reaction intermediates be elucidated for small systems,[18] but also these reactions should prove extremely useful in structural determinations of gas-phase ions.

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Ion Cyclotron Resonance Study of the Mechanism of Chemical Ionization. Mass Spectroscopy of Selected Hydrocarbons Using Methane Reagent Gas

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Abstract: A four-section ion cyclotron resonance (icr) cell with independent trapping capabilities in the source and the reaction-analyzer regions has been used to study mechanisms of chemical ionization (CI) processes. A pressure dependence study on pure methane (a frequently used reagent gas) has shown that CI conditions approximating those of conventional high source pressure mass spectrometers can be obtained at a pressure of around 1×10^{-4} Torr using icr techniques. Through the use of trapping field ejection, the role of the principal reagent ions in methane, CH_5^+ and $C_2H_5^+$, in producing the various CI products from some C_6 hydrocarbons has been ascertained and mechanisms for such processes have been deduced. Results indicate that, with minor exceptions, only those CI reactions which are exothermic for ground state ion energetics actually occur. With the C_6 paraffins, $C_5H_{11}^+$ is a major CI product and is produced exclusively from CH_5^+ reagent ion; the other CI products, in the order of decreasing intensities, are $C_6H_{13}^+$, $C_4H_9^+$, $C_3H_7^+$, and $C_4H_8^+$ or $C_3H_6^+$, which have varying but systematic contributions from both CH_5^+ and $C_2H_5^+$. The CI of cyclohexane produced primarily $C_6H_{11}^+$, having both CH_5^+ and $C_2H_5^+$ as reagent ions, but the fragments $C_3H_7^+$, $C_4H_8^+$, and $C_4H_9^+$ came exclusively from CH_5^+. The CI of benzene produces primarily $C_6H_7^+$ with minor amounts of $C_7H_7^+$. The former had mostly CH_5^+ as progenitor ion while $C_7H_7^+$ had the third reagent ion in methane, $C_3H_5^+$, as its primary precursor. The results of this study are compared with related work and generally acceptable agreement was found despite widely variant experimental parameters.

A survey of recent literature[2] reveals that the ion cyclotron resonance (icr) technique has played an ever increasing part in the study of gas phase ion–molecule reactions. It has proven its value by elucidating complex reaction mechanism and by determining the endothermicity or exothermicity of ion–molecule reactions through ion cyclotron double resonance. More recently, quantitative determinations of reaction rate constants and energy dependence of some ion–molecule reactions have been reported. In this paper, we will present another extension of icr spectroscopic techniques to elucidate the mechanism of chemical ionization (CI) mass spectroscopy of selected C_6 hydrocarbons.

Even though chemical ionization studies in conventional high pressure source mass spectrometers are done in the 0.5–1 Torr range, comparable studies can be performed in the icr at around 1×10^{-4} Torr. This is possible because of the long ion residence times associated with weak electric and strong magnetic fields of an ion cyclotron resonance mass spectrometer. For the drift parameters used in this investigation, for example, the ion residence time at the magnetic field to detect m/e 85 is 14 msec.[3] Since this is about five orders of magnitude higher than the ion residence times in a conventional high pressure source, chemical ionization experiments can be readily performed at a pressure of around 1×10^{-4} Torr in an icr instrument.

In this study, methane was used as the reagent gas. It was chosen for this investigation both because ion–molecule reaction products for this system have been well characterized and because it has been used most extensively as the reagent gas in chemical ionization studies. It has, however, been impossible to determine which one of the two major ion–molecule products in methane (CH_5^+ and $C_2H_5^+$) are responsible for the various chemical ionization products. The technique of ion cyclotron resonance using trapping field ion ejection was used to resolve individual contributions from these principal secondary ions in high pressure methane.

The ion-ejection technique used in this research was developed by Beauchamp and Armstrong.[4a] The principles of ion ejection have been discussed and its

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(1) Alfred P. Sloan Fellow, 1968–1972.

(2) J. D. Baldeschwieler, *Science*, **159**, 263 (1968); J. D. Baldeschwieler and S. S. Woodgate, *Accounts Chem. Res.*, **4**, 114 (1971), and references cited therein.

(3) Techniques recently developed for the experimental measurement of residence times (R. P. Clow and J. H. Futrell, *Int. J. Mass Spectrom. Ion Phys.*, **8**, 119 (1972)) have demonstrated that residence times are somewhat less than 14 msec under these conditions. The general conclusion of this paragraph nevertheless applies.

(4) (a) J. L. Beauchamp and J. T. Armstrong, *J. Rev. Sci. Instrum.*, **40**, 123 (1969); (b) M. T. Bowers, D. D. Ellemen, and J. King, *J. Chem. Phys.*, **50**, 4787 (1969).

