reciprocals of the specific rate constants. The equilibrium constants are the negatives of the abscissa intercepts. The equilibrium constants can also be calculated by dividing the ordinate intercepts, $1/k$, by the slopes, $1/kK_2$. The values of K_2 and k obtained for the three temperatures are listed in Table II.

TABLE II
SPECIFIC RATE AND EQUILIBRIUM CONSTANTS FOR THE PYROSULFATE DECOMPOSITION IN EQUIMOLAR $(Na,K)NO_3$

T, °C.	$k \times 10^3$, min.$^{-1}$	$K \times 10^2$, ref. 3	$K \times 10^2$, this study
250	31 ± 6	26	7.2 ± 0.7
275	74 ± 3		21.8 ± .2
300	162 ± 1		50.8 ± .1

The concentration of total acid, T_a, present at any time was determined by an iodometric titration.[3] Six or seven samples were taken at each of two temperatures, 250 and 300°, and the corresponding potentials recorded. The constant K_1 was determined from each sample with the aid of eq. 9. At both temperatures it was observed that the dissociation constant K_1 increased with time. This increase can probably be explained by taking into account the increase in sulfate ion concentration which had been assumed to be constant in the derivation of eq. 9. Since the sulfate ion concentration was known accurately initially, the data at each temperature were extrapolated back to zero time. The experimentally determined values of K_1 are listed in Table III. The values of K_1 at zero time are

$$K_1 (250°) = (2.7 \pm 0.3) \times 10^{-26}$$

$$K_1 (300°) = (5.7 \pm 0.1) \times 10^{-24}$$

If the assumption is made that the enthalpy of dissociation is constant over the temperature range 250–300°, the enthalpy of dissociation can be calculated from the Clausius–Clapeyron equation. The $\Delta H°$ value thus obtained and the $\Delta G°$ and $\Delta S°$ values for the nitrate ion dissociation are given in Table IV.

TABLE III
VARIATION OF K_1 WITH TIME

T, °C.		$K_1 \times 10^{27}$	T, °C.		$K_1 \times 10^{23}$
250	60 min.	3.79	300	6 min.	2.32
	75 min.	3.98		10 min.	3.54
	90 min.	4.93		16 min.	5.48
	105 min.	5.01		25 min.	8.36
	4 hr.	6.74		30 min.	9.89
	5 hr.	7.89		38 min.	11.91
	6 hr.	10.40			

TABLE IV
VALUES OF $\Delta H°$, $\Delta G°$, AND $\Delta S°$ FOR THE NITRATE ION DISSOCIATION

T, °C.	$\Delta G°$, kcal.	$\Delta H°$, kcal.	$\Delta S°$, e.u.
250	60.9		4.6
275		63.3	
300	60.6		4.7

No mention has been made as to what form the oxide ion takes when in solution in fused nitrates. The measurements so far involved only require the oxide ion to exist as such on the electrode surface and an equilibrium between the oxide ion and any solvated species. It seems reasonable that in a solution of alkali nitrates the oxide ion could exist in forms containing Na^+, K^+, or NO_3^-. The existence of an orthonitrate ion, NO_4^{-3}, has been postulated by several workers, among the more recent of which is Kohlmuller,[7] who prepared both sodium and potassium orthonitrates by dissolving alkali oxides in alkali nitrates. It may be that the orthonitrate ion can exist in solution in alkali nitrate solvents, at least in small concentrations. However, a spectroscopic analysis of such a solution would be needed to establish unequivocally the existence of the orthonitrate ion.

(7) R. Kohlmuller, *Ann. chim.* (Paris), **4**, 1183 (1959).

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, AMERICAN OIL CO., WHITING, IND.]

Organic Ions in the Gas Phase. XIII. Cycloheptatriene-7-d; Decomposition of C₇H₈⁺ and C₇H₈⁺⁺ from Cycloheptatriene and Toluene

BY SEYMOUR MEYERSON

The mass spectra of cycloheptatriene unlabeled and -7-d show that, as in other C_7H_8 isomers, the eight hydrogen atoms lose positional identity in nearly all the decomposition reactions of singly ionized molecules produced by electron impact. Such loss of identity occurs also in decomposition of doubly ionized cycloheptatriene to $C_7H_7^+{}^+$ and to $C_7H_6^{++}$ and of doubly ionized toluene to $C_7H_6^{++}$, but, in the process whereby doubly ionized toluene loses a hydrogen atom to form $C_7H_7^-{}^+$, any one hydrogen in the methyl group is about four times as likely to be lost as one in the ring. Thus the distinction between methyl and ring hydrogens survives in the excited doubly ionized state or states involved.

