largely isomerized before reaching the collision region. This is consistent with the observation of complete scrambling in the $C_7H_7^+$ ions formed by unimolecular metastable decomposition of toluene $M\cdot^+$ ions.[14c] Assuming that the CA spectrum of cycloheptatriene ions is representative of that of the isomerized toluene ions, the data indicate that approximately half of the undecomposed toluene ions formed by 70-eV electrons have isomerized after 10^{-5} sec.

Other icr studies of Bursey and coworkers have shown[15] that $C_7H_8\cdot^+$ ions from *n*-butylbenzene cannot have the toluene structure. This is borne out by the CA spectra of these ions and the analogous ones from 2-phenylethanol. However, these spectra are identical with that of cycloheptatriene within experimental error; although this could be a coincidence, it suggests that the bulk of these $C_7H_8\cdot^+$ ions have isomerized to the common cycloheptatriene-like structure after 10^{-5} sec. Contrary to previous suggestions,[15] we reason that $C_7H_8\cdot^+$ ions produced by rearrangement of *n*-butylbenzene $M\cdot^+$ ions should exhibit a *higher* average internal energy than $C_7H_8\cdot^+$ from toluene. There should be fewer $C_7H_8\cdot^+$ ions of low energy, as these will be formed from lower energy $M\cdot^+$ ions in competition with other low energy processes. More importantly, the *P*(E) function of the nondecomposing $C_7H_8\cdot^+$ ions should not have a region of low probability at higher energies as is indicated for the *P*(E) function of toluene ions.[14c] Hydrogen–deuterium scrambling in $C_7H_8\cdot^+$ ions formed from 2-phenylethanol is complete in those ions undergoing unimolecular metastable decomposition;[16] therefore it is probable that the similarity of the CA spectra of $C_7H_8\cdot^+$ ions from cycloheptatriene, *n*-butylbenzene, and 2-phenylethanol (Table III) is due to the fact that the bulk of these ions which reach the collision region have isomerized to a common structure.

Meyerson and coworkers have suggested that the unusually high abundance of the $(M - C_2H_2)\cdot^+$ ion in the EI spectrum of norbornadiene is due to elimination of acetylene from molecular ions which have not isomerized.[17] This is also indicated in the CA spectrum of norbornadiene ions, which shows a substantial increase in the abundance of *m/e* 66.[17a]

$C_{13}H_9^+$ Ions. These even-electron ions have been reported in the EI spectra of diphenylmethane,[18] the isomeric diphenylethanes and -ethenes,[18,19] fluorene,[20] 9,10-dihydrophenanthrene,[21] and in a variety of diphenylheterocyclic compounds.[22] Although isomerization to a stable fluorenyl ion structure (h) has been proposed for many of these precursors,[18–22] a pre-



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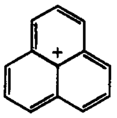
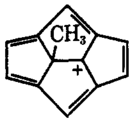


i



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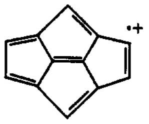

k

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(17a) Note Added in Proof. A recent communication (R. C. Dunbar and E. W. Fu, *ibid.*, 95, 2716 (1973)) presents evidence from photodissociation studies utilizing ion cyclotron resonance spectroscopy that $C_7H_8\cdot^+$ ions from toluene, cycloheptatriene, and norbornadiene do not undergo interconversion on a time scale of seconds.

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liminary report by Kinstle[23] favors a phenalenium structure (i) for the $C_{13}H_9^+$ ions from phenalene and acenaphthylenes. Conflicting labeling evidence and interpretations have been presented concerning the $C_{13}H_9^+$ ions from stilbene.[1,24,25] ^{2}H and ^{13}C labeling studies and MI spectral data have led Güsten and coworkers to the conclusion that $C_{13}H_9^+$ from stilbene contains 75% h plus 25% of an ionic species with a much higher tendency to form $C_7H_5^+$.[25]

MI spectra of $C_{13}H_9^+$ ions from a variety of compounds are listed in Table IV. Güsten and coworkers found that [139+]/[115+] for fluorene and stilbene is 0.48 and 4.4,[25b] respectively, under their experimental conditions; in contrast, our values (1.3 and 1.0) differ very little. Other differences in our MI spectra do not appear to justify further conclusions concerning the structure(s) of the respective $C_{13}H_9^+$ ions.