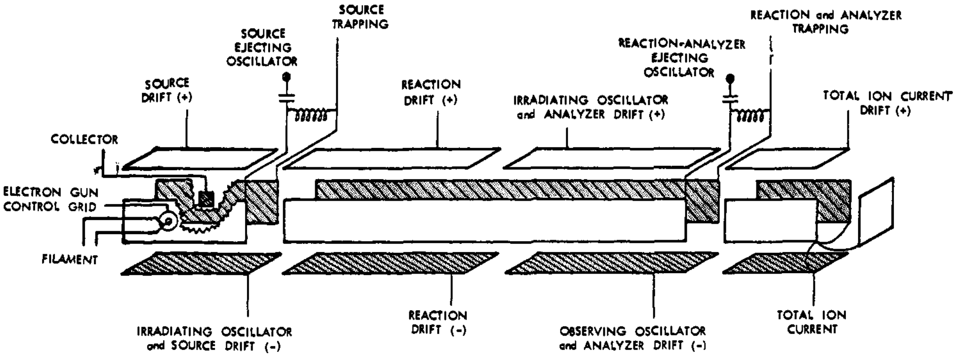

Figure 1. Schematic view of the four-section chemical ionization icr cell.

application to the study of concurrent ion–molecule reactions has been illustrated[4b] and will not be presented here. It will be sufficient to state that ions are ejected from the icr cell by increasing the amplitude of the natural oscillatory motion of an ion in the trapping field with a radio frequency (rf) signal generator until it is neutralized on a trapping plate. Since the frequency of this harmonic oscillation is given approximately by the expression

$$\omega_T = (4qV_T/md^2)^{1/2} \qquad \text{(A)}$$

(where q is the ion charge, V_T the trapping potential, m the ion mass, and d the distance between the trapping plates) which depends inversely on the square root of mass, a particular ion may be selectively ejected.

Experimental Section

The icr spectrometer used in this study has been described elsewhere.[5] Particular features are the use of a 12-in. magnet, heated dual gas inlets with variable leaks, and a newly designed four-section icr cell which can be operated at elevated temperatures. A schematic of this cell, similar in design with the ceramic-mounted, bakeable flat Varian cell, is shown in Figure 1. The unique features of this cell are (1) an extra 6.35-cm reaction zone between the source and the analyzer regions, (2) separate trapping plates in the source and the reaction-analyzer regions such that trapping fields can be independently varied and ejection applied to either region, (3) closure of the total ion current collector plates to enhance collection efficiency, and (4) independently variable positive and negative drift potentials for the various regions of the cell.

The mixture of the C_6 analytical gas being investigated with methane reagent gas was prepared in the analyzer chamber using the two gas inlet systems. The analytical gas was introduced into the analyzer through one inlet to an ionization gauge pressure reading of around 1.3×10^{-6} Torr. The total pressure was then taken up to 9.2×10^{-5} Torr by leaking methane into the analyzer chamber through the second inlet. The partial pressure of benzene was greatest at 0.33% while that of others was around 0.27% after correcting for relative total ionization cross sections. In all the experiments, the ionizing electron beam was operated at 70-eV energy and the trap current (*ca.* 1.0 nA) adjusted to give a total ion current of around 4 pA and always less than 5 pA.

The typical electrostatic potentials used in this study are presented in Table I. Under these conditions (as will be shown later) the primary electron impact ions in methane, CH_4^+ and CH_3^+, are essentially quantitatively converted to CH_5^+ and $C_2H_5^+$, respectively. These secondary ionic products were then selectively ejected in the reaction-analyzer region utilizing trapping field ejection. The ejection frequencies calculated from eq A are 21.1 and 16.2 kHz for CH_5^+ and $C_2H_5^+$, respectively, for the parameters of Table I. The experimental values were obtained by varying the frequency to obtain a minimum icr signal. These frequencies were 28.5 ± 0.50 and 21.1 ± 0.50 kHz. (There was a small deviation from the theoretical frequency in the work of Beauchamp and Armstrong as well, and its source is still unknown. It is probably related to the field distortion resulting from the cell geometry and the relatively large trapping potential of 0.50 V necessary for ion ejection work.) The amplitude of the ejection rf was 0.50 V peak to peak.

Table I. Typical Drift and Trapping Conditions

Source region	Reaction region	Analyzer region	
0.25	0.50		Trapping voltage
0.13	0.08	0.08	Positive drift voltage
0.08	0.08	0.08	Negative drift voltage

The ion–molecule reaction study for methane and the chemical ionization studies of C_6 hydrocarbons using methane reagent gas were performed both at room temperature and at 95°. The detector marginal oscillator was operated at 216 kHz and the magnetic field was swept to obtain the mass spectra through magnetic field modulation. All the intensity values presented have been corrected for the first-order mass discrimination in an icr resulting from sweeping the magnetic field.[6] This correction was made by multiplying each intensity by a correction factor proportional to the reciprocal of the ionic mass.[7]

Results and Discussion

Pure Methane. Because of its role as reagent gas, ion–molecule reactions in methane were briefly reexamined. The pressure dependence of major primary ions, CH_2^+, CH_3^+, and CH_4^+, which makes up approximately 99% of the total electron impact ionization, and their reaction products CH_5^+, $C_2H_5^+$, $C_2H_4^+$, and $C_3H_5^+$ are displayed in Figures 2 and 3. As has been shown earlier by high source pressure techniques,[5–7] the primary ions react rapidly in methane. The falloff of CH_2^+ intensity is accompanied by its reaction with methane to give $C_2H_3^+$ and $C_2H_4^+$. The other two primary ionization products, CH_3^+ and CH_4^+, likewise react rapidly to produce $C_2H_5^+$ and CH_5^+, respectively. Above a pressure of 6×10^{-5} Torr, the intensities of primary ions are negligible and the intensities of products $C_2H_5^+$ and CH_5^+ remain constant, indicating that they do not react further with methane. The secondary species $C_2H_4^+$ also does not react and

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[5] J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **89**, 4569 (1967).

(6) A. G. C. Goode, R. M. O'Malley, A. J. Ferrer-Correia, R. I. Massey, K. R. Jennings, J. H. Futrell, and P. M. Llewellyn, *Int. J. Mass Spectrom. Ion Phys.*, **5**, 393 (1970).

