Chemical Ionization Mass Spectrometry. VI. C_7H_8 Isomers. Toluene, Cycloheptatriene, and Norbornadiene

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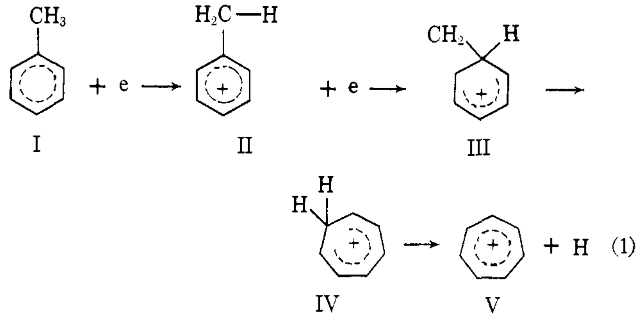
Abstract: Chemical ionization mass spectra are reported for toluene, toluene-α-d_3, cycloheptatriene, cycloheptatriene-7-*d*, and norbornadiene. The spectra of toluene, cycloheptatriene, and norbornadiene differ significantly from each other in that the amount of fragment ions increases as one progresses from toluene to norbornadiene. Ionization processes which involve quite conventional carbonium ion chemistry are postulated for the formation of the major fragment ions. In the deuterated toluene and deuterated cycloheptatriene, D^- abstraction occurs in amounts which are disproportionately high when compared with the relative amounts of deuterium and hydrogen in the molecules, and it is concluded that in the hydride abstraction process by chemical ionization the hydrogens do not become equivalent. The abstraction occurs from the methyl group of toluene and from the methylene group of cycloheptatriene. The formation of the $(MW - 1)^+$ (or $(MW - 2)^+$ in the deuterated compounds) ions occurs by direct hydride ion abstraction either by $C_2H_5^+$ or CH_5^+. Protonation of the toluene or cycloheptatriene followed by loss of H_2 does not seem to occur. However, hydrogen migration does seem to occur in the processes involved in the formation of benzenium and propyl ions from cycloheptatriene.

One of the most interesting discoveries in modern mass spectrometry is that of Meyerson and co-workers[1] concerning the structural rearrangements which occur in aromatic molecules under electron impact. In particular the $C_7H_7^+$ ion is formed from toluene by removal of a hydrogen atom at random from the ring or side chain, and further decomposition of the $C_7H_7^+$ ion is such as to show that the $C_7H_7^+$ ion has a completely symmetrical structure. Meyerson and co-workers explained these phenomena by postulating that the $C_7H_8^+$ ion formed initially from toluene undergoes a rearrangement to an ion containing a seven-membered ring of carbon atoms and equivalent hydrogens, and they further postulate that the $C_7H_7^+$ ion formed by hydrogen loss is the tropylium ion. Somewhat more recently, Meyer and Harrison[2] have postulated a more detailed mechanism, which can be represented by the sequence in eq 1. The toluene ion (II) is converted to the intermediate ion (III) by a hydrogen atom shift to the 1-carbon atom, and IV is formed from III by insertion of the CH_2 group into the ring. Experiments with methylethylbenzenes indicate that the insertion into the several C–C bonds of the ring occurs at random.



Meyerson[3] found that in cycloheptatriene-7-*d* the loss of hydrogen to form the tropylium ion (V) occurs at random, that is, without regard to the positional identity of the atoms in the original molecule. This behavior, the behavior in toluene, and the behavior in the methylethylbenzenes all indicate that the hydrogen atoms in the cycloheptatriene ion (IV) move easily around the ring. Obviously one does not know the detailed path or mechanism by which this occurs, but it is convenient to think of it as involving a series of 1,2 hydride ion shifts.

It is also of interest that mass spectra of all the C_7H_8 isomers which have been investigated (listed by Meyerson[3]) are very similar, and Meyerson suggests that the different isomers decompose under electron impact largely by common reaction paths *via* common intermediates. From the deuterium-labeling experiments, one concludes that one of the intermediates is the cycloheptatriene ion and the other is the tropylium ion.[4]

Recently we have been engaged in an investigation of chemical ionization mass spectrometry,[5-8] and in the course of this work it has become clear that the spectra generated by this technique are quite different from those encountered in electron-impact mass spectrometry. Thus it is of interest to investigate the mass spectrometry of C_7H_8 isomers by means of chemical ionization mass spectrometry, and the compounds that we have chosen for study are toluene, cycloheptatriene, and norbornadiene. Toluene-α-d_3 and cycloheptatriene-7-*d* were also included in the study.

Experimental Procedure

The apparatus, experimental procedures, and experimental conditions are generally the same as those described in previous communications.[5,6] Methane was used as the reactant gas, and its pressure was maintained at 1.00 ± 0.02 torr. The ionization chamber was maintained at a temperature of 225°, and the gas-

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[1] 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.

[2] F. Meyer and A. G. Harrison, *J. Am. Chem. Soc.*, **86**, 4757 (1964).

[3] S. Meyerson, *ibid.*, **85**, 3340 (1963).

[4] See ref 1, pp 507, 508.

[5] (a) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **88**, 2621 (1966); (b) *ibid.*, **88**, 4337 (1966).

[6] F. H. Field, M. S. B. Munson, and D. A. Becker, Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., 1966.