The CA spectra (Table IV) are closely similar for all ions, except for small variations in *m/e* 139 and 115 which result from low-energy processes of the MI spectrum, and fluctuations of *m/e* 150. For diphenylmethane and stilbene, lowering the electron energy causes dramatic increases in the relative abundance of *m/e* 150, indicating the presence of a second isomeric $C_{13}H_9^+$ ion. This ion has a very distinctive CA spectrum, but one which is incompatible with the additional ion structure proposed by Güsten,[25b] as this was thought to give abundant *m/e* 89 and 115 ions.

The formation of abundant odd-electron ions from the decomposition of even-electron ions is unusual, as this involves loss of a neutral radical species with concomitant electron unpairing. The favored loss of hydrogen from the even-electron $C_{13}H_9^+$ ion probably is due to the low bond strength of C–H in comparison to the C–C bonds, all of which presumably are of higher bond orders. The unusually abundant *m/e* 150 peak of the second $C_{13}H_9^+$ ion could correspond to the cleavage of a carbon–carbon *single bond;* a possible rationalization is the loss of $CH_3\cdot$ from structure j to give k.[26] The close resemblance in Table IV for the CA spectra of $C_{13}H_9^+$ ions produced by 70-eV electrons indicates that these largely have a common structure, such as h or i; even the $C_{13}H_9^+$ ions from 2-methylbiphenyl must contain <10% of the second ion structure.

Relationship of the Structure and the CA Spectrum of an Ion. When an ion cannot be identified by direct matching of its CA spectrum with that of an ion of known structure, it still should be possible to gain structural information from the nature of the fragment ions in the CA spectrum; the ion decomposition pathways resemble those of EI mass spectra,[3] so that the extensive correlations developed for EI spectra[4a] can be used directly. For example, a major difference in the CA spectra of the $C_2H_5O^+$ isomers (Table II) is the abundant *m/e* 15 ion produced by $CH_3O^+{=}CH_2$; the

Table IV. Metastable Ion and Collisional Activation Spectra of $C_{13}H_9^+$ Ions

m/e	Ph$_2$CH$_2$ 70 eV	Ph$_2$CH$_2$ 19 eV[b]	1,2-Diphenylethane	1,1-Diphenylethane	*cis*-Stilbene	*trans*-Stilbene 70 eV	*trans*-Stilbene 16 eV	*trans*-Stilbene 14.5 eV	1,1-Diphenylethylene	Fluorene 70 eV	Fluorene 16 eV	2-Methylbiphenyl	2-Bromofluorene	(p-ClC$_6$H$_4$)$_2$-CH$_2$	9,10-Dihydrophenanthrene	2,5-Diphenyloxazole	4,5-Ph$_2$-imidazole 70 eV	4,5-Ph$_2$-imidazole 22 eV	2-Phenylindole
Metastable Ion Spectra[a]																			
115	0.19		0.42	0.16	0.70	0.62			0.73	0.54		0.22	0.67	0.38	0.66	0.12	0.72		
139	0.19		0.41	0.17	0.89	0.79			0.93	0.54		0.24	0.78	0.46	0.98	0.18	0.92		
163	3.6		1.9	2.5	*a*	*a*			3.2	*a*		3.8	1.7	1.7	9.5	<1.8	1.8		
164	100		100	100	100	100			100	100		100	100	100	100	100	100		
Collisional Activation Spectra[b]																			
27	0.4		0.2	0.4	0.4	0.3	0.4		0.4	0.4	0.4	0.4	0.3	0.3	0.4	0.5	0.3	0.6	0.3
39	5	4	5	5	5	5	5	3	6	6	5	5	5	6	5	5	6	5	5
51	8	9	7	8	8	8	9	5	8	8	9	8	7	8	8	8	8	7	8
63	20	19	20	21	20	20	20	17	20	20	20	21	20	20	20	19	21	20	20
75	17	17	17	17	17	17	17	17	17	17	18	17	17	16	17	16	17	17	17
87	21	18	21	20	20	20	20	21	20	21	21	21	20	21	20	20	20	19	21
99	11	10	11	11	10	10	10	12	10	10	10	11	11	10	11	11	10	10	11
115	32	32	34	32	32	32	22	19	33	35	28	33	34	28	31	33	37	26	39
125	18	23	19	18	20	20	19	25	19	18	17	18	19	19	19	21	18	22	17
139	71	55	72	71	71	71	51	74	70	76	57	74	73	81	66	69	79	58	90
150	85	429	58	68	57	57	130	615	57	46	47	88	53	51	57	56	46	47	43

[a] Abundances normalized to *m/e* 164 = 100 as some *m/e* 163 peaks were not resolvable; [*m/e* 150] = <10% [*m/e* 139]. [b] Abundances normalized to the sum of all ions except *m/e* 115, 139, and 150; *m/e* 164 not resolved except in the 19-eV spectrum of diphenylmethane in which it has an abundance value of 9000; values for *m/e* 115 and 139 have been corrected for unimolecular metastable contributions except for low-energy data.