(7) Ths correction is appropriate for single-resonance spectra but not, in general, for ion–molecule reaction products. For the latter, as pointed out in ref 6, multiplication by m^2 is appropriate in the low conversion limit; a better correction takes into account measured residence times as a function of magnetic field (J. H. Futrell, to be published). The present experimental conditions, involving hundreds of collisions, do not correspond to these limits, and no simple procedure for quantitative correction of the data is proposed. Consequently only a qualitative comparison with previous data is possible, and the good agreement with other experiments must be regarded to some extent as fortuitous.

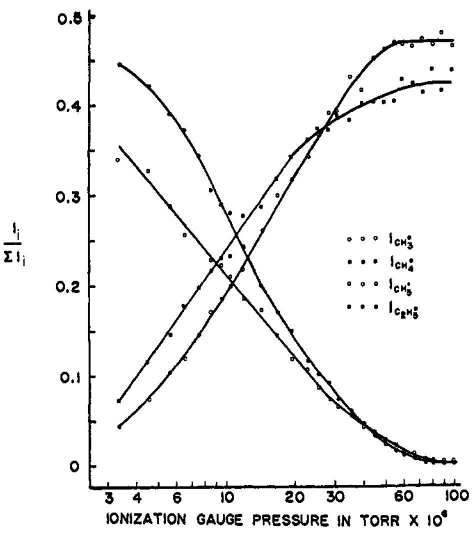

Figure 2. Relative intensities of CH_3^+, CH_4^+, CH_5^+, and $C_2H_5^+$ as a function of methane pressure.

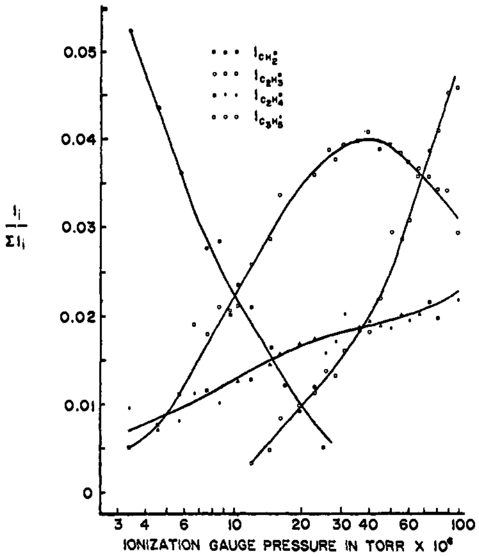

Figure 3. Relative intensities of CH_2^+, $C_2H_3^+$, $C_2H_4^+$, and $C_3H_5^+$ as a function of methane pressure.

gradually increases with methane pressure. The secondary product ion $C_2H_3^+$, on the other hand, reaches a maximum at a pressure of about 4 × 10^{-5} Torr and decreases in intensity with higher pressure. It apparently reacts with methane to form $C_3H_5^+$ whose steeper pressure dependence is indicative of a third-order contribution to its production.

The results plotted in Figures 2 and 3 are those obtained at a temperature of 95°. The operation of the icr cell at room temperature coupled with the inlet being used at ambient temperature produced a highly complex mass spectrum at elevated pressure. The ionic species found (ranging from m/e of 43 to as high as 107) and their relative intensities correlate excellently with those reported by several workers.[8-10] The absence of ionic species with more than three carbons at elevated analyzer and inlet temperatures, and at ambient analyzer temperature after it has been baked for several days at temperatures of 250°, indicates that these products are not formed by consecutive ion–molecule reactions,[8] nor from contaminants in the methane sample,[10] but are probably due to the desorption of absorbed substances on the inlet and/or the analyzer chambers walls as postulated by Field, *et al.*[9]

In Table II, the mass distribution at chemical ionization condition (9.2 × 10^{-5} Torr by ionization gauge and some parameters as Table I) of pure methane is tabulated along with the results of ejecting selectively the principal ions, $C_2H_5^+$ and CH_5^+. As can be seen in Table II, the intensities of CH_5^+ and $C_2H_5^+$ make up approximately 90% of the total ionic product. This is to be expected in that their precursors, CH_4^+ and CH_3^+, made up around 90% of the electron impact ionization products. The ion $C_2H_5^+$ can be ejected with 95% efficiency without affecting the intensity of CH_5^+. The ion CH_5^+ can in turn be ejected with 91% efficiency with an accompanying reduction in the $C_2H_5^+$ intensity of 15%. This results from the ejection of unreacted CH_3^+ which has entered the reaction-analyzer trapping region along with CH_5^+ (same could be said of $C_2H_3^+$, $C_2H_4^+$, and $C_3H_5^+$ and their precursors CH_2^+ and $C_2H_3^+$).

Table II. Relative Ion Intensities Resulting from the Ejection of CH_5^+ and $C_2H_5^+$ in Pure Methane at a Pressure of 9.1 × 10^{-5} Torr

	CH_5^+	$C_2H_3^+$	$C_2H_4^+$	$C_2H_5^+$	$C_3H_5^+$
No ejection	46.98	3.79	2.53	42.40	4.27
Eject $C_2H_5^+$	46.3	0	0	2.15	2.34
Eject CH_5^+	3.39	2.82	2.15	36.0	3.94

Even though the ejection of CH_5^+ and $C_2H_5^+$ does not appear to be 100% efficient, it is actually better than the values cited in Table II under true chemical ionization conditions. This apparent contradiction arises from the fact that, at the observing frequency of 216 kHz used in this experiment, magnetic field values of 2.4 kG and 4.1 kG are necessary for cyclotron resonance of CH_5^+ and $C_2H_5^+$, respectively. However, the chemical ionization products investigated in the C_6 hydrocarbons range in masses from 42 to 91 or 5.9 to 12.9 kG. As a consequence of the direct proportionality between ion residence time and magnetic field, the ion residence time for CH_5^+ and $C_2H_5^+$ at the magnetic fields to detect the chemical ionization products is much longer than at the fields used to detect their resonance signals of the reagent ions themselves. Consequently the ejection efficiencies are expected to be much better at the higher magnetic fields, probably approaching 100% ejection.