Loss of a hydrogen atom from toluene under electron impact—to give a $C_7H_7^+$ ion that most probably has the symmetrical tropylium structure[1,2]—is preceded or accompanied by a rearrangement in which the eight hydrogen atoms lose identity, as shown by the mass spectra of variously deuterated species of toluene.[1,2] The questions raised by this finding transcend the toluene system in which they originated. Eight other C_7H_8 isomers have been subjected to electron impact in a mass spectrometer: cycloheptatriene-1,3,5,[2–4] bicyclo-[2.2.1]heptadiene-2,5,[2,4,5] spiro[2.4]heptadiene-1,3,[2,4,6] 1-ethinylcyclopentene,[2,4] 3-ethinylcyclopentene,[2,7] methylfulvene,[8] quadricyclene,[8] and heptadiyne-1,6.[9] All of them have spectra remarkably similar to that of toluene. Moreover, the two ethinylcyclopentenes have

(1) P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957).

(2) H. M. Grubb and S. Meyerson, in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, Inc., New York, N. Y., 1963, p. 453.

(3) S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957).

(4) V. Hanuš and Z. Dolejšek, *Kernenergie*, **3**, 836 (1960).

(5) S. Meyerson, J. D. McCollum, and P. N. Rylander, *J. Am. Chem. Soc.*, **83**, 1401 (1961).

(6) V. Hanuš, *Nature*, **184**, 1796 (1959).

(7) V. Hanuš and Z. Dolejšek, *Jaderná energie*, **6**, 350 (1960).

(8) V. Hanuš and Z. Dolejšek, *Collection Czechoslov. Chem. Commun.*, **28**, 652 (1963); Z. Dolejšek, V. Hanuš, and H. Prinzbach, *Angew. Chem.*, **74**, 902 (1962).

(9) R. F. Kendall, F. O. Cotton, N. G. Foster, and B. H. Eccleston, presented before ASTM Committee E-14, New Orleans, La., June 1962.

been labeled with deuterium in the β-position, and the mass spectra of both, like those of deuterated toluenes, show essentially statistical loss of protium and deuterium in the primary cleavage.[4,7] Finally, appearance-potential measurements on toluene, cycloheptatriene, and bicycloheptadiene lead to nearly identical values for the energy of the lowest excited ionized state $C_7H_8^{+*}$ from which decomposition to $C_7H_7^+$ occurs.[2,3,5] Thus, the nine isomers seem to decompose largely by common reaction paths *via* common intermediates.

The labeling data call for high symmetry in $C_7H_8^{+*}$. In terms of classical structures, such an intermediate might resemble the ground-state cycloheptatriene molecule more closely than any of the other isomers. If so, cycloheptatriene itself might be expected to lose a hydrogen atom from the 7-position before equilibration with the remaining atoms. Such a reaction would parallel the hydride transfer by which cycloheptatriene can be converted to tropylium ion in solution.[10] The hope of testing this possibility and perhaps of gaining some additional insight into the chemical species involved prompted study of the mass spectra of cycloheptatriene unlabeled and -7-*d*.

The data obtained opened another area to at least preliminary exploration. The spectrum of cycloheptatriene contains a group of peaks at m/e 42 to 46 due solely to doubly charged ions. Such a group, free of interference from singly charged ions, offers an unusual opportunity to learn something of the decomposition reactions of a doubly ionized molecule. Realization of this possibility prompted study also of the corresponding regions in the spectra of deuterated toluenes. Attention was focused on the loss of hydrogen to produce $C_7H_7^{++}$ and $C_7H_6^{++}$.

Experimental

The author is indebted to A. P. ter Borg, H. Kloosterziel, and A. F. Bickel, of the Koninklijke/Shell-Laboratorium, Amsterdam, The Netherlands, for the generous gift of the cycloheptatriene samples. Isotopic purity of the deuterated species, by low-voltage mass spectrometry,[11] was $94.0 \pm 0.5\%$, in agreement with the Shell measurements of 93.9% by mass spectrometry and 94.0% by electrical integration of the n.m.r. spectrum.[12]

In accord with recommended precautions,[12] the vials in which the cycloheptatriene-7-*d* was repackaged, the syringe used to transfer it, and the micropipet used to introduce it into the spectrometer were all pretreated with alkali to avoid possible hydride exchange on acid sites. To reduce the likelihood of thermal isomerization, the ion-source heating coil was disconnected and the source was allowed to cool to its equilibrium temperature of 140°. At this temperature, the half-life of cycloheptatriene-7-*d* with respect to isomerization to other deuterated species is about 150 hr.[12]; thus no appreciable thermal isomerization should occur during the few milliseconds spent in transit through the source. Reducing the source temperature was later found to have been unnecessary; the spectrum measured at the normal operating temperature of 250°—as well as derived label retentions in fragment ions—was almost exactly the same as that at 140°. After the mass-spectral measurements were completed, the material was examined by n.m.r. spectroscopy, which gave no evidence for deuterium in any position other than the original methylene group.

Mass spectra were measured on a Consolidated model 21-103c instrument with 70-v. electrons. Possible voltage-dependence of label retention in $C_7H_7^+$ and $C_5H_5^+$ was checked by measuring the C_7 and C_5 spectral regions repeatedly as ionizing voltage was increased stepwise from the appearance potentials of these respective ions to 70 v. For these measurements, the repellers were maintained at a potential of 3 v. Procedures used to calculate label retention in fragment ions and voltage dependence of label retentions have been described elsewhere.[2,13–15]

(10) H. J. Dauben, F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957); Z. N. Parnes, M. E. Vol'pin, and D. N. Kursanov, *Tetrahedron Letters*, **21**, 20 (1960); K. Conrow, *J. Am. Chem. Soc.*, **83**, 2343 (1961).

(11) D. P. Stevenson and C. D. Wagner, *ibid.*, **72**, 5612 (1950); R. E. Honig, *Anal. Chem.*, **22**, 1474 (1950).

(12) A. P. ter Borg, H. Kloosterziel, and A. F. Bickel, private communication; A. P. ter Borg, H. Kloosterziel, and N. van Meurs, *Proc. Chem. Soc.*, 359 (1962); *Rec. trav. chim.*, **82**, 717 (1963).

In the study of doubly charged ions, deuteriotoluene spectra reported in earlier work[1] were remeasured to ensure that they all correspond to uniform instrumental conditions and were supplemented by spectra of toluene-2,3-d_2 and -2,3,4,5,6-d_5. The author is indebted for the gift of the former to L. C. Leitch,[16] of the National Research Council of Canada, and of the latter to F. R. Jensen, of the University of California. Isotopic analysis of these species, made by low-voltage mass spectrometry,[11] gave: toluene-2,3-d_2, 0.3% unlabeled, 17.0% d_1, 82.7% d_2; toluene-2,3,4,5,6-d_5, 1.9% d_4, 98.1% d_5.

Results

Table I shows the cycloheptatriene mass spectra, corrected for naturally occurring C^{13} and D,[17] and for contributions of the unlabeled species in the labeled material. Except for the excess intensity at m/e 42 in the spectrum of the labeled species beyond that in the spectrum of the unlabeled one, the peaks of m/e 42 to 47 inclusive were assumed due solely to doubly charged ions and corrected accordingly for naturally occurring heavy isotopes. At all other masses, contributions of doubly charged ions are evidently small and were ignored in making the corrections.

Metastable peaks[2] establish the decomposition paths

$$C_7H_8^+ \xrightarrow{-H} C_7H_7^+ \xrightarrow{-C_2H_2} C_5H_5^- \xrightarrow{-C_2H_2} C_3H_3^-$$
$$92 \qquad 91 \qquad 65 \qquad 39$$

$$C_7H_8^{++} \xrightarrow{-H_2} C_7H_6^{-+}$$
$$92 \qquad 90$$

The first of these is known from metastable-peak evidence to occur in all C_7H_8 isomers that have been studied in the mass spectrometer.[1,2,4,5,7–9] The second finds similar support in the spectra of toluene and bicycloheptadiene measured in this Laboratory; it has not been reported in the other isomers.

Table II shows label retentions in several fragment ions in the spectrum of the deuterated species. Values in the column headed "Statistical" were calculated on the assumption that the eight hydrogen atoms in the molecule are fully scrambled in forming the fragment ions. In all except four ions, the value so calculated is close to the observed retention. In two of these, $C_2H_3^+$ and CH_3^+, the "observed" values may be in error due to neglect of isotope effects on relative intensities of the various ions that enter into the calculation.[2] Total intensities in the two- and one-carbon regions differ appreciably between the two spectra; which specific ion yields are implicated is not known. For the ions in question, the first "observed" value was obtained by a calculating sequence starting at the high-mass end of the two- or one-carbon region; the second, at the low-mass end. The discrepancy corresponds to the cumulative errors caused by neglect of isotope effects. The differences between observed and statistical retentions in the other two ions, $C_6H_6^+$ and $C_6H_5^+$, are greater and cannot be so accounted for; they require another explanation.

Label retentions in both $C_7H_7^+$ and $C_5H_5^+$ were found constant at about 90% and 60%, respectively, throughout the entire range of ionizing voltage, except possibly for slightly lower values in the long shallow tail of the $C_5H_5^+$ ionization-efficiency curve immediately above the appearance potential.

Table III shows partial spectra of doubly charged ions from the cycloheptatrienes, recalculated to a scale on which relative intensity of $C_7H_8^{++}$ equals 100. Table

(13) S. Meyerson and P. N. Rylander, *J. Phys. Chem.*, **62**, 2 (1958).

(14) S. Meyerson, *J. Chem. Phys.*, **34**, 2046 (1961).

(15) S. Meyerson, T. D. Nevitt, and P. N. Rylander, in "Advances in Mass Spectrometry," Vol. 2, R. M. Elliott, Ed., Pergamon Press, New York, N. Y., 1963, p. 313.

(16) R. N. Renaud, D. Kovachic, and L. C. Leitch, *Can. J. Chem.*, **39**, 21 (1961).

(17) J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," D. Van Nostrand Co., Princeton, N. J., 1960.

TABLE I
MASS SPECTRA OF CYCLOHEPTATRIENES

m/e^a	Unlabeled	7-d	m/e	Unlabeled	7-d
12	0.71	0.72	47.3 m	...	0.20
13	.68	.62	48	0.36	0.32
14	.84	.66	49	2.48	2.07
15	3.60	2.51	50	13.0	10.4
16	0.07	1.81	51	18.7	15.7
			52		5.32	9.58
23.4 m	.02	...	53	3.71	3.96
24	.18	0.24	54	...	2.41
25	1.12	1.04			
25½ d	0.07	0.04			
26	9.08	7.17	60	0.93	0.86
26½ d	...	0.02	61	6.28	5.08
27	18.1	12.9	62	11.6	8.86
28	0.66	9.76	63	23.4	16.5
29	.09	0.42	64	4.23	10.6
30	..	.04	65	45.2	19.0
31 d	.57	.56	66	4.30	28.1
31½ d	.11	.22	67	...	3.42
32 d	.23	.34	72	0.05	0.04
32½ d	.01	.04	73	0.37	0.36
33	...	.02	74	1.41	1.12
			75	0.98	0.94
35.0 m	.04	.02	76	0.77	0.70
36	.73	.80	77	2.98	1.89
37	8.37	7.23	78	0.52	1.71
37½ d	0.07	0.04	79	.04	0.14
38	16.7	13.8	80	.01	0.02
38½ d	...	0.04			
39	58.3	40.0	84	.57	0.46
40	6.24	26.3	85	1.59	1.06
41	4.08	4.80	86	2.03	1.43
42 {	...	2.45	87	1.11	1.06
42 { d	0.26	0.26	88	0.18	0.52
42½ d	0.30	0.16	88.0 m	0.45	...
43	3.78	3.07	89	9.36	3.01
43½ d	0.57	1.27	89.0 m	...	0.44
44 d	1.48	0.80	90	2.28	6.29
44.0 m	0.32	...	90.0 m	4.44	...
44.5 d	0.89	0.90	91	257	28.7
44½ m	...	0.38	91.0 m	...	3.42
45 d	7.60	2.35	92	100.0	229
45½ d	2.98	6.15	93	...	100.0
46 d	4.14	2.65			
46.4 m	0.30	...			
46½ d	...	4.22			

Metastable transitions

23.4	(65^+)	→ (39^-)	+ 26
35.0	(39^+)	→ $(37')$	+ 2
44.0	(92^{+-})	→ (90^{-+})	+ 2
44.5	(93^{--})	→ (91^{++})	+ 2
46.4	(91^+)	→ (65^+)	+ 26
47.3	(92^+)	→ (66^-)	+ 26
88.0	(92^+)	→ (90^-)	+ 2
	or (90^-)	→ (89^+)	+ 1
89.0	(93^-)	→ (91^-)	+ 2
	or (91^+)	→ (90^+)	+ 1
90.0	(92^+)	→ (91^+)	+ 1
91.0	(93^+)	→ (92^-)	+ 1

[a] m denotes a metastable peak; d denotes a peak due to a doubly charged ion.

TABLE II
LABEL RETENTIONS IN FRAGMENT IONS FROM CYCLOHEPTATRIENE-7-d

Ion	Observed, %	Statistical, %	Ion	Observed, %	Statistical, %
$C_7H_7^+$	89.1	87.5	$C_2H_4^+$	56	50.0
$C_6H_6^+$	27	75.0	$C_2H_3^-$	52.3, 39.9	37.5
$C_6H_5^+$	45	62.5	CH_2^+	50, 44	37.5
$C_5H_6^+$	79.5	75.0	$C_7H_7^{+-}$	88.8	87.5
$C_5H_4^+$	60.1	62.5	$C_7H_6^{++}$	76.6	75.0
$C_4H_5^+$	65.0	62.5			
$C_4H_4^+$	50.0	50.0			
$C_3H_5^+$	60.0	62.5			
$C_3H_4^-$	50.8	50.0			
$C_3H_3^+$	39.8	37.5			

the labeled species than in that of the unlabeled one. All the labeled toluenes similarly show $C_7H_8^{++}$:$C_7H_8^+$ intensity ratios slightly higher than that of the unlabeled species.

TABLE III
PARTIAL SPECTRA OF CYCLOHEPTATRIENES

m/e	Unlabeled	7-d
44½	21.5	21.3
45	184	55.8
45½	72.0	145.8
46	100.0	62.9
46½	...	100.0

TABLE IV
PARTIAL SPECTRA OF TOLUENES

m/e	Un-labeled	2-d	3-d	4-d	α-d	2,3-d_2	α-d_1[a]	2,3,4,5,6-d_5[b]
44½	13.8	22.4	23.1	22.1	21.4	9.6	8.8	c
45	157.6	58.3	53.4	48.0	40.6	21.3	12.0	c
45½	61.4	120.8	122.8	120.9	128.1	61.3	23.3	c
46	100.0	57.7	58.4	58.6	49.0	94.7	78.6	c
46½	...	100.0	100.0	100.0	100.0	52.5	91.4	49.5
47	...	...	...	...	...	100.0	26.2	78.8
47½	...	...	...	...	...	...	100.0	35.3
48	...	...	...	...	...	...	...	43.8[d]
48½	...	...	...	...	...	...	...	100.0

[a] Uncorrected for 5.1% toluene-d_2 and 0.1% -d_1. [b] Uncorrected for 1.9% toluene-d_4. [c] Omitted because of probable interference from singly charged ions at integral values of m/e 46 and less. [d] Corrected for estimated contribution of C_4^+.

TABLE V
LABEL RETENTIONS IN DOUBLY CHARGED IONS

	—$C_7H_7^{++}$, %—		—$C_7H_6^{++}$, %—	
	Obsd.	Calcd.[a]	Obsd.	Calcd.[b]
Cycloheptatriene-7-d	87.4	87.5	75.0	75.0
Toluene-2-d	94.0	94	74.3	75.0
-3-d	95.1	94	76.0	75.0
-4-d	95.4	94	74.9	75.0
α-d	79.8	77	73.4	75.0
-2,3-d_2[c]	85.5	88	54.4	53.6
-α-d_3[c]	33.9[d]	31	32.2[d]	35.7
-2,3,4,5,6-d_5[c]	68.2[d]	70	9.5[d]	10.7

[a] Calculated on assumption that probability of losing each ring hydrogen atom in toluene is 6%; each methyl hydrogen, 23%. In cycloheptatriene, the eight hydrogen atoms were assumed equivalent. [b] Calculated on assumption of random loss of two of the eight hydrogen atoms. [c] Retention of all the original deuterium atoms. [d] Includes approximate corrections for isotopic impurities.

IV shows partial spectra of the toluenes similarly calculated. Label retentions derived from Tables III and IV are collected in Table V in the columns headed "Observed." Differences between the cycloheptatriene-7-d values in Tables II and V result from the change in scale of relative intensities[15] and reflect the slightly higher $C_7H_8^{++}$:$C_7H_8^+$ intensity ratio in the spectrum of

Label retentions in $C_7H_7^{++}$ and $C_7H_6^{++}$ from cycloheptatriene-7-d and in $C_7H_6^{++}$ from the deuterated toluenes imply that formation of these ions, as of most of the singly charged ions in the spectra, is preceded or accompanied by loss of identity of the eight hydrogen atoms. Retentions that would follow from such randomization are listed in Table V in the columns headed "Calculated." Discrepancies between observed and

calculated values may arise in part from experimental uncertainties; in part from unknown isotope effects; and in part, in the cases of toluene-α-d_3 and -2,3,4,5,-6-d_5, from approximations made in correcting for isotopic impurities.

Discussion

The general agreement between observed and calculated values in Table II implies that nearly all fragment ions formed from cycloheptatriene arise in decomposition paths in which the eight hydrogen atoms lose positional identity. Some disagreement, however, shows that nonrandomizing paths also exist.

Radomizing Processes.—Constancy of label retention in $C_7H_7{}^+$ and $C_5H_5{}^+$ as ionizing voltage is varied from the appearance potential to 70 v. suggests that randomization in forming these ions is effected by a single reaction path, rather than by a fortuitous combination of multiple contributing paths. The primary decomposition step is apparently preceded or accompanied by rearrangement of the parent ion to a configuration of higher symmetry than that of the original molecule. This behavior of cycloheptatriene-7-d parallels that of labeled species of other C_7H_8 isomers.

Present data thus add support to the idea that the nine isomers studied decompose largely *via* common intermediates - of which $C_7H_8{}^{+*}$ refers to the one of lowest energy—characterized by higher symmetry than that of any of the original molecules. The intermediate $C_7H_8{}^{+*}$ is perhaps best represented as a tropylium ion with an extra hydrogen atom that is bonded equally to — or that spends equal time on—each of the seven carbon atoms.

Randomization in the $C_7H_8{}^+$ ion may have a bearing on the mechanism by which bitropyl is formed in the radiolysis of cycloheptatriene. In bitropyl so derived from cycloheptatriene-7-C^{14}, the label is distributed randomly throughout the cycloheptatrienyl group.[18] This finding has been interpreted as evidence for a radical-combination mechanism

$$2C_7H_7 \longrightarrow C_7H_7C_7H_7$$
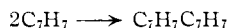
rather than a reaction involving an excited or ionized molecule

$$C_7H_8{}^* + C_7H_8 \longrightarrow C_7H_7C_7H_7 + H_2$$
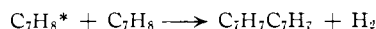
because "it is . . . difficult to see how the primary process, *i.e.* the formation of a positively charged radical ion, could be responsible for the randomization."[18] The matter would seem now to merit reconsideration.

Nonrandomizing Processes.—Although the nine C_7H_8 spectra show striking similarities, they are not identical. Spectral differences and associated label retentions in five of the isomers—toluene,[2,3,19] bicycloheptadiene,[2,4,5] 1-ethinylcyclopentene,[4] quadricyclene,[8] and heptadiyne-1,6[9]—have been accounted for by competing reaction paths specifically related to the initial structures. In cycloheptatriene, also, a small part of the total ion yield apparently arises by decomposition of the parent ion without prior rearrangement.

The observed retentions in $C_6H_6{}^+$ and $C_6H_5{}^+$ indicate preferential loss of the elements of the original methylene group. Formation of $C_6H_6{}^+$ from cycloheptatriene
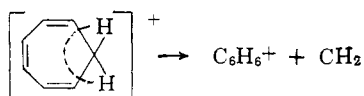
thus resembles—except for the net charge on the molecule—the reverse of the synthesis of cycloheptatriene from benzene and photolyzed diazomethane.[18] This is

(18) G. Juppe and A. P. Wolf, *J. Am. Chem. Soc.*, **83**, 337 (1961).

(19) P. N. Rylander and S. Meyerson, *J. Chem. Phys.*, **27**, 1116 (1957).

the first clear case, to the author's knowledge, of loss of CH_2 from the parent ion of a hydrocarbon other than ethylene[20,21] and cyclopropane.[20,22] Such a reaction may be regarded as analogous to the loss of CO from aromatic carbonyl compounds and quinones[23]; of CF_2 from perfluoroxylenes, perfluorotoluene, and benzotrifluoride[24]; and of CCl_2 from hexachlorocyclopropane.[25] The differences in frequency and intensity with which these processes are observed in mass spectra of appropriate compounds seem to parallel differences in stability of the four divalent species.

Relative label retentions in $C_7H_7{}^+$ and $C_5H_5{}^+$ from cycloheptatriene-7-d suggest that a small part of the $C_5H_5{}^+$ yield arises by a nonrandomizing process. If $C_5H_5{}^+$ arose solely by decomposition of a completely symmetrical $C_7H_7{}^+$ ion, retention in $C_5H_5{}^+$ should be $5/7 \times 89.9\%$ or 63.6%; if the reaction involves an isotope effect, the figure would be expected to be slightly higher.[26] The observed retention of 60.1% can be accounted for by assuming that 5.5% of the $C_5H_5{}^+$ yield arises by an alternative path directly from the unrearranged parent ion
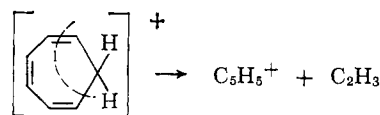

Similar discrepancies suggested that 4 to 9% of the $C_5H_5{}^+$ yields from labeled toluenes—the specific amount depending on the isomer—are formed from the parent ions by loss of the original methyl group and the attached ring carbon.[3]

Doubly Charged Ions.—In view of the known randomization of hydrogen atoms in singly ionized C_7H_8 molecules, and of the even greater disturbance of the electronic structure expected to result from double ionization, the evidence for complete randomization in the reactions

$$\text{cycloheptatriene}^{+-} \longrightarrow C_7H_7{}^{+-} + H$$
$$\text{cycloheptatriene}^{+-} \longrightarrow C_7H_6{}^{--} + H_2$$
$$\text{toluene}^{++} \longrightarrow C_7H_6{}^{++} + H_2$$

is interesting but not unexpected. Far more surprising is the finding that the reaction

$$\text{toluene}^{++} \longrightarrow C_7H_7{}^{-+} + H$$
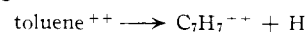
is not accompanied by such randomization. Any one hydrogen atom in the methyl group is about four times as likely to be lost in this reaction as one in the ring. Thus, the distinction between methyl and ring hydrogens survives in the excited doubly ionized state or states involved.

Available energetics data on doubly charged hydrocarbon ions[27] suggest that the appearance potential of $C_7H_7{}^{++}$ is about 30 e.v., some 18 e.v. greater than that of $C_7H_7{}^+$.[3] Thus, loss of identity of hydrogen atoms in ionic decomposition processes cannot be explained simply by invoking high mobility brought on by ionization-excitation to a high energy level. Rather, an explanation must be sought in terms of specific changes

(20) American Petroleum Institute, Research Project 44, "Catalog of Mass Spectral Data," Chemical Thermodynamics Properties Center, Agricultural and Mechanical College of Texas, College Station, Tex., 1947-1962.

(21) V. H. Dibeler, F. L. Mohler, and M. de Hemptinne, *J. Research Natl. Bur. Standards*, **53**, 107 (1954).

(22) P. Natalis, *Bull. Soc. Roy. Sci. Liège*, **29**, 94 (1960).

(23) J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, **63**, 1861 (1959).

(24) J. R. Majer, *J. Appl. Chem.* (London), **11**, 141 (1961).

(25) E. K. Fields and S. Meyerson, *J. Org. Chem.*, **28**, 1915 (1963).

(26) D. P. Stevenson and C. D. Wagner, *J. Chem. Phys.*, **19**, 11 (1951); D. P. Stevenson, *ibid.*, **19**, 17 (1951).

(27) F. L. Mohler, E. G. Bloom, E. J. Wells, J. H. Lengel, and C. E. Wise, *J. Research Natl. Bur. Standards*, **42**, 369 (1949).

in molecular geometry occurring in response to specific driving forces.[28] The stability of the tropylium ion could furnish the driving force for rearrangement of the $C_7H_8^{+*}$ ions derived from the various isomers to a complex of a tropylium ion and a hydrogen atom. The corresponding doubly ionized species evidently does not have the same driving force to attain a configuration of such high symmetry.

Extension to Other Sets of Isomers

Available data on at least three other sets of isomers—allene, propyne,[20,29,30] and cyclopropene[31]; but-1-yne, but-2-yne, buta-1,2-diene, and buta-1,3-diene[20,29,32,33]; and styrene, cyclooctatetraene,[20,34] and benzocyclobutene[35]—suggest interrelationships similar to those linking the several C_7H_8 isomers. In all three cases, the isomeric spectra are strikingly similar. The spectra of propyne-3-d_3, buta-1,3-diene-1,4-d_4, and five deuterated styrenes show essentially complete loss of positional identity of hydrogen atoms before or during primary decomposition steps. Finally, summing the appearance potential of $C_3H_3^+$ derived from each C_3H_4 and C_4H_6 molecule in turn and the heat of formation of the molecule gives virtually identical values for the members of each set of isomers. Each such sum is

the energy of the lowest ionized state of the molecule accessible by electron impact and able to undergo whatever rearrangement and decomposition is required to produce a $C_3H_3^+$ ion.

If decomposition of such isomers does involve prior rearrangement to a common intermediate at a common energy level, the appearance potentials of the fragment ions can be used to calculate differences in stability of the isomers,[2,3,5] but not bond-dissociation energies in the original molecules. If this view is correct, agreement of bond-dissociation energies derived from appearance potentials with values found by other means[36] must be regarded as fortuitous. A similar conclusion was arrived at earlier from consideration of discrepancies between directly and indirectly measured ionization potentials of free radicals, coupled with labeling evidence of rearrangements in molecule-ions as well as fragment ions.[1,2,37] If a group of isomers all go over into a common intermediate before decomposing, the identities of the decomposition products must reflect the structure of the intermediate rather than that of the original molecule subjected to electron impact. Moreover, no *a priori* reason is apparent for supposing that the structure of such an intermediate is more-closely related in any unique fashion to the original structure of one isomer than of another.[37a]

(28) Compare S. Meyerson and R. W. Vander Haar, *J. Chem. Phys.*, **37**, 2458 (1962).

(29) J. Collin and F. P. Lossing, *J. Am. Chem. Soc.*, **79**, 5848 (1957).

(30) J. Collin and F. P. Lossing, *ibid.*, **80**, 1568 (1958).

(31) K. B. Wiberg, W. J. Bartley, and F. P. Lossing, *ibid.*, **84**, 3980 (1962).

(32) F. H. Coats and R. C. Anderson, *ibid.*, **79**, 1340 (1957).

(33) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 138.

(34) E. I. Quinn and F. L. Mohler, *J. Research Natl. Bur. Standards*, **62**, 39 (1959).

(35) Unpublished spectrum, this Laboratory. The sample was kindly furnished by F. R. Jensen of the University of California.

(36) See, for example, R. Schaffer, Ph.D. Thesis, McGill University, Montreal, Can., 1961.

(37) S. Meyerson, P. N. Rylander, E. L. Eliel, and J. D. McCollum, *J. Am. Chem. Soc.*, **81**, 2606 (1959).

(37a) NOTE ADDED IN PROOF.—The mass spectrum of a tenth C_7H_8 isomer, $\Delta^{2,6}$-bicyclo[3.2.0]heptadiene, and appearance potentials of selected ions in the spectrum, were reported recently (C. Lifshitz and S. H. Bauer, *J. Phys. Chem.*, **67**, 1629 (1963)). This spectrum also resembles closely those of the other isomers. Following the suggestion made previously,[2,4,5] the appearance potential of the $C_7H_7^+$ ion was used to estimate the heat of formation of the bicyclo[3.2.0]heptadiene as 2.7 ± 0.2 kcal. per mole.

Cage Combination and Disproportionation of CH₃ + C₂H₅ → Products. The Effect of Solvents and Temperature
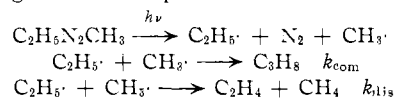
BY P. S. DIXON, A. P. STEFANI, AND M. SZWARC

The cage interaction of methyl and ethyl radicals was investigated over a wide temperature range (-191 to $+85°$). The radicals were produced by photolysis of $CH_3N_2C_2H_5$ in isooctane or in glycol. It was shown that the ratio $k_{dis}/k_{com} = C_2H_4/C_3H_8$ increases with decreasing temperature, the temperature dependence being given by the relation $k_{dis}/k_{com} \sim T^{-0.85}$ for the isooctane reaction and $k_{dis}/k_{com} \sim T^{-0.6}$ for the glycol reaction. At all temperatures k_{dis}/k_{com} is larger for the reaction in glycol than for that in isooctane, although at the lowest temperature, $-191°$, their values differ insignificantly. The observed values of k_{dis}/k_{com} in solution are greater than those reported for the gas phase reaction. The observed features of the reaction Me + Et resemble those described earlier for the reaction Et + Et, and it appears therefore that they are characteristic for the interaction of radicals in solution.

In an earlier study of the cage interaction of ethyl radicals,[1] we attempted to determine whether their combination, $2C_2H_5 \rightarrow C_4H_{10}$, and disproportionation, $2C_2H_5 \rightarrow C_2H_4 + C_2H_6$, involve a common transition state, or whether each reaction proceeds through its own activated complex. Although the results of these investigations did not permit an unambiguous distinction between these two alternatives, they revealed some new features of these processes which are of considerable interest. (1) The ratio k_{dis}/k_{com} was found to be affected by the solvent, its value being greater for a solution reaction than for the gaseous interaction. Its value seems to increase with the internal pressure of the solvent. (2) A definite temperature dependence of

(1) P. S. Dixon, A. P. Stefani, and M. Szwarc, *J. Am. Chem. Soc.*, **85**, 2551 (1963).

the ratio k_{dis}/k'_{com} was observed, disproportionation being favored by lower temperatures in both the gaseous and solution reactions.

It was with the intention of determining whether these phenomena are peculiar to the cage interaction of ethyl radicals or whether they are common to other similar systems that we undertook the present work. The cage interaction of methyl and ethyl radicals produced by photolysis of $C_2H_5N_2CH_3$ solutions was therefore investigated. The process involves the steps

$$C_2H_5N_2CH_3 \xrightarrow{h\nu} C_2H_5\cdot + N_2 + CH_3\cdot$$
$$C_2H_5\cdot + CH_3\cdot \longrightarrow C_3H_8 \quad k_{com}$$
$$C_2H_5\cdot + CH_3\cdot \longrightarrow C_2H_4 + CH_4 \quad k_{dis}$$

and hence the value of k_{dis}/k_{com} is determined by the ratio ethylene/propane.