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Chemical Ionization Mass Spectrometry. IV. Aromatic Hydrocarbons

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Abstract: Chemical ionization spectra with methane as a reactant gas are reported for 21 alkylbenzenes and 2 alkylnaphthalenes. Proton and ethyl addition reactions are observed for the aromatic hydrocarbons in contrast with the previously reported aliphatic hydrocarbons. Hydride abstraction appears to occur for the aliphatic but not aromatic hydrogens. Alkyl ion and olefin displacement reactions are noted for some of the branched alkylbenzenes; for *t*-amylbenzene, $C_5H_{11}^+$ is about 80% of the additive ionization.

In the previous papers of this series we have given a general introduction to the technique of chemical ionization mass spectrometry¹ and then discussed in detail the spectra of several esters² and saturated hydrocarbons.³ The purpose of this paper is to present the chemical ionization mass spectra of a series of aromatic hydrocarbons and to discuss the reactions involved in the formation of these ions. We shall speculate on the mechanisms, choosing the ones which seem most plausible. We feel that this speculation is worthwhile to provide a framework to show the general usefulness of the method. Isotope studies are planned as future experiments.

Although the technique has been discussed in detail previously,¹⁻³ it is still sufficiently new that a brief review is perhaps in order. A high pressure of reactant gas (1.0 torr of CH_4 in these experiments) and a low pressure of additive (of the order of 10^{-3} torr) are mixed and allowed to flow through the source of a mass spectrometer. Because of the large excess of CH_4 , electron impact produces almost exclusively ions from CH_4 . These ions react with CH_4 at essentially every collision to give product ions which react slowly, if

at all, with CH_4 . Thus, at pressures of pure CH_4 greater than about 0.5 torr within the source of the mass spectrometer and for reaction times of the order of 10^{-6} sec, CH_5^+ , $C_2H_5^+$, $C_3H_5^+$, $C_2H_4^+$, and $C_3H_7^+$ are the major ions.⁴ When another molecular species is present in small concentration in the present experiments, the product ions from methane may react readily with the additive to produce ions which are characteristic of the added material. A spectrum of ions is produced by chemical reaction in the gas phase; hence the name chemical ionization mass spectrometry.

Experimental Procedure

The apparatus and experimental procedures have been described previously¹⁻³ and the experimental conditions are the same as those used previously,^{2,3} except that the source temperature was 185° in the present experiments. The chemicals used in these experiments were API samples whenever possible. Commercial samples of highest purity were used without purification in the other cases.

Results

Table I shows the distribution of additive ions obtained with methane as a reactant gas for 21 alkylbenzenes and 2 alkylnaphthalenes. The ions are listed according to what we feel are their compositions rather than values of m/e , because this method greatly sim-











(1) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **88**, 2621 (1966).

(2) M. S. B. Munson and F. H. Field, *ibid.*, **88**, 4337 (1966).

(3) F. H. Field, M. S. B. Munson, and D. A. Becker, *Advances in Chemistry Series*, No. 58, American Chemical Society, Washington, D. C., 1966, p 167.

(4) F. H. Field and M. S. B. Munson, *J. Am. Chem. Soc.*, **87**, 3289 (1965).

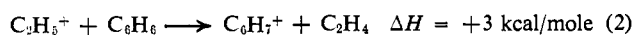
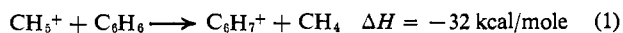
Table I. Chemical Ionization Spectra (CH₄ Reactant). Relative Abundances of Ions in Alkylaromatic Hydrocarbons^a