Chemical Ionization of C_6 Paraffins. The utilization of ion–molecule reaction products in methane as reagent ions to generate an analytical mass spectrum produces a characteristic pattern which is considerably different from that produced by electron impact ionization. The ions found in the chemical ionization of *n*-hexane with methane are presented in Table III and show that the mass distribution is considerably less complex (only about five CI products compared to over 30 by 70-eV electron impact[11]). The only CI

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(8) S. Wexler and N. Jesse, *J. Amer. Chem. Soc.*, **84**, 3425 (1962).

(9) F. H. Field, J. L. Franklin, and M. S. B. Munson, *ibid.*, **85**, 3575 (1963).

(10) R. M. Haynes and P. Kebarle, *J. Chem. Phys.*, **45**, 3899 (1966).

(11) API Research Project 44, "Catalog of Mass Spectra Data," Texas A and M University, College Station, Texas, 1963.

Table III. Relative Intensities from the Chemical Ionization of *n*-Hexane with Methane Reagent Gas

	CH_5^+	$C_2H_5^+$	$C_3H_5^+$	$C_3H_7^+$	$C_4H_8^+$	$C_4H_9^+$	$C_5H_{11}^+$	$C_6H_{13}^+$	$C_6H_{14}^+$
1.3×10^{-6} Torr *n*-hexane, 9.2×10^{-5} Torr total	39.84	37.74	4.97	4.51	0.63	3.49	1.61	6.53	0.17
Eject $C_2H_5^+$	40.00	0	1.06	2.14	0.66	2.10	1.27	3.48	0.03
Eject CH_5^+	2.44	30.62	3.79	2.50	0.66	1.61	0	2.61	0.09

products found in *n*-hexane were $C_6H_{13}^+$, $C_5H_{11}^+$, $C_4H_9^+$, $C_4H_8^+$, and $C_3H_7^+$ after corrections were made for the methane ion–molecule reaction products and isotopic contributions. (Field and Munson[12] discussed the behaviors of only $C_6H_{13}^+$ and $C_5H_{11}^+$ intensities as a function of total pressure in their CI work on *n*-hexane with methane reagent.) This large simplification in mass pattern is accompanied by an equally large change in the relative intensities as exemplified by the intense CI peak at m/q 95, the (M − 1) ion, where M represents molecular mass. In the electron impact spectrum, this mass makes up less than half of 1% of total ionization[11] while chemical ionization produces approximately 38% of the (M − 1) ion. The large rate for CI reactions is also evident in Table III. Even though *n*-hexane makes up only about 0.3% of the gas mixture, the CI products from *n*-hexane constitute approximately 17% of the spectrum under the stated conditions.

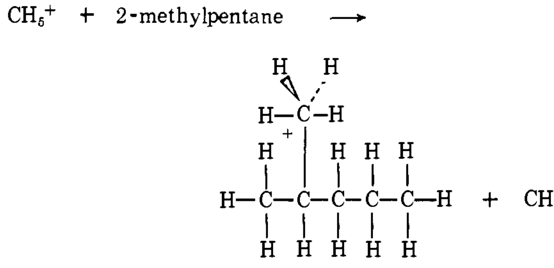
The results of ejecting $C_2H_5^+$ and CH_5^+ in the chemical ionization of *n*-hexane are also presented in Table III. The CI products left after the removal of $C_2H_5^+$ are attributed to CH_5^+ reactions. Similarly, the ejection of CH_5^+ gives a CI mass distribution which has had $C_2H_5^+$ as the precursor ion. With the exception of $C_5H_{11}^+$ all the chemical ionization products in *n*-hexane appear to have both CH_5^+ and $C_2H_5^+$ as precursor ions. The formation of $C_5H_{11}^+$, however, proceeds exclusively from CH_5^+. The chemical ionization results for all the C_6 hydrocarbons obtained from ejection experiments similar to that illustrated for *n*-hexane in Table III are summarized in Table IV.

As can be seen in Table IV, with minor exceptions chemical ionization of all the C_6 paraffins gives ionic products which are same as those for *n*-hexane. The possible CI reactions of CH_5^+ and $C_2H_5^+$ with *n*-hexane to give the observed products are summarized in Table V along with their heats of reactions. Quoted enthalpies of reaction are based upon thermochemical data of Franklin, *et al.*[13] For CH_5^+, a heat of formation value of 229 kcal mol^{-1} was used.[14] Entirely analogous reactions can be written for all the C_6 paraffins since the same reactions are energetically allowed. This generalization can be made because the heats of formation of these compounds range between the values −40 for *n*-hexane to −44 for 2,2-dimethylbutane.

$C_6H_{14}^+$. A trace of the molecular mass ion is present in some of the chemical ionization of C_6 paraffins. Its formation probably can be attributed to primary ionization by electron impact or to charge exchange from CH_2^+ and CH_4^+ ions from methane.