[7] M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **89**, 1047 (1967).

[8] F. H. Field and M. S. B. Munson, *ibid.*, **89**, 4272 (1967).

Table I. Chemical Ionization Mass Spectra[a]

	$C_6H_5CH_3$		$C_6H_5CD_3$		cyclo-C_7H_8		cyclo-C_7H_7D		Norbornadiene	
Ion	*m/e*	*I*	*m/e*	*I*	*m/e*	*I*	*m/e*	*I*	*m/e*	*I*
MW + 43	135	0.002	138	0.001	135	0.001				
MW + 41	133	0.023	136	0.023	133	0.005	134	0.005	133	0.002
MW + 29	121	0.099	124	0.099	121	0.030	122	0.031	121	0.010
MW + 27	119	0.002	122	0.003	119	0.001			119	0.002
MW + 15	107	0.002	110	0.001	107	0.005	108	0.001	107	0.009
MW + 13	105	0.006	108	0.001	105	0.004	106	0.003	105	0.006
MW + 12			107	0.006			105	0.001		
MW + 1	93	0.709	96	0.684	93	0.580	94	0.566	93	0.458
MW	92	0.040	95	0.050	92	0.046	93	0.072	92	0.045
MW − 1	91	0.039	94	0.006	91	0.092	92	0.060	91	0.180
MW − 2			93	0.043			91	0.035		
MW − 13					79	0.084	80	0.064	79	0.072
MW − 14							79	0.016		
MW − 25					67	0.006	68	0.003	67	0.028
MW − 26							67	0.003		
MW − 27					65	0.003			65	0.001
MW − 37					55	0.016	56	0.006	55	0.038
MW − 38							55	0.011		
MW − 49					43	0.065	44	0.021	43	0.046
MW − 50							43	0.045		
Ions attributed to impurities	79	0.003	123 79	0.002 0.002	69	0.001	107	0.001	117 69	0.001 0.001

[a] Reactant = CH_4, P_{CH_4} = 1.00 torr.

handling reservoir containing the compound investigated was maintained at 130°. This relatively low temperature of the reservoir was used to diminish the possibility of thermal redistributions of the deuterium atoms in the deuterated toluene and cycloheptatriene. From the rate constant given by ter Borg, Kloosterziel, and van Meurs[9] for the thermal isomerization of cycloheptatriene-7-*d*, one calculates a half-life at 140° of 60 hr for the isomerization of the deuterium atom away from the 7 position. In our experiments the cycloheptatriene was maintained in the reservoir of the mass spectrometer at 140° for about 20 min, and thus a quite negligible amount of thermal isomerization occurred. Meyerson[8] found that in his apparatus the spectrum of the deuterated cycloheptatriene measured with an ionization chamber temperature of 250° was not different from that measured with a temperature of 140°. Thus we believe that no significant amount of thermal isomerization occurred in the ionization chamber of our mass spectrometer at 225°.

The toluene was reagent-grade material obtained from Allied Chemical, and no impurities were detected by gas chromatographic measurements. The cycloheptatriene was obtained from Aldrich Chemical Co., and the sample used in the mass spectra measurements was purified by preparative-scale gas chromatography. The norbornadiene was Practical Grade obtained from Matheson Coleman and Bell, and it was distilled and a center cut collected immediately before use in the mass spectrometer. The toluene-α-d_3 was obtained from the Isomet Corp., Palisades Park, N. J.; it is represented by the manufacturer to have an isotopic purity of 98%. The sample used for the mass spectra measurements was purified by preparative-scale gas chromatography. The cycloheptatriene-7-*d*, which was obtained from Dr. B. Franzus of these laboratories, was prepared by the reduction with $LiAlD_4$ of 7-acetoxynorbornadiene in tetrahydrofuran as described by Franzus and Snyder.[10] The sample used in the mass spectral measurements was purified by preparative-scale gas chromatography. An nmr spectrum of the cycloheptatriene-7-*d* was obtained, and it indicated that within the limits of accuracy of the measurement (probably a few per cent at worst) the sample was pure cycloheptatriene-7-*d*.

Results

The chemical ionization mass spectra for the five compounds studied are given in Table I. The values given are the relative intensities of the ions from the substances under investigation with *m/e* values of 43 and greater. For simplicity of tabulation C^{13} ions are omitted from Table I, and the tabulated intensities have been corrected for interferences from C^{13} isotopic ions of lower masses. This correction is usually of significance only for the MW^+ ions. However, the C^{13} isotopic ions are taken into account in calculating relative intensities, and thus the values given in Table I do not sum to unity for each compound. Duplicate determinations were made on each compound, and the reproducibility of the spectra was very satisfactory.

Toluene

The chemical ionization spectrum of toluene has been given previously,[7] and it was redetermined here as a check and is given here for comparison purposes. The spectrum is dominated by ions formed by the addition of reactant ions or H^+ to toluene, and the only fragment ion formed is the MW − 1 ion. The intensity of this ion (0.039) is rather low.