Compound										
(MW + C ₃ H ₇) ⁺	0.0030	0.0038	0.016	...	0.0056	0.0060	0.0057	0.0043	0.0020	0.0068
(MW + C ₃ H ₅) ⁺	0.030	0.033	0.007	0.027	0.0080	0.027	0.026	0.018	0.0015	0.029
(MW + C ₂ H ₅) ⁺	0.124	0.134	0.0024	0.112	0.0023	0.092	0.092	0.021	0.0002	0.117
(MW + H) ⁺	0.72	0.69	0.24	0.61	0.22	0.43	0.44	0.20	0.14	0.54
MW ⁺	0.034	0.031	0.024	0.028	0.020	0.029	0.026	0.022	0.016	0.028
(MW - H) ⁺	...	0.028	0.057	0.125	0.073	0.075	0.096	0.051	0.047	0.071
(MW - CH ₃) ⁺	0.068	0.0012	0.055	0.032	0.034	0.053	0.059	0.046
(MW - C ₂ H ₅) ⁺	0.011	...	0.005	0.019	0.019	0.003	0.030	0.003
(MW - C ₃ H ₇) ⁺	0.009	0.004	0.002	0.018	0.012	...
(MW - C ₄ H ₉) ⁺
Olefin	...	0.0003	0.040	0.005	0.136	0.033	0.027	0.039	0.082	?
displacement by C ₂ H ₅ ⁺	...	0.0005	0.124	...	0.294	0.114	0.095	0.020	0.048	0.029
Olefin displace- ment by H ⁺	...	?	0.33	?	0.091	0.053	0.041	0.46	0.45	?
R ⁺	...	?	0.33	?	0.091	0.053	0.041	0.46	0.45	?

^a ... , was not observed, less than 0.0005 of additive ionization; ?, could not be observed because of interferences.

plifies the tabulation and discussion. The relative abundances that are listed in the tables are the fractions of additive ionization. ¹³C isotope ions are excluded and the relative abundances of MW⁺ ions have been corrected for ¹³C ion currents from (MW - 1)⁺. This tabulation includes all of the ions greater than 0.01 in relative abundance except for occasional values of 0.01-0.02 which obviously came from impurities. We shall explain the formation of these ions in terms of reactions between the neutral aromatic hydrocarbons and CH₅⁺ (48% of the CH₄ ionization at 1.0 torr), C₂H₅⁺ (40%), C₃H₅⁺ (6%), C₂H₃⁺ (2%), and C₃H₇⁺ (1%).

The (MW + H)⁺ ion is very prominent in the spectra of all but three of these aromatic hydrocarbons. The formation of protonated aromatic hydrocarbons is certainly to be expected and agrees well with the observations of these ions as stable species in concentrated acidic solutions. Since ΔH_f(C₆H₇⁺), presumably protonated benzene, has been determined from electron-impact measurements,⁵ it is possible to calculate the heats of proton transfer from the two major Brønsted acids.



Proton transfer from CH₅⁺ is exothermic, but proton transfer from C₂H₅⁺ is apparently slightly endothermic. However, it is unlikely that ΔH_f(C₆H₇⁺) is known with this high an accuracy, and kinetic studies to establish the occurrence or nonoccurrence of (2) would be useful in determining a limit for the proton affinity of benzene. These experiments have not yet been done.

The heats of formation of the higher homologs, protonated toluene, etc., are not known; therefore, energetics for these reactions cannot be calculated. However, the methyl inductive effect would lead one to expect that the alkylbenzenes would all be stronger bases than benzene, and replacement of H atoms by CH₃ groups has been shown to increase the relative basicity for gaseous proton transfer for other nucleophilic systems.⁶

(5) J. L. Franklin, F. W. Lampe, and H. E. Lumpkin, *J. Am. Chem. Soc.*, **81**, 3152 (1959).

Also, in solutions, increasing alkyl substitution increases the base strength.⁷ Consequently, we expect that proton transfer from CH₅⁺ and C₂H₅⁺ to all of the alkylbenzenes will be exothermic.