$C_6H_{13}^+$. The (M − 1) ion makes up a significant part of the chemical ionization spectra in all the C_6 paraffins. Its production is very exothermic from either precursor. The relative intensity decreases with branching (39% for *n*-hexane to 27% for 2,2-dimethylbutane) and the relative contribution by CH_5^+ to this (M − 1) ion also decreases from a high of 0.57 in *n*-hexane to 0.42 in 2,2-dimethylbutane. This systematic variation in the intensity of (M − 1) peak was observed by Field[15] in CI of larger hydrocarbons also. One can infer from this that the (M − 1) ion is produced by hydride abstraction from a secondary position of the C_6H_{14} molecule by $C_2H_5^+$ and CH_5^+ to give this ion and C_2H_6, and CH_4 and H_2 as neutrals, respectively. This systematic decrease in the intensity of this ion could be accounted for by the decreasing number of *sec*-hydrogens and the crossover in the relative contributions from CH_5^+ to $C_2H_5^+$ probably results from a competing reaction channel (to be discussed later) favorable only to CH_5^+.

$C_5H_{11}^+$. The intensity of this ion changes dramatically in the chemical ionization of C_6 paraffins. As shown in Table IV, its relative intensity goes up from a value of 10% in *n*-hexane to a high of 51% in 2,2-dimethylbutane. Furthermore, Table IV shows that $C_5H_{11}^+$ is produced only by CH_5^+. A contribution of up to 0.08 observed for 2,3-dimethylbutane could easily be accounted for by the incomplete ejection of CH_5^+, reaction during ejection, or reaction in the source region before ejection. The systematic behavior of $C_5H_{11}^+$ intensity with branching, coupled with the



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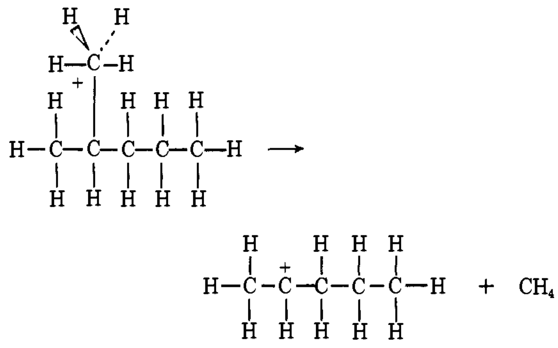

(1b)

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

(13) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," U. S. Department of Commerce, NBS, Washington, D. C., 1969.

(14) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **87**, 3294 (1965).

(15) F. H. Field, *Accounts Chem. Res.*, **1**, 42 (1968).

Table IV. Relative Ion Intensities in Selected C_6 Hydrocarbons with Methane Reagent[a]

m/e	Ion	n-Hexane	3-Methylpentane	2-Methylpentane	2,3-Dimethylbutane	2,2-Dimethylbutane	Cyclohexane	Benzene
42	$C_3H_6^+$			4.2 [0.49] (0.51)	7.1 [0.47] (0.53)			
43	$C_3H_7^+$	26.8 [0.46] (0.54)	16.4 [0.36] (0.64)	19.7 [0.43] (0.57)	12.4 [0.37] (0.63)	8.7 [0.43] (0.57)	8.4 [1.00]	
55	$C_4H_7^+$						Trace	
56	$C_4H_8^+$	3.8 [0.50] (0.50)	7.1 [0.50] (0.50)			2.6 [0.51] (0.49)	3.7 [1.00]	
57	$C_4H_9^+$	20.7 [0.57] (0.43)	19.0 [0.59] (0.41)	12.9 [0.52] (0.48)	6.4 [0.27] (0.73)	12.0 [0.49] (0.51)	6.8 [1.00]	
71	$C_5H_{11}^+$	9.6 [1.00]	23.1 [0.94] (0.06)	26.7 [0.93] (0.07)	42.8 [0.92 (0.08)	51.0 [0.94 (0.06)		
78	$C_6H_6^+$							8.6 [0.80] (0.20)
79	$C_6H_7^+$							87.5 [0.72] (0.28)
80	$C_6H_8^+$							Trace
83	$C_6H_{11}^+$						75.7 [0.58] (0.42)	
84	$C_6H_{12}^+$						3.9 [0.54] (0.46)	
85	$C_6H_{13}^+$	38.9 [0.57] (0.43)	34.4 [0.57] (0.43)	36.7 [0.54] (0.46)	31.1 [0.50] (0.50)	26.6 [0.42] (0.58)	0.9 [1.00]	
86	$C_6H_{14}^+$	Trace		Trace	Trace	Trace		
91	$C_7H_7^+$							4.2 [0.2] (0.2) {0.6}

[a] The relative intensities in per cent total chemical ionization products are tabulated vertically for each C_6 hydrocarbon studied. The values in brackets, parentheses, and braces which follow the per cent ion intensities represent contributions from CH_5^+, $C_2H_5^+$, and $C_3H_5^+$, respectively. For example, the relative intensity of $C_3H_7^+$ for n-hexane is 26.8% of total CI products. Of this 26.8%, 0.46 has CH_5^+ as the precursor reagent ion while the balance, 0.54, is due to CI from $C_2H_5^+$ reagent ion.