In $C_6H_5CD_3$ the intensity at *m/e* 93, which corresponds to abstraction of a D^- from the molecule, is 0.043, but the intensity at *m/e* 94, corresponding to H^- abstraction, is 0.006. Thus the ratio of H loss to D loss is 0.14, which is to be compared with the value 5/3 = 1.67 for the ratio of H loss to D loss if the loss ratio depended only upon the relative numbers of H and D atoms in the parent molecule. We conclude that the ring and side-chain hydrogens in toluene do not become equivalent in the generation of chemical ionization mass spectra, and the probability of hydride ion abstraction from the side chain in forming $(MW - 1)^+$ is much larger than that of removal from the ring.

We do not know with surety what the origin or significance of the $C_7H_4D_3^+$ (*m/e* 94) from $C_6H_5CD_3$ is, for several possibilities exist. The ion may result from the occurrence of some loss of identity of the ring and side-chain hydrogen atoms in toluene. Some abstraction of H from the ring may occur, although it is pointed out later that this is unlikely. Another possibility is that exchange with the reactant ions occurs in the chemical ionization process, or alternatively (or possibly in addition) the ions formed by the chemical

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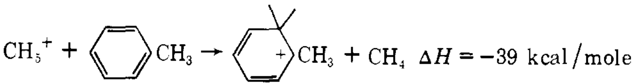
[9] A. P. ter Borg, H. Kloosterziel, and N. van Meurs, *Rec. Trav. Chim.*, **82**, 717 (1963).

[10] B. Franzus and E. I. Snyder, *J. Am. Chem. Soc.*, **85**, 3902 (1963).

ionization exchange with methane molecules as the ions pass out of the ionization chamber. We point out that in previous work with perdeuteriocyclohexane (cyclo-C_6D_{12}) we found[8] no evidence for exchange either in the initial chemical ionization process or in the passage of the ions out of the ionization chamber. A fourth possibility for the formation of the *m/e* 94 ion is that it results from an isotopic impurity in the $C_6H_5CD_3$. However, in Table I one observes that an intensity of 0.002 exists in the spectrum of $C_6H_5CD_3$ at *m/e* 123. This ion would be formed from the addition of $C_2H_5^+$ ion to $C_6H_5CD_2H$, and from the relative intensities observed at *m/e* 123 and 124 one concludes that the $C_6H_5CH_3$ contained about 2% of $C_6H_5CD_2H$ as an impurity. Obviously this amount of impurity would account for only a small fraction of the intensity observed at *m/e* 94.

It is of value to consider the reactions and energies which are involved in the chemical ionization of toluene. From Table I it may be seen that proton transfer to toluene is the most important reaction occurring, since the intensity of the $(MW + 1)^+$ ion accounts for approximately 70% of the toluene ionization. One also observes in the spectrum a moderate amount of $C_2H_5^+$ addition to toluene and smaller amounts of addition of $C_3H_5^+$ and $C_3H_7^+$. The proton affinity of toluene is not known, but it is reasonable to estimate it to be somewhat greater than the proton affinity of benzene (*vide infra*). Thus we guess that the heat of formation of protonated toluene is about 220 kcal/mole, and with this value proton transfer from both CH_5^+ and $C_2H_5^+$ is exothermic, *i.e.*



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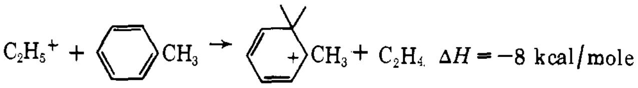
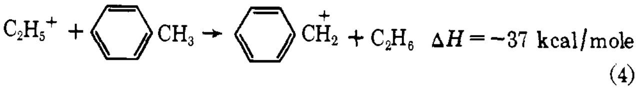


(3)

The occurrence of proton transfer from $C_2H_5^+$ is also indicated by the fact that 70% of the toluene ionization occurs in the form of $(MW + 1)^+$ ions, but roughly only 45% of the methane ionization is in the form of CH_5^+. Thus some of the $(MW + 1)^+$ ions must come from reactions of the other major ion in the methane plasma, namely, $C_2H_5^+$.

The $(MW - 1)^+$ ion from toluene can be thought of as occurring in either or both of two different ways. One of these ways is a hydride ion abstraction from toluene by one of the reactant ions, which would give $(MW - 1)^+$ directly. $C_2H_5^+$ ion is an obvious choice for one of the reactants which will effect hydride ion abstraction, but we have shown[8] that CH_5^+ can abstract hydride from cyclohexane, and it is reasonable to think that it can do the same with toluene. The ion produced by abstracting H^- from the methyl group is the benzyl ion (assuming that no rearrangement occurs) and the preferred value for the heat of formation of benzyl ion is[11] 220 kcal/mole. The formation of this ion from toluene is highly exothermic for both $C_2H_5^+$ and CH_5^+, thus



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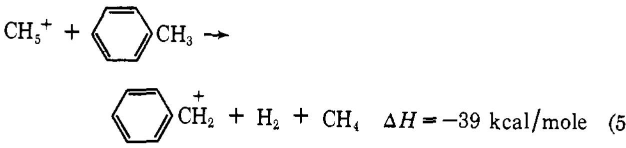
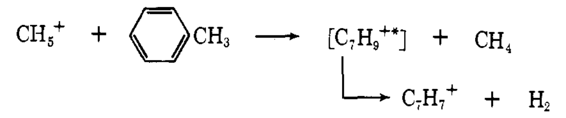


(5)

The heat of formation of tropylium ion is[12] 217 kcal/mole, and the formation of this ion by hydride ion abstraction from toluene would also be strongly exothermic. On the other hand, the abstraction of a ring hydrogen to form a methylphenyl ion is almost surely strongly endothermic and highly unlikely. The heat of formation of phenyl ion is not known with certainty, but values of $\Delta H_f(C_6H_5^+)$ are found[11] to range from 285 to 300 kcal/mole, and some of these values may apply to phenyl ions. It is reasonable to suggest that the heat of formation of the methylphenyl ion is of the order of 285 kcal/mole, and using this figure abstraction of H^- by $C_2H_5^+$ and CH_5^+ is endothermic by about 25 kcal/mole.

The other general process by which $(MW - 1)^+$ ions can be formed from the toluene involves protonation to form $C_7H_9^+$ followed by elimination of H_2 to give $C_7H_7^+$. Thus we may write



(6)

$\Delta H = -39$ kcal/mole ($C_7H_7^+$ = benzyl)
$= -42$ kcal/mole ($C_7H_7^+$ = tropylium)

The corresponding reaction involving $C_2H_5^+$ as reactant ion would be 30 kcal/mole less exothermic.

The fact that very little mixing of H and D is observed in the formation of $(MW - 2)^+$ ion from $C_6H_5CH_3$ (86% of the hydrogen removed is in the form of D entities) is related to the question of the extent to which hydride abstraction processes (reactions 4 and 5) and protonation–H_2 loss processes (reaction 6) are involved in the formation of $(MW - 1)^+$ in toluene. In particular, we think that the occurrence of reaction 6 would offer an opportunity for hydrogen–deuterium mixing in $C_6H_5CD_3$, and we think that the very small amount of mixing observed indicates that reaction 6 does not occur to a significant extent in spite of its large exothermicity. From the heats of formation of CH_5^+, toluene, and methane, we can calculate that the heat of formation of the excited protonated toluene ($C_7H_9^{+*}$) written in reaction 6 is 259 kcal/mole. From the appearance potential of $C_7H_9^+$ from cycloheptadiene reported by Lifshitz and Bauer[13] and the heat of formation of cycloheptadiene given by the same workers, we calculate a heat of formation for $C_7H_9^+$, which presumably has the protonated cycloheptatriene structure, of 231 kcal/mole. Alternatively, using the Franklin[14] group equivalent method we calculate values of 219 or 230 kcal/mole for the heat of formation of

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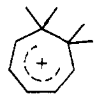
(11) J. L. Franklin, F. H. Field, and co-workers, revision of Table 45 in ref 20, to be published.

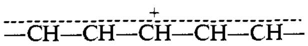
(12) A. G. Harrison, L. R. Honnen, H. J. Dauben, and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960).

(13) C. Lifshitz and S. H. Bauer, *J. Phys. Chem.*, **67**, 1629 (1963).

(14) J. L. Franklin, *J. Chem. Phys.*, **21**, 2029 (1953).

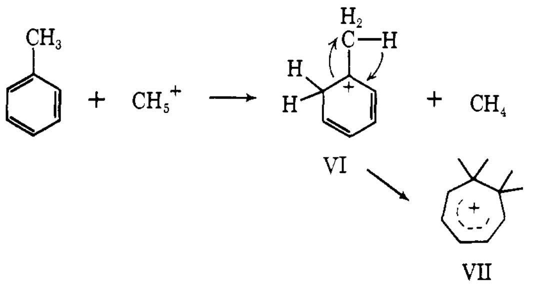


The two values result from different values assigned to the energy of the



$$\overset{+}{-CH-CH-CH-CH-CH-}$$

group, and these in turn depend upon whether one uses a heat of formation of protonated benzene ($\Delta H_f(C_6H_7^+)$) of 235 kcal/mole[15] or 224 kcal/mole.[13] For our purposes it is adequate to take the heat of formation of protonated cycloheptatriene to be 230 kcal/mole, and consequently it is energetically possible (and even probable) that the $C_7H_9^{+*}$ ion formed by the reaction of toluene and CH_5^+ (reaction 6) will isomerize to form protonated cycloheptatriene. A possible mechanism analogous to reaction 1 is



(7)

Ion VII retains the energy of the reaction, and thus it is highly excited, containing 29 kcal/mole in excess of $\Delta H_f(\text{cyclo-}C_7H_9^+)$ = 230 kcal/mole. With this degree of excitation, migration of hydrogen atoms around the ring must be considered as a distinct possibility, and such migration would give rise to isotopic mixing of hydrogens and deuteriums in $C_6H_5CD_3$. Loss of hydrogen molecule from VII produces tropylium ion, which would be isotopically mixed when starting with $C_6H_5CD_3$.

Since isotopic mixing does not in fact occur to any significant extent in the formation of $(MW - D)^+$, we conclude that reaction 6 does not occur. We speculate that the reaction does not occur because of the existence of an activation energy barrier which could exist in reaction 7 or in the loss of hydrogen molecules from VII to form tropylium. The excitation energy in ion VII is 29 kcal/mole, and thus the magnitude of the activation energy barrier must be greater than this amount. The existence of an activation energy in the formation of $C_7H_7^+$ is also strongly indicated by the very large intensity of $(MW + 1)^+$ ions in the toluene mass spectrum since some barrier must be present preventing them from undergoing the very exothermic decomposition to $C_7H_7^+$.