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[23] T. H. Kinstle and P. J. Ihrig, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, No. O110.

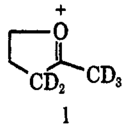
[24] P. F. Donaghue, P. Y. White, J. H. Bowie, B. D. Roney, and H. J. Rodda, *Org. Mass Spectrom.*, **2**, 1061 (1969); J. H. Bowie and P. Y. White, *Aust. J. Chem.*, **24**, 205 (1971); *Org. Mass Spectrom.*, **6**, 135 (1972).

[25] (a) H. Güsten, L, Klasinc, J. Marsel, and D. Milivojevic, *Org. Mass Spectrom.*, **5**, 357 (1971); (b) **6**, 175 (1972).

[26] Recently, Dr. J. Winkler has determined CA and MI spectra of ions from $C_6H_5CD_2C_6H_5$. These data are qualitatively consistent with complete hydrogen scrambling in the formation of $C_{12}H_6^+$; the CA spectral peaks are too broad for accurate results. We are indebted for Dr. D. M. Jerina for synthesis of this compound.

loss of CH_2O from such oxonium ions of ethers is well known.[4a]

CA spectra provide support for the structures postulated for the isomeric ions formed by the competing methyl-loss decompositions of 2-hexanone.[27] Structures l and m were presumed to be formed in the losses



l

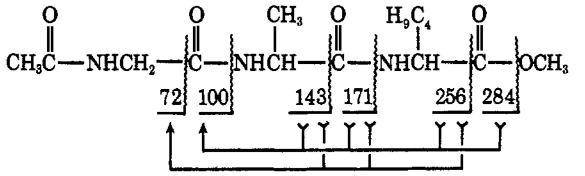
$CH_3CH_2CH_2CD_2CO^+$

m

of $CH_3\cdot$ and $CD_3\cdot$, respectively, from $CH_3CH_2CH_2CD_2COCD_3$.[28] The largest peak in the CA spectrum of m is at *m/e* 59, presumably $C_3H_7CD_2^+$, corresponding to the expected[4a] loss of CO; a peak of 9% of its abundance occurs at *m/e* 43, presumably $C_3H_7^+$. On the other hand, the largest peaks (and their probable assignments) in the CA spectrum of l are *m/e* 46 (CD_3CO^+), 62 (loss of C_2H_4), and 72 (loss of $CD_3\cdot$). The presence of these peaks in the normal EI spectrum would not be indicative of the structures of l or m, of course, as other precursors are possible in the EI spectrum. In addition, the *m/e* 72 peak is present in only 0.06% abundance in the EI spectrum, probably because l can only be formed with relatively low internal energies. (The rearrangement formation of l from 2-hexanone is the lowest energy process;[27] the appearance potential for the prominent $(M - C_3H_6)\cdot^+$ ion is only 0.6 eV higher, so that formation of the latter ion should compete effectively with the formation of higher energy l ions.) Thus, in this case collisional activation apparently gives l ions of higher internal energies than those achieved in the electron-impact formation of l.

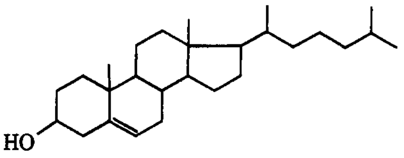
Loose-Complex Reactions. A useful difference in MI and CA spectra is that in the latter simple cleavage reactions are more favored in comparison to reactions with tight activated complexes such as rearrangements.[6,14c] A variety of examples show that [loose]/[tight] values are often an order of magnitude larger in CA spectra, although these values may still not be as large as those of EI mass spectra. Examples of these ratios for MI, CA, and EI spectra, respectively, are: nitrobenzene, $[(M - NO_2)^+]/[(M - NO)\cdot^+]$, 0.05, 8, 10; *n*-butyrophenone, $[(M - C_3H_7)^+]/[(M - H_2O)\cdot^+]$, 0.6, 5, 100; phenyl butyrate, $[(M - C_6H_5O)^+]/[(M - C_4H_6O)\cdot^+]$, 0.1, 0.6, 0.6; and triphenylcarbinol, $[(M - C_6H_5)^+]/[(M - C_7H_6O)\cdot^+]$, 0.1, 1.4, 4.

The mass spectral elucidation of amino acid sequences in oligopeptides utilizes the characteristic peaks arising from simple cleavages of the polyamide chain. MI spectra have been utilized for this,[29] especially for the sequencing of mixtures;[30] as expected, these reactions are more favored in CA spectra. Thus the MI spectra of the EI ions of Ac-Gly-Ala-Leu-OCH_3 only showed the sequence peak *m/e* 143 → 100 corresponding to Ac-Gly-Ala$^+$ → Ac-Gly$^+$, while their CA spectra gave sufficient peaks for elucidation of the complete sequence.[31] This method could also be applied to peptide ions formed by chemical ionization[30] or field ionization.[32] Beckey's "field desorption" technique gives molecular ion information on samples of very low volatility, such as an underivatized nonapeptide, but fragmentation is insufficient for sequence determination;[32] CA spectra could supply this information.

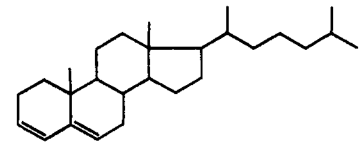


$$CH_3\overset{O}{\overset{\|}{C}}-NHCH_2-\overset{O}{\overset{\|}{C}}-NH\overset{CH_3}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-NH\overset{H_9C_4}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-OCH_3$$

Other Applications to Molecular Structure Determination. The usefulness of metastable ion information concerning reaction pathways for structure elucidation is well known;[4] CA spectra should be much more useful in this application because of the larger number of pathways observable.[33] The increased tendency in CA spectra for simple cleavage reactions has obvious advantages for structure characterization. It may also be possible to gain information on the relationship of structural features of unknown larger molecules by observing the effect of their presence on the CA spectra of analogous ions. For example, the EI spectrum of cholesterol (n) shows significant $(M - CH_3)^+$ and $(M - H_2O)\cdot^+$ peaks indicative of the presence of methyl and hydroxyl groups in the molecule. In the CA spectra of the $(M - H_2O)\cdot^+$ ion (possibly o) the peak corresponding to the loss of CH_3 is of almost the same abundance (1.1%) relative to the precursor as that (1.0%) of the methyl-loss peak in the CA spectrum of the molecular ion. This is consistent with the fact that the OH group of n is sufficiently removed from the sites of potential CH_3 loss that the structural change accompanying H_2O loss has little effect on the methyl-loss peak of the CA spectrum.



n



o

Further studies utilizing CA spectra in the elucidation of ion and molecular structures and ion decomposition pathways will be reported separately.

Acknowledgments. We are indebted to Drs. Ian Howe, Chava Lifshitz, D. J. McAdoo, and Timothy Wachs for helpful discussions.

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(27) F. W. McLafferty, D. J. McAdoo, and J. S. Smith, *J. Amer. Chem. Soc.*, **91**, 5400 (1969).

(28) Abundances in the EI spectrum relative to the base peak, $C_2D_3O^+$, are h, 3%, and i, 9%.

(29) M. M. Shemyakin, Y. A. Ovchinnikov, and A. A. Kiryushkin in "Mass Spectrometry: Techniques and Applications," G. W. A. Milne, Ed., Wiley-Interscience, New York, N. Y., 1972, p 289.

(30) F. W. McLafferty, R. Venkataraghavan, and P. Irving, *Biochem. Biophys. Res. Commun.*, **39**, 274 (1970); H.-K. Wipf, P. Irving, M. McCamish, R. Venkataraghavan, and F. W. McLafferty, *J. Amer. Chem. Soc.*, in press.

(31) A more thorough study of this application will be reported separately: K. Levsen, H.-K. Wipf, and F. W. McLafferty, *Org. Mass Spectrom.*, submitted for publication.

(32) H. U. Winkler and H.-D. Beckey, *Biochem. Biophys. Res. Commun.*, **46**, 391 (1972).

(33) The elemental composition of the neutral lost in a particular CA reaction can sometimes be determined by examining the CA spectrum of the precursor ion containing a natural isotope. Thus the $C_3H_5^+$ product ion (*m/e* 41) in the MI and CA spectra of $C_3H_7O^+$ (*m/e* 59) does not shift to *m/e* 43 in the spectra of $C_3H_7{}^{18}O^+$ (*m/e* 61).