Table V. Possible Chemical Ionization Reactions of n-Hexane to Give the Observed Products and the Heats of Reactions for These CI Processes[a]

Eq no.		ΔH
1	$CH_5^+ + n\text{-}C_6H_{14} \rightarrow n\text{-}C_6H_{13}^+ + CH_4 + H_2$	−37
2	$\rightarrow n\text{-}C_5H_{11}^+ + 2CH_4$	−54
3	$\rightarrow n\text{-}C_4H_8^+ + CH_4 + C_2H_6$	−9
4	$\rightarrow trans\text{-}2\text{-}C_4H_8^+ + 2CH_4 + CH_3$	24
5	$\rightarrow n\text{-}C_3H_7^+ + CH_4 + C_3H_8$	−23
6	$C_2H_5^+ + n\text{-}C_6H_{14} \rightarrow n\text{-}C_6H_{13}^+ + C_2H_6$	−29
7	$\rightarrow n\text{-}C_5H_{11}^+ + C_3H_8$	−28
8	$\rightarrow n\text{-}C_5H_{11}^+ + C_2H_6 + CH_2$	66
9	$\rightarrow n\text{-}C_4H_9^+ + C_2H_6 + C_2H_4$	31
10	$\rightarrow t\text{-}C_4H_9^+ + C_2H_6 + C_2H_4$	−11
11	$\rightarrow trans\text{-}2\text{-}C_4H_8 + C_2H_6 + C_2H_5$	34
12	$\rightarrow i\text{-}C_3H_7^+ + C_2H_6 + C_3H_6$	−4
13	$\rightarrow n\text{-}C_3H_7^+ + C_2H_6 + C_3H_6$	15

[a] Chupka and Berkowitz[17] have recently obtained ΔH_f $(CH_5^+) \leq 223$ kcal mol^{-1} at 0°K using the inherently more accurate technique of photoionization. However, excited ions are present under the experimental conditions of this work, which are more analogous to those of Munson and Field,[11] and their value of ΔH_f $(CH_5^+) = 229$ kcal mol^{-1} was used in constructing the present table. Conclusions would not be substantively altered by using the photoionization result.

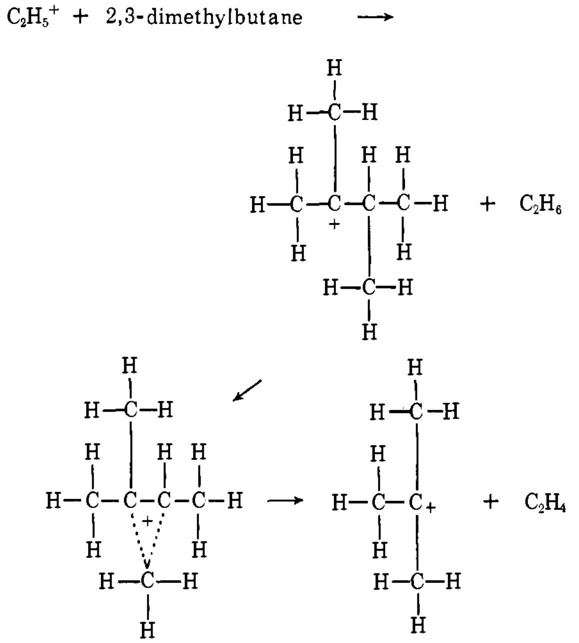
fact that CH_5^+ is only precursor, suggests for its formation the mechanism[16] which is shown in eq 1a and 1b. The reaction of CH_5^+ initially to protonate a methyl group which in turn dissociates to give $C_5H_{11}^+$ and CH_4 accounts for the dramatic increase in the relative intensities of $C_5H_{11}^+$ with branching. Moreover, the concept of competing reaction channels with this dependence on molecular structure rationalizes the apparent anomalous behavior found for the CH_5^+ contribution to the (M − 1) ion which was discussed previously.

$C_4H_9^+$. The formation of $C_4H_9^+$ from the CI of these C_6 paraffins is also exothermic, and its relative intensity varies from a high of 21% for n-hexane to a low of 6% for 2,3-dimethylbutane. The relative intensity appears to drop off systematically with branching except in the case of 2,3-dimethylbutane, where $C_4H_9^+$ is disproportionately small. A careful consideration of this structure reconciles this discontinuity. In order to produce $C_4H_9^+$ from 2,3-dimethylbutane, a carbon rearrangement must take place. Further evidence for the unique nature of this species from 2,3-dimethylbutane is the fact that 0.73 of its intensity is derived from $C_2H_5^+$, while the contribution of $C_2H_5^+$ to $C_4H_9^+$ formation from other C_6 paraffins ranges from 0.4 to 0.5. These suggest the methyl migration mechanism (eq 2a,b), which has its analog in solution chemistry.[16,17] This appears to be a further verification of the fact that $C_2H_5^+$ preferentially reacts by hydride abstraction while CH_5^+ reacts by a highly exoergic proton transfer reaction.

$C_3H_7^+$. The reaction to produce $C_3H_7^+$ is another chemical ionization process which is exothermic with both principal methane reagent ions CH_5^+ and $C_2H_5^+$, provided $i\text{-}C_3H_7^+$ is assumed to be the product ion. Its relative intensity also varies systematically with increasing branching going from a high of 27% total

(16) Additional experiments with CD_5^+ and $C_2D_5^+$ reagent ions (T. Elwood and J. H. Futrell, to be published) support this mechanism in that no deuterium incorporation is observed.

(17) R. T. Morrison and R. N. Boyd, "Organic Chemistry," Allyn and Bacon, Boston, Mass., 1963, p 259.