Thus the important aspects of the chemical ionization of toluene using methane as a reactant are as follows. The dominant reaction occurring is proton transfer to form $C_7H_9^{+*}$, and this ion has enough energy that it may isomerize to the protonated cycloheptatriene ion. Mixing of hydrogen isotopes present may occur by hydride transfer reactions around the ring, but hydrogen molecule loss to give the $C_7H_7^+$ ion does not occur to a significant extent. The $C_7H_7^+$ ion observed in the spectrum is formed by hydride ion abstraction direct from the toluene side chain, and the evidence from our study here with toluene-α-d_3 and our prior study with perdeuteriocyclohexane[8] indicates that isotopic mixing does not occur in this process.

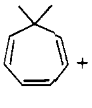
Cycloheptatriene

As can be seen from Table I, the chemical ionization mass spectrum of cycloheptatriene differs significantly from that of toluene. The intensities of the cycloheptatriene ions with *m/e* values greater than MW^+ are smaller than the intensities of the corresponding ions in toluene, the amounts being approximately 20, 300, and 500% for $(MW + 1)^+$, $(MW + 29)^+$, and $(MW + 41)^+$, respectively. These decreases are balanced by an increase in the intensity of $(MW - 1)^+$ and by the appearance of ions with *m/e* values less than $(MW - 1)^+$, especially *m/e* 79 and 43 (I = 0.084 and 0.065, respectively). These ions would enable one to distinguish mass spectrometrically between toluene and cycloheptatriene quite easily. On the other hand, electron-impact spectra of toluene and cycloheptatriene differ significantly only in the relative intensity of the MW^+ ion (46% larger in toluene[1]), and distinguishing between the two compounds would be more difficult.

The $(MW - 1)^+$ ion in cycloheptatriene has an intensity of 0.092, which is approximately twice the intensity of the ion in toluene. In monodeuteriocycloheptatriene one observes ions which can be attributed to loss either of H or D, namely, $(MW - 1)^+$ = 0.060 (formed by H loss) and $(MW - 2)^+$ = 0.035 (formed by D loss). We call attention at this point to the fact that the sum of the intensities of the ions observed at *m/e* 91 and 92 in cyclo-C_7H_7D is equal to the intensity of the *m/e* 91 ion in cyclo-C_7H_8. In general, similar good agreement is to be observed in Table I for the total intensities of the ions of a given structure but distributed over different mass numbers because of different isotope content.

The intensities at *m/e* 91 and 92 in cyclo-C_7H_7D show that in the formation of tropylium ion H is removed from the parent molecule 1.7 times as often as D. However, the ratio of H to D in the parent molecule is 7, and thus the hydrogens in cycloheptatriene are not equivalent in chemical ionization. By contrast, with electron impact all the hydrogen became equivalent. Thus Meyerson[3] found that the ratio of intensities of the *m/e* 92 and 91 ions is 92/91 = 7.9. We have determined the electron-impact spectrum of cyclo-C_7H_7D by electron impact using the Esso mass spectrometer operated in the electron-impact mode. Our results corroborate those of Meyerson, for we find that 92/91 = 7.3.

As was the case with toluene, formation of the $(MW - 1)^+$ ion from cyclo-C_7H_8 can be effected by direct hydride ion abstraction from cycloheptatriene or by protonation of cycloheptatriene followed by loss of hydrogen molecule. If the hydride ion abstraction occurs from the methylene group in cycloheptatriene to form tropylium ion, the reactions are 71 kcal/mole exothermic when $C_2H_5^+$ is the reagent and 73 kcal/mole exothermic when CH_5^+ is the reagent. The removal of a vinyl hydrogen to form an ion such as



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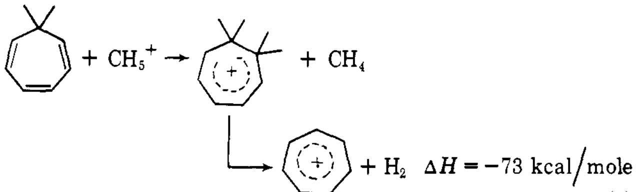
[15] F. W. Lampe, J. L. Franklin, and F. H. Field, *Progr. Reaction Kinetics*, 1, 69 (1961).

will obviously require much more energy than the formation of tropylium, but we cannot say with certainty how much. A rough group equivalent estimate made using the value $\Delta H_f(\text{-CH=C-}) = 265$ kcal/mole gives the result that the ionization process will be somewhat endothermic for either $C_2H_5^+$ or CH_5^+ as reagents. Thus we would expect that hydride abstraction from the methylene group would be much more probable. In this case, except for the operation of the isotope effect, hydride ion and deuteride ion abstraction should occur from cyclo-C_7H_7D in equal amounts. The hydride or deuteride abstraction reaction constitutes in effect a three-center process, and from the discussion given by Melander,[16] for such processes the operation of the isotope effect results in abstraction of H atoms or ions from two to five times more rapidly than abstraction of D atoms or ions. Thus it seems reasonable to attribute the fact that in our experiments H^- is abstracted 70% more often than D^- to the isotope effect and to conclude that isotopic mixing in the formation of tropylium ions is absent.

However, we face with cycloheptatriene the same problem that we face with toluene, namely, the possibility that isotopic mixing can occur through protonation followed by loss of hydrogen molecule; and the problem is worse in cycloheptatriene because the energies are higher. We write

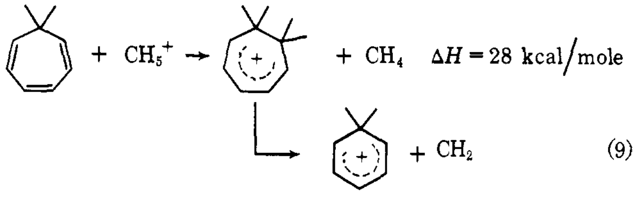


(8)

The energy content of the $C_7H_9^+$ intermediate written in reaction 8 is 290 kcal/mole, which is to be compared with the value of 259 kcal/mole in the intermediate of reaction 6. Thus the intermediate in reaction 8 is excited 290 − 230 = 60 kcal/mole above the ground state of $C_7H_9^+$, and it is surely to be expected that hydrogen migration around the ring and the concomitant isotopic mixing occurs. Nevertheless, the tropylium ion formed from cyclo-C_7H_7D shows no evidence of isotopic mixing, and we must conclude that the formation of tropylium by reaction 8 does not in fact occur. This indicates that the activation energy for H_2 elimination from $C_7H_9^+$ is greater than 60 kcal/mole, which seems rather high. However, 58% of the total ionization of cycloheptatriene exists as the $(MW + 1)^+$ ion, and some strong activation barrier must stand in the path of the occurrence of reaction 8.

The third most intense ion in the cycloheptatriene spectrum ($I = 0.084$) appears at m/e 79, which corresponds to the ion $C_6H_7^+$. We shall assume that the ion is the cyclic benzenium ion, for the noncyclic $C_6H_7^+$ ion would be much higher in energy. In cyclo-C_7H_7D one finds the intensity at m/e 80 is 0.064 and that at m/e 79 is 0.016. Thus the deuterium is retained in the benzenium ion four times as often as it is lost.

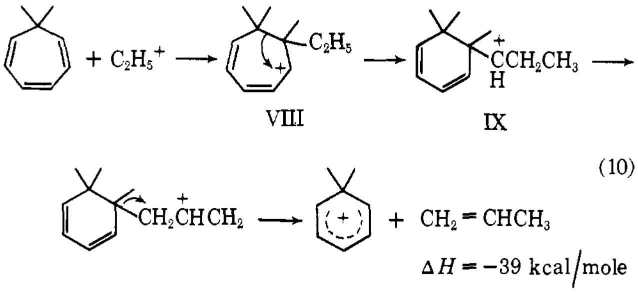
One can write reactions for the production of $C_6H_7^+$ involving either of the major reactant ions in the methane plasma. Considering CH_5^+ first, we write



(9)

The heat of reaction given in reaction 9 is calculated using the value $\Delta H_f(CH_2) = 94$ kcal/mole,[17] and $\Delta H_f(C_6H_7^+) = 224$ kcal/mole,[13] and it is seen that the reaction is rather strongly endothermic (because of the high heat of formation of methylene). Thus the probability of occurrence of reaction 9 is low.

We consider the possibility that $C_6H_7^+$ is formed by a reaction of $C_2H_5^+$, and we write



(10)

The energetics of reaction 10 are favorable for its occurrence. The over-all reaction is strongly exothermic, but in addition the energy content of VIII–X as formed in reaction 10 is 272 kcal/mole, which is 40 kcal/mole greater than the minimum energy of IX and X ($\Delta H_f(\text{IX}) = \Delta H_f(\text{X}) = 232$ kcal/mole) as calculated from group equivalents. Thus unless unexpectedly large activation energy barriers are present, more than enough energy is available for the isomerization of VIII to IX to X, followed by the decomposition of X. In reaction 10 the original methylene group of the cycloheptatriene is retained in the benzenium ion, and complete retention of the deuterium in cyclo-C_7H_7D is to be expected in the absence of hydrogen migrations. If randomization of the ring hydrogens occurs, the D atom will be retained in 7/8 = 87.5% of the ions, and if some randomization of the ethyl group hydrogen atoms occurs, D-atom retention will be somewhat lower. The observed D-atom retention of 80% is compatible with the occurrence of reaction 10 with some ethyl hydrogen randomization. It should be pointed out that 78% of the benzenium ions produced from cyclo-C_7H_7D by means of reaction 9 will contain D atoms if randomization of the ring hydrogens occurs. Thus the observed D-atom content cannot be used to distinguish between reactions 9 and 10, but, regardless of which reaction occurs, randomization is indicated.

It is of interest to attempt to rationalize the fact that m/e 79 ions are not observed in the chemical ionization mass spectrum of toluene (except in a small amount which might well be a result of the presence of an impurity). $C_6H_7^+$ ions could possibly be formed from toluene by the reaction

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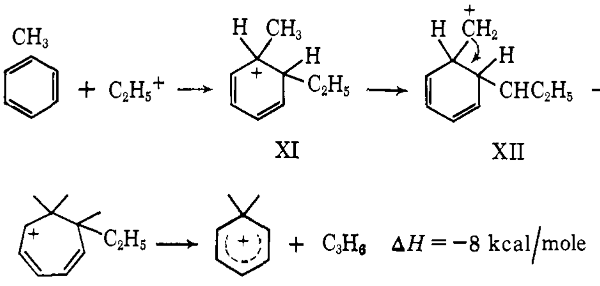
[16] L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Co., New York, N. Y., 1960, pp 67 ff, 117–119.

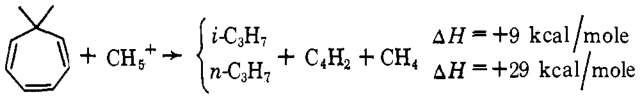
[17] D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, National Bureau of Standards, Technical Note 270-1, U. S. Government Printing Office, Washington, D. C., 1965.



(11)

However, from group equivalents we calculate that the heat of formation of XII is 256 kcal/mole, which is 19 kcal/mole greater than the energy content (237 kcal/mole) of XI as formed by addition of $C_2H_5^+$ to toluene. Thus, reaction 11 entails an activation energy which can be expected effectively to prevent its occurrence.

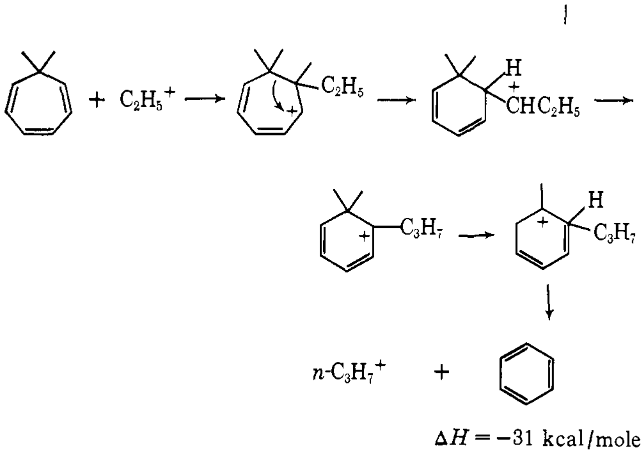
The other fragment ion of significant intensity in the spectrum of cycloheptatriene is *m/e* 43, $C_3H_7^+$, I = 0.065. In cyclo-C_7H_7D the peak divides and one finds I = 0.045 at *m/e* 43 and I = 0.021 at *m/e* 44. As was the case with the $C_6H_7^+$ ion, one can write reactions for the formation of this ion using either CH_5^+ or $C_2H_5^+$ as reactant ions. With CH_5^+ we write



(12)

The heat of reaction is calculated using a value of $\Delta H_f(C_4H_2)$ = 104 kcal/mole as given by Coats and Anderson.[18] One can conceive of a mechanism by which the transformation given in reaction 12 is accomplished, but, since the rearrangement involved is quite profound, a large number of steps is required, which we shall not give here.

Using $C_2H_5^+$ as a reactant, we may write



(13)

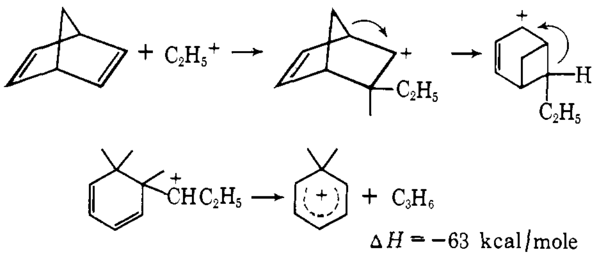
Reaction 13 is strongly exothermic, whereas reaction 12 is endothermic. Reaction 13 as written is not a simple reaction, but it is a good deal less complicated than any mechanism we have been able to conceive for reaction 12. Furthermore, reaction 13 leading to the production of propyl ion and benzene is almost the mirror image of reaction 11 leading to the production of benzenium ion and propylene, and we consider this to add somewhat to the probability that reaction 13 actually occurs. In cyclo-C_7H_7D it may be shown that if randomization is assumed not to occur, the ratio $I_{44}/I_{43} = \infty$ on the basis of reaction 12 and 0 on the basis of reaction 13. On the other hand, if randomization does occur, I_{44}/I_{43} = 3.5 on the basis of reaction 12 and 0.33 on the basis of reaction 13. The actual value is 0.47, which may be taken as providing evidence for the occurrence of randomization and reaction 13.

Norbornadiene (Bicyclo[2.2.1]heptadiene-2,5)

The spectrum of norbornadiene (Table I) when compared with the spectra of cycloheptatriene and toluene exhibits smaller intensities for the addition ions, that is, ions with *m/e* values greater than MW, and correspondingly larger intensities of ions with *m/e* less than MW. However, the (MW + 1)$^+$ ion with intensity 0.458 still dominates the spectrum. The heat of formation of norbornadiene (ΔH_f(norbornadiene) = 67 kcal/mole)[19] is 24 kcal/mole higher than that of cycloheptatriene and 55 kcal/mole higher than that of toluene. This higher energy will make the various chemical ionization processes occurring more exothermic and can be expected to lead to a greater degree of fragmentation.

The ions that one finds in the mass spectrum of norbornadiene have the same *m/e* values as those found in cycloheptatriene, and as such the spectrum of norbornadiene does not differ from that of cycloheptatriene as much as the spectrum of cycloheptatriene differs from that of toluene. However, the intensities of the *m/e* 91 and 67 ions in norbornadiene are respectively twice and four times as large as the intensities of these ions in cycloheptatriene, and one would be able easily to distinguish between the two compounds from their mass spectra.

The *m/e* 91 ion in norbornadiene is doubtless formed by some combination of H$^-$ abstraction of ethyl ions and reaction with CH_5^+. The formation of $C_6H_7^+$ can be easily rationalized by the sequence



(14)

The presence of the *m/e* 67 ion ($C_5H_7^+$) in the chemical ionization mass spectra of norbornadiene and the presence of the *m/e* 66 ion ($C_5H_6^+$) in the electron-impact spectrum is of interest because it offers a point of comparison of the two modes of ionization. Meyerson, McCollum, and Rylander[19] find that the *m/e* 66 ion is the second most intense ion in the spectrum, with an intensity approximately half that of the dominant $C_7H_7^+$ ion. They point out that if one assumes the ion to have the cyclopentadiene structure (without further evidence other structures are possible) the formation of this ion can be looked upon as a kind of reverse Diels–Alder reaction producing cyclopentadiene ion and acetylene from norbornadiene molecule ion. From the relatively high intensity of the *m/e* 66 ion,

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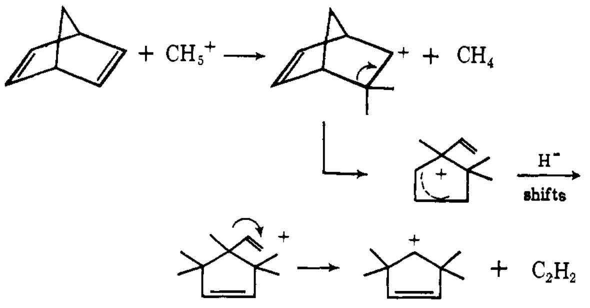
(18) F. H. Coats and R. C. Anderson, *J. Am. Chem. Soc.*, **79**, 1340 (1957).

(19) S. Meyerson, J. D. McCollum, and P. N. Rylander, *ibid.*, **83**, 1401 (1961).

one concludes that this is a fairly high probability process. By comparison the $C_5H_7^+$ ion formed by chemical ionization from norbornadiene can be looked upon as having the protonated cyclopentadiene structure, and one can write a plausible reaction sequence producing the ion. Thus



(15)

$\Delta H \cong -25$ kcal/mole

Taking the value $\Delta H_f(C_5H_7^+)$ = 235 cal/mole from Field and Franklin,[20] the reaction is seen to be quite exothermic and thus probably must be considered as allowed in spite of the fact that the mechanism given involves an unconventional hydride shift across a double bond. However, because one starts the reaction with protonated norbornadiene, a reverse Diels–Alder reaction is not possible, and the multistep process written in reaction 15 occurs with a relatively low probability (ion intensity = 0.028).

The intensity of the *m/e* 55 ion is large enough (0.038) in norbornadiene to be considered, but we are unable to advance a mechanism for its formation. The *m/e* 43 ion can be formed by a process which is related to reaction 14 in the same way that reaction 13 is related to reaction 10. Alternatively, one can write an exothermic reaction for the production of isopropyl ion from norbornadiene and CH_5^+.

$$\text{bicyclo-}C_7H_8 + CH_5^+ \longrightarrow i\text{-}C_3H_7^+ + C_4H_2 + CH_4 \qquad \Delta H = -15 \text{ kcal/mole} \quad (16)$$

but the process requires a very extensive set of rearrangements of atoms.

Conclusion

We conclude from this study that in one respect the phenomenon of isotopic mixing in chemical ionization is different from that in electron-impact ionization, but in another respect it is the same. In the formation of $(MW - 1)^+$ ions isotopic mixing does not occur by chemical ionization, which is in contrast to the electron-impact behavior. This seems to be the consequence of the fact that $(MW - 1)^+$ ion formation by chemical ionization occurs by H^- abstraction by a Lewis acid, a process which does not seem to involve isotopic mixing and exchange. No analog for this process exists in electron-impact ionization. However, from the isotopic distributions observed in the formation of benzenium and propyl ions from cyclo-C_7H_7D we conclude, although quite tentatively, that randomization of hydrogens occurs in the processes forming these ions. We have suggested that these processes involve the addition of $C_2H_5^+$ (or, less likely, H^+) to the cycloheptatriene, which is followed by rearrangement leading to the formation of the product ion. It would appear that the ions involved in these transformations are sufficiently activated and have lifetimes prior to ultimate decomposition long enough to permit migration of hydrogen atoms around the molecule. In this respect, these chemical ionization processes conform on the one hand to the mobility observed in electron-impact ionization and dissociation of C_7H_8 isomers, and on the other hand they conform to the very well-known lability of carbonium ions in condensed phase organic chemistry.

Acknowledgment. The author thanks Mr. Frank C. Petronis for the experimental measurements in this work, Dr. Boris Franzus of these laboratories, who kindly supplied the deuterated cycloheptatriene, and Dr. Franzus and Dr. George M. Kramer, also of these laboratories, for valuable conversations concerning these studies.

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(20) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957.