In previous studies^{3,8} we reported that the stabilities of protonated paraffins become vanishingly small for molecules larger than ethane. We also postulated^{4,3} that the chemical ionization process in paraffins involved random attack and localized reaction of the reactant ion. It is reasonable to extend these concepts to the alkyl aromatics, and thus we postulate that the (MW + H)⁺ ions formed in the alkyl aromatics result from proton transfer to the aromatic ring portion of the molecule and that the intensities of the (MW + H)⁺ ions can be related to the relative number of ring and side-chain carbon atoms in the molecules. The intensity of (MW + H)⁺ in benzene is 0.72, and the (MW + H)⁺ intensity in an alkylbenzene should be given by the expression $I = (0.72)(6/N)$, where N is the number of carbon atoms in the alkylbenzene. Intensities of selected alkylbenzenes calculated using this expression are given in Table II along with the corresponding experimental values. The compounds chosen contain only methyl or ethyl side chains, which give maximum (MW + H)⁺ intensities. As may be seen from Table I and will be discussed later, larger side chains, particularly if branched, are stripped from the ring in the form of alkyl ions; this decomposition lowers the (MW + H)⁺ intensity and vitiates the calculated intensities.

The agreement between experimental and calculated intensities given in Table II suggests that the postulates on which the calculations are based are reasonably valid. The experimental values are uniformly slightly higher than the calculated values, which can be interpreted as meaning that a small preference exists for attack of the reactant on the ring.

An inspection of Table I shows that ethyl addition is a prominent process for the majority of the aromatics studied. The formation of the (MW + C₂H₅)⁺ ions

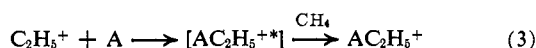
(6) M. S. B. Munson, *ibid.*, **87**, 2332 (1965).

(7) L. J. Andrews, *Chem. Rev.*, **54**, 713 (1954).

(8) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **87**, 4242 (1965).

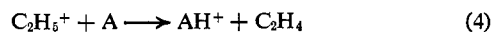
0.0050	0.0037	0.0040	0.0050	0.0051	0.0005	0.0030	0.0042	...
0.028	0.026	0.026	0.023	0.020	0.011	0.022	0.031	0.018
0.113	0.112	0.102	0.096	0.058	0.069	0.092	0.156	0.112
0.54	0.52	0.54	0.49	0.25	0.50	...	0.0022	0.48	0.003	0.28	0.63	0.51
0.025	0.028	0.026	0.024	0.020	0.058	...	0.010	0.029	0.010	0.026	0.042	0.047
0.097	0.119	0.097	0.138	0.090	0.24	0.031	0.065	0.164	0.053	0.160	0.022	0.064
0.043	0.057	0.026	0.030	0.011	0.002	0.050	0.075	0.060	0.096	0.121	...	0.014
0.002	0.002	0.008	...	0.032	0.0005	0.0007	0.0011	...	0.0030	0.006
...	0.010	...	0.008	0.0010	...	0.0003	0.003	...	0.040
...	0.073	...	0.008	0.0010	...	0.0005
?	?	?	?	0.024	0.007	?	...	0.101	...	0.010
0.024	0.026	0.023	0.018	0.007	...	0.0010	0.008	0.006	...	0.151	...	0.018
?	?	?	?	0.33	?	0.80	0.79	?	0.79	<0.001	?	0.002

probably involves the collision-stabilized addition of $C_2H_5^+$ to the aromatic hydrocarbon, *i.e.*



where A is an aromatic molecule. The kinetic measurements necessary to establish the dependence on CH_4 pressure of the $AC_2H_5^+$ intensities were not made, but the CH_4 pressure is sufficiently high to allow reaction 3 to occur with reasonable probability. Reaction 3 is analogous to the classical organic process of alkylation of aromatic hydrocarbons by carbonium ion.

In general, when $(MW + H)^+$ is an abundant ion, $(MW + C_2H_5)^+$ is also abundant; that is, the stability of the ethylated aromatic hydrocarbon parallels that of the protonated hydrocarbon. The ratio of ethyl addition to proton addition is about 0.19. If all the ethyl ion in the methane plasma in the mass spectrometer reacted *via* the addition reaction 3 and if all $(MW + H)^+$ ions were formed by proton transfer from CH_5^+ (reactions analogous to (1)), one would expect the intensity ratio $(MW + C_2H_5)^+ / (MW + H)^+$ to approximate the ratios of intensities of $C_2H_5^+$ to CH_5^+ in the methane plasma, namely, $40/48 = 0.83$. The much lower value of 0.19 actually observed can be explained in part by the possibility that other reactions are consuming $C_2H_5^+$, especially



which is analogous to reaction 2.

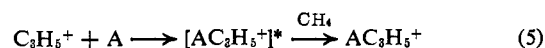
There is a slight decrease in relative abundance of $(MW + C_2H_5)^+$ ions with increasing number of alkyl carbon atoms in the aromatic molecule. This trend is similar to that shown for $(MW + H)^+$ ions in Table II and may be explained in the same manner; that is, attack at the alkyl groups of the aromatic hydrocarbon does not give rise to ethyl addition. For four compounds there is an appreciable amount of $(MW + H)^+$ and virtually no $(MW + C_2H_5)^+$: isopropylbenzene, 1-methyl-2-isopropylbenzene, *sec*-butylbenzene, and 1,3,5-triisopropylbenzene. One can perhaps rationalize that lack of ethyl addition to the triisopropylbenzene on the basis of steric hindrance to the addition of an ethyl group but not for the addition of a proton.

Table II. Relative Abundances of $(MW + H)^+$ Ions

Compound	Intensities of $(MW + H)^+$ Calcd	Exptl
	0.62	0.69
	0.48	0.61
	0.43	0.54
	0.40	0.50
	0.36	0.48

However, we have no explanation for the special instabilities of $(MW + C_2H_5)^+$ for the other three compounds.

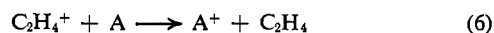
In addition to $(MW + C_2H_5)^+$ ions, there are small amounts of $(MW + C_3H_5)^+$ ions formed by reactions analogous to (3)



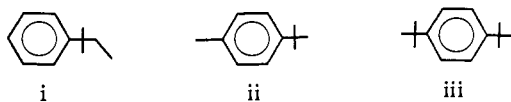
and even smaller amounts of $(MW + C_3H_7)^+$ formed by a similar reaction with $C_3H_7^+$. There is a parallelism between the abundances of the $(MW + C_3H_5)^+$ ions, the $(MW + C_2H_5)^+$ ions, and $(MW + H)^+$ ions. For these compounds $(MW + C_3H_5)^+ / (MW + C_2H_5)^+$ is reasonably constant at 0.25, and the ratio $(C_3H_5^+) / (C_2H_5^+)$ is about 0.15 in pure methane at these pressures. The relative concentrations of $(MW + C_3H_7)^+$ ions are always low as one would expect since the concentration of $C_3H_7^+$ in pure methane is quite low, about 0.01.

MW^+ ions are observed for all except one of the alkylbenzenes (i), but the concentrations are small, 0.02–0.03 of the additive ionization with only a few exceptions. The ionization potentials of all of the alkylbenzenes are lower than that of benzene, 9.25 v, and this value is below the ionization potential of ethylene, 10.51

v.⁹ Consequently, the most reasonable mode of formation is charge exchange with the ethylene ion¹⁰ (formed in methane with a concentration of 0.02 of the total ionization).

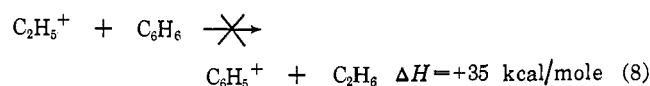
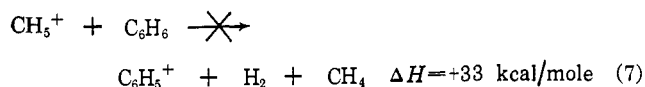


The somewhat larger value, 0.058, for pentamethylbenzene is perhaps the result of a small amount of charge exchange from the ethyl ion since from comparison with the other polymethylbenzenes the ionization potential of pentamethylbenzene should be about 8.0 v and the ionization potential of the ethyl radical is 8.3–8.8 v.¹¹ A similar explanation can be advanced for the high MW⁺ abundances for the two naphthalenes.

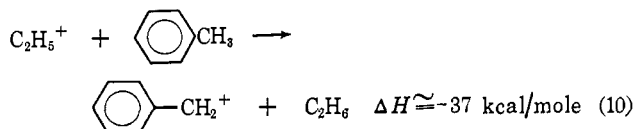
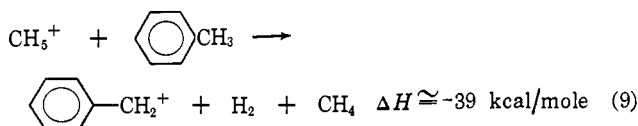


The relative abundances of molecular ions for 1-methyl-4-*t*-butylbenzene (ii) and 1,4-di-*t*-butylbenzene (iii) are lower than the relative abundances of molecular ions for the other alkylbenzenes, and the molecular ion for 2-phenyl-2-methylbutane (i) is essentially absent. These observations are surprising and do not result from an inherent instability of the molecular ions, since the molecular ions are relatively abundant for these compounds in the electron-impact spectra.¹²

In the row for (MW – H)⁺ ions in Table I, it will be noted that only benzene does not give this ion. Consequently we consider that the hydrogen is removed from the side chain for all of the alkylbenzenes. This difference between ring and side chain is expected from the energetics of the reactions, since removal of ring hydrogen is endothermic



but abstraction from the α position of the side chain is exothermic



The presence of an alkyl substituent will not alter the energetics of (7) and (8) to any appreciable extent. In addition, it is very apparent from previous work that hydrogens may be removed from aliphatic carbon

(9) K. Watanabe, T. Nakayama, and J. Mottl, "Final Report on Ionization Potentials of Molecules by a Photoionization Method," Army Project No. 5B99-01-004, 1959.

(10) N. A. Boelrijk and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 730 (1962).

(11) C. E. Melton and W. H. Hamill, *J. Chem. Phys.*, **41**, 3464 (1964).

(12) API Project 44, Tables of Mass Spectral Data, Texas A & M.

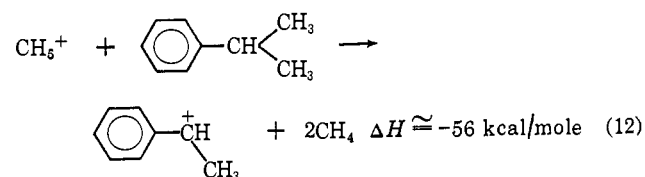
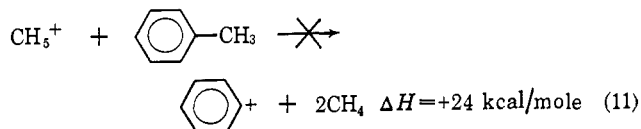
atoms.³ The C₇H₇⁺ ions in (9) and (10) are written as benzyl ions, but the possibility that they are tropylium ions must be entertained.

From Table I it may be seen that approximately a tenfold variation in (MW – H)⁺ intensity occurs, ranging from 0.028 for toluene to 0.24 for pentamethylbenzene. We have not been successful in rationalizing these variations in terms of a general principle, but a few qualitative observations can be made. Intensities of (MW – H)⁺ ions tend to increase as the number of substituents on the benzene ring increases. This increase is most noticeable in the compounds toluene, mesitylene, and pentamethylbenzene for which the relative intensities of (MW – H)⁺ ions are 1:4.5:8.6. This increase in intensity is appreciably greater than the increase in the number of methyl groups in the molecules (from which the H[•] ions are presumably abstracted), and this suggests that an interaction such as hyperconjugation may be operating. The quite low (MW – H)⁺ intensities observed for



which have no benzyl hydrogens, show that the probability for abstracting these hydrogens is low. In a previous study on paraffin hydrocarbons³ it was assumed that hydrogens could not be abstracted from aliphatic methyl groups (primary hydrogens). The formation of (MW – H)⁺ ions from iii indicates that this assumption is not strictly valid. The results in Table I offer some indication that hydrogens on alkyl-substituted benzyl carbon atoms (secondary and tertiary benzyl hydrogens) are abstracted more easily than primary benzyl hydrogens. This is to be anticipated on the basis of established chemical principles. Finally, the variations in the (MW – H)⁺ intensities for 1,2-, 1,3-, and 1,4-diethylbenzene (0.071, 0.097, and 0.119, respectively) indicate that unknown factors are operating.

From an inspection of the abundances of the (MW – CH₃)⁺ ions for the first four compounds listed in Table I, it is apparent that loss of CH₃ does not come from decomposition of the rings or from a methyl group attached to the ring, but comes only from methyl groups bonded to another alkyl carbon atom. This difference is expected on the basis of the energetics of the reactions



Loss of alkyl fragments from aliphatic hydrocarbons has been previously established.³

It is also apparent that there is a correlation between the number of methyl groups in the aliphatic chain of *n*

Table III. Comparison of Abundance of (MW - CH₃)⁺ Ions

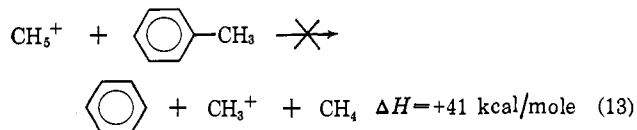
Compound	Exptl	Calcd
	0.068	0.061
	0.055	0.055
	0.032	0.028
	0.034	0.028
	0.053	0.055
	0.059	0.055
	0.046	0.055
	0.043	0.055
	0.057	0.055
	0.026	0.028
	0.030	0.028
	0.011	0.025
	0.050	0.075
	0.075	0.075
	0.060	0.069
	0.096	0.118
	0.121	0.110

carbon atoms ($n \geq 2$) and the abundance of (MW - CH₃)⁺ ions without much regard for the structure of the resulting ion. We take the abundance of (MW - CH₃)⁺ ions to be proportional to the ratio of aliphatic methyl groups to the total number of carbon atoms and calculate the value of the proportionality constant for several compounds. These values are averaged, and the (MW - CH₃)⁺ abundances calculated using this average are given in Table III.

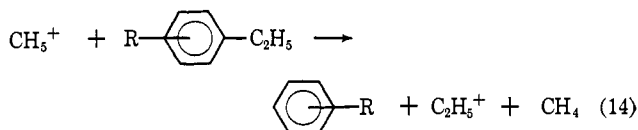
Table I also shows the loss of ethyl, propyl, and butyl groups. The loss of these higher alkyl groups follows essentially the same path as methyl loss—only from an aliphatic side chain and not the loss of the whole group attached to the ring. That is, ethyl loss from the diethylbenzenes is small, but it is 0.02–0.03 for the *n*-propyltoluenes and *sec*-butylbenzene. Loss of ethyl groups is much smaller for isopropyl- and isobutylbenzene, for which no C₂H₅⁺ loss may occur without rearrangement.

Let us now consider the last row in Table I, the formation of alkyl ions, R⁺, from the alkylbenzenes in which R refers to the largest alkyl group if more than

one are present. Small concentrations of CH₃⁺ ions could be missed because this ion reacts rapidly with methane, but the formation of methyl ion from reaction with toluene is vigorously endothermic and we feel that it does not occur at all.

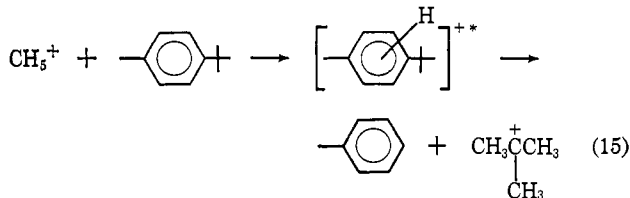


Formation of ethyl ions by a reaction of CH₃⁺ analogous to (13) is exothermic and probably occurs to a small extent. However, because of the large ion current for C₂H₅⁺ from reactions in methane alone, we could not detect reaction 14 in these experiments, although experiments with alkyl-deuterated compounds could establish the occurrence or nonoccurrence of



The most striking of these dealkylation reactions are those for the three molecules which may form tertiary alkyl ions by simple bond fission: *t*-amylbenzene, 1-methyl-4-*t*-butylbenzene, and 1,4-di-*t*-butylbenzene. For these compounds C₅H₁₁⁺ or C₄H₉⁺ is the dominant reaction product, about 0.8 of the additive ionization. This dealkylation reaction is the obvious explanation for the failure to observe (MW + H)⁺ ions for these compounds; all of the (MW + H)⁺ ions decompose. The virtually complete extent of decomposition is surprising. However, it has also been observed in condensed-phase chemistry that the *t*-butyl group is easily removed from an aromatic ring by acid-catalyzed reactions.¹³

The alkyl group cannot be displaced by attack at only the substituted position, because the relative abundance of the tertiary alkyl ions is much too large to be formed from attack at one of six nearly equivalent ring carbon atoms. Consequently, we are obliged to assume that attack by either CH₃⁺ or C₂H₅⁺ (displacement of *t*-butyl by the ethyl ion is also exothermic) at any ring position is effective for displacement.



Either the proton is capable of rapid migration about the ring, or the protonation must be nearly symmetrical in the plane perpendicular to the plane of the ring.

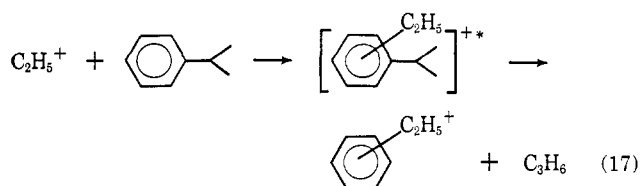
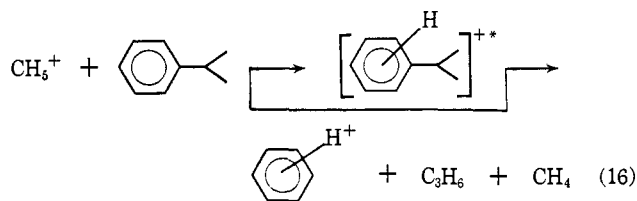
The rapid proton mobility in our experiments is different from the slow proton exchange observed in cold acidic solutions of aromatic hydrocarbons.¹⁴ However, in these experiments rapid exchange reactions began to occur as the solutions were warmed, and our experiments are at 185°. Part of the differences may

(13) M. J. Schlatter, *J. Am. Chem. Soc.*, **76**, 4952 (1954).
 (14) G. A. Olah, *ibid.*, **87**, 1103 (1965).

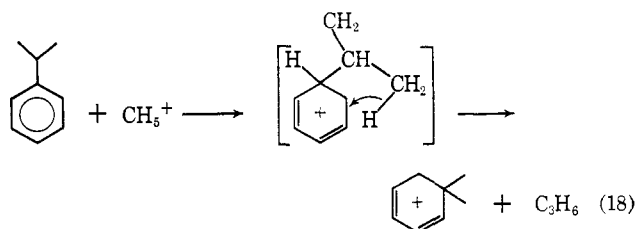
also be the result of the much greater acid strength of CH_5^+ than the solution acids.

The probability for formation of alkyl ions decreases in the order tertiary > secondary > primary, as may be deduced from the differences in abundances of alkyl ions for *t*-butyltoluene, isopropyltoluene, and *n*-propyltoluene. This order is the same as that observed in condensed-phase dealkylation. The presence of large amounts of C_4H_9^+ ions in isobutylbenzene suggests that the alkyl ion may rearrange during the decomposition to give the *t*-butyl ions.

The dealkylation reactions just mentioned are analogous to known condensed-phase reactions. However, there are two other processes which occur which have no solution analogs, and these processes compete with alkyl ion formation as decomposition processes of the protonated aromatic hydrocarbons. These reactions are illustrated for cumene



These olefin displacement reactions are effective dealkylation reactions since an alkyl group is removed from the ring. Reaction 16 is exothermic by about 8 kcal/mole, and (17) is probably exothermic as well. The variation in relative amounts of alkyl ion formation, olefin displacement by protons, and olefin displacement by ethyl ions cannot be explained in detail at present. A plausible reaction mechanism can be written for olefin displacement.



The increase in olefin elimination brought about by alkyl substitution on the ring (as in methylcumene) may be the result of stabilization of charge in the intermediate written above by the alkyl groups.

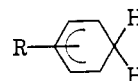
For 1-methyl-4-*t*-butylbenzene, and di-*t*-butylbenzene, the decompositions of the protonated hydrocarbons, to give *t*- C_4H_9^+ and toluene or *t*-butylbenzene, are 40–50 kcal/mole more exothermic than any other decomposition reaction. One may reasonably expect

that these low-energy processes will be the ones which will be observed, as is in fact the case. However, the variation of the relative amounts of dealkylation or loss of olefin for the propyl and butyl aromatic hydrocarbons must be due to subtle differences in energy or structure, and there are not enough data for a trend to be apparent.

The spectra of the two naphthalenes agree well with expectations from the considerations presented for the alkylbenzenes, present no complications, and will not be discussed.

Discussion

The structure of the protonated species cannot be determined from the spectra. However, it is very tempting to consider that these species are similar to the protonated intermediates which are observed or postulated in solution chemistry



particularly in view of the similarity of the reactions observed in common in gaseous and condensed-phase proton transfer to give stable species, alkylation by carbonium ions, and acid-catalyzed dealkylation.

The electron-impact mass spectra of alkylbenzenes have been summarized in a recent review.¹⁵ This work includes studies on deuterium and ^{13}C -labeled compounds and interpretations of metastable peaks. It provides a detailed picture of the dissociation processes occurring after electron impact. Most of the data were obtained from conventional instruments at high electron energy. Because the ionization and activation of molecules by electron impact and chemical ionization are quite different, it is of interest to compare briefly the two kinds of spectra. Thus, more decomposition products are produced by electron impact and more extensive ionic rearrangements occur in electron-impact spectra than in chemical-ionization spectra. There is no evidence for any ring-opening reaction in the chemical ionization mass spectra in contrast to the high-energy electron-impact spectra.¹⁵ Chemical ionization spectra contain reasonably large amounts of $(\text{MW} - \text{H})^+$ ions, depending upon the kind and number of nonaromatic hydrogen atoms, but electron-impact spectra generally contain only small amounts of $(\text{MW} - \text{H})^+$ ions. β cleavage to form benzyl ions is common to both types of spectra. There is no evidence for ring expansion in the chemical ionization mass spectra although a small amount of C_7H_7^+ (0.01 of additive ionization) is observed in benzene, which might involve this phenomenon.

Acknowledgment. The authors are very grateful to Mr. W. C. Gieger for performing these experiments with his accustomed skill.

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