(2a)

(2b)

CI intensity for n-hexane to a low of 9% with 2,2-dimethylbutane. The ion $C_2H_5^+$ consistently contributes more than half of $C_3H_7^+$ intensity and probably reflects the fact that there are other more favored reactive channels (such as the reaction to form $C_5H_{11}^+$) available to CH_5^+. The production of $C_3H_7^+$ from 2,2-dimethylbutane requires a carbon chain rearrangement and occurs with very low probability. A scheme very similar to that for the formation of $C_4H_9^+$ from 2,3-dimethylbutane may be written.

$C_4H_8^+$ and $C_3H_6^+$. These chemical ionization products are the only endothermic species (assuming ground state ions) found in the C_6 paraffins. The endothermicity for unexcited ions is reflected in the low relative intensities of these ions, which is less than 7% of the total CI products. It is interesting to note that 2-methylpentane and 2,3-dimethylbutane give $C_3H_6^+$ while the others give $C_4H_8^+$, with the precursor ions being equally CH_5^+ and $C_2H_5^+$. This illustrates the influence of structure of the neutral molecule in determining the CI products formed. The presence of an isopropyl group R-CH$(CH_3)_2$ favors $C_3H_6^+$; otherwise, $C_4H_8^+$ is produced. Mechanisms analogous to those already given can be invoked to rationalize this behavior.

In summary, the chemical ionization of the C_6 paraffins by methane reagent gives primarily products which are produced from exothermic reaction channels. The observation of $C_3H_6^+$ and $C_4H_8^+$ are exceptions and can be used to put a lower limit on the internal excitation of CH_5^+ and $C_2H_5^+$. Thus, reaction 8 of Table V can be used to establish that some $C_2H_5^+$ ions have up to 2.5-eV internal excitation. The systematic variation of relative intensities with branching suggests that $C_5H_{11}^+$ is produced exclusively from the initial attack of CH_5^+ on a methyl group at the expense of other CI products which in general have both CH_5^+ and $C_2H_5^+$ as precursors. The formation of $C_4H_9^+$ from 2,3-dimethylbutane illustrates that structural rearrangement occurs but the formation of $C_3H_6^+$ from only 2-methylpentane and 2,3-dimethylbutane suggests that this is an unfavorable reactive channel.

Chemical Ionization of Cyclohexane and Benzene. The cyclic compounds cyclohexane and benzene behaved very differently from the C_6 paraffins discussed previously. In cyclohexane, the CI products from methane reagent are shown in Table IV. A small amount of parent ion also formed can be attributed to charge transfer and primary ionization and is not included among the CI products. Even though the (M − 1) ion, which makes up 76% of total CI products, has contributions from both CH_5^+ and $C_2H_5^+$, all the smaller fragment ions and the protonated cyclohexane ion come exclusively from CH_5.$^+$ This can be rationalized through thermodynamic considerations as follows.

$$CH_5^+ + c\text{-}C_6H_{12} \longrightarrow c\text{-}C_6H_{11}^+ + CH_4 + H_2 \quad (3)$$

$$C_2H_5^+ + c\text{-}C_6H_{12} \longrightarrow c\text{-}C_6H_{11}^+ + C_2H_6 \quad (4)$$

The reactions to form $C_6H_{11}^+$ (M − 1) ion from CH_5^+ and $C_2H_5^+$ are exothermic by 33 and 2 kcal mol^{-1}, respectively. However, the presence of the (M + 1) ion, which has CH_5^+ as precursor, suggests the following set of reactions.

$$CH_5^+ + c\text{-}C_6H_{12} \longrightarrow [c\text{-}C_6H_{13}^+]^* + CH_4 \quad (5a)$$

$$[c\text{-}C_6H_{13}^+]^* + CH_4 \longrightarrow c\text{-}C_6H_{13}^+ + (CH_4)^* \quad (5b)$$

$$[c\text{-}C_6H_{13}]^* \longrightarrow c\text{-}C_6H_{11}^+ + H_2 \quad (5c)$$

(In reaction 5c, c-$C_6H_{11}^+$ is considered as the logical dissociation product; moreover, thermochemical data for other $C_6H_{11}^+$ are not available.) The unimolecular dissociation of the $C_6H_{13}^+$ is endothermic by about 15 kcal mol^{-1} but could be driven by the very energetic protonation reaction 5a which is exothermic by 47 kcal mol^{-1}. If equal partition of energy takes place among the various degrees of freedom, the (M + 1) ion would retain about 41 kcal mol^{-1} of this energy, which is more than sufficient to drive the endothermic H_2 elimination reaction to form c-$C_6H_{11}^+$. This mechanism is further supported by consideration of the relative intensities of the (M + 1) ion found in this study and in the study by Field and Munson.[18] They find this intensity to be around 9% while we find only 1%. There is, however, excellent agreement for the (M − 1) ion intensity (74 *vs.* 76%). This difference in the (M + 1) ion probably results from the different experimental parameters of the two studies. The high source pressure and corresponding high collision frequency used by Field and Munson would favor the collisional deexcitation of the (c-$C_6H_{13}^+$)* species and explain the observed difference in its intensity.

Even though (M − 1) production is very exothermic, the formation of fragment ions found in this study are near thermoneutral only for CH_5^+ precursor.

$$CH_5^+ + c\text{-}C_6H_{12} \longrightarrow n\text{-}C_4H_9^+ + CH_4 + C_2H_4 \quad (6)$$

$$\longrightarrow 1\text{-}C_4H_8^+ + CH_4 + C_2H_5 \quad (7)$$

$$\longrightarrow n\text{-}C_3H_7^+ + CH_4 + C_3H_5 \quad (8)$$

These heats of reactions are 12, 12, and −4 kcal mol^{-1}, respectively. However, the production of corresponding ions from $C_2H_5^+$ are 62, 76, and 44 kcal mol^{-1} endothermic.

In addition to the CI products found in this study, Field and Munson[18] listed $C_5H_9^+$ as a CI product of c-C_6H_{12}. This discrepancy cannot be easily explained

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[18] F. H. Field and M. S. B. Munson, *J. Amer. Chem. Soc.*, **89**, 4272 (1967).

in that its formation from CH_5^+ is 42 kcal mol^{-1} exothermic. One can speculate that the low pressure and long reaction times of icr may permit this ion to dissociate to $C_3H_7^+$. The unimolecular dissociation

$$C_5H_9^+ \longrightarrow C_3H_7^+ + C_2H_2 \qquad (9)$$

is only about 30 kcal mol^{-1} endothermic (assuming $C_5H_9^+$ from CI of *c*-C_6H_{12} has the properties of $C_5H_9^+$ from the ionization of the molecules *cis*- and *trans*-1,2-dimethylcyclohexane[10]) and there is sufficient energy from the proton transfer reaction for the overall reaction sequence to occur as postulated. It should also be pointed out that high pressure chemical ionization experiments are usually carried out under conditions such that CH_5^+ and $C_2H_5^+$ will undergo many collisions with methane prior to reaction with the additive molecule. Consequently, reagent ions in the present experiments may possess a broader distribution of excitation energy than in the Field and Munson experiments.

The chemical ionization of benzene with methane reagent produced $C_6H_7^+$, $C_7H_7^+$, and $C_6H_6^+$. The latter probably is a charge-transfer or primary ionization product. Using a value of 235 kcal mol^{-1} for the heat of formation of $C_6H_7^+$,[19] CI reactions to produce $C_6H_7^+$ from CH_5^+ and $C_2H_5^+$ are 30 kcal mol^{-1} exothermic and 12 kcal mol^{-1} endothermic, respectively.

$$CH_5^+ + C_6H_6 \longrightarrow C_6H_7^+ + CH_4 \qquad (10)$$

$$C_2H_5^+ + C_6H_6 \longrightarrow C_6H_7^+ + C_2H_4 \qquad (11)$$

The observation of protonated benzene from $C_2H_5^+$ may result from internally excited $C_2H_5^+$ or may simply reflect an uncertainty in the heat of formation of $C_6H_7^+$. In any case, of the 88% of CI products which make up $C_6H_7^+$, only about 28% of it is produced *via* this thermodynamically less favored route.

The only other CI product found for benzene was $C_7H_7^+$. However, the ejection results suggested that CH_5^+ and $C_2H_5^+$ make only a minor contribution to the production of the tropylium ion. The plausible alternative reaction

$$C_3H_5^+ + C_6H_6 \longrightarrow C_7H_7^+ + C_2H_4 \qquad (12)$$

which is exothermic by 15 kcal mol^{-1} suggests that the third reagent ion in methane, $C_3H_5^+$, may be responsible for the reaction product. This possibility was further investigated by examining a mixture of benzene and 3-bromopropene. The latter is an excellent source for $C_3H_5^+$, even though there are minor amounts of $C_3H_3^+$ and $C_3H_5Br^+$ as well.

At a benzene pressure of 1.8×10^{-6} Torr, the mass spectrum is that expected from a 70-eV electron impact ionization. However, the addition of small amounts of 3-bromopropene produced the anticipated $C_7H_7^+$ product in amounts directly proportional to added 3-bromopropene. Finally, the more conventional ion cyclotron double resonance (icdr) verified the link between $C_3H_5^+$ and the tropylium ion.

In addition to the protonated benzene ion, $C_6H_7^+$, Munson and Field[17] observed the addition products $C_9H_{13}^+$, $C_9H_{11}^+$, and $C_8H_{11}^+$; however, no $C_7H_7^+$ was observed. These higher mass adduct ions which are not observed in this study were interpreted as addition products of major product ions in methane with benzene. The conflicting results between high pressure source and icr CI studies can be reconciled by considering the different experimental parameters; the icr experiments are performed at a pressure which is four orders of magnitude lower but with ion residence times correspondingly longer. For the addition product $C_9H_{11}^+$ the data indicate that the unimolecular dissociation to $C_7H_7^+$

$$C_9H_{11}^+ \longrightarrow C_7H_7^+ + C_2H_4 \qquad (13)$$

occurs with a lifetime of the intermediate which is short compared with icr observation times ($\sim 10^{-3}$ sec) but long compared with collision times in high pressure CI ($\sim 10^{-6}$ sec). Similar decomposition reactions can be written for other addition products found by Munson and Field involving dissociation products $C_7H_7^+$ and methane for ($C_8H_{11}^+$) and $C_7H_7^+$ and ethane for ($C_9H_{13}^+$). Alternative low-energy dissociation pathways leading to protonated benzene, $C_6H_7^+$, and corresponding neutral products may also be invoked.

These low-energy unimolecular dissociation channels should be especially favored under icr experimental conditions. However, the high source pressure CI technique and short ion transit time used by Munson and Field would render collisional stabilization and detection of short-lived excited addition products such as $C_9H_{11}^+$ especially probable. The tandem results of Bone and Futrell[20] lend support to the interpretation of these results as competition between collisional stabilization and dissociation of the addition products. In their study, $C_3H_5^+$ was impacted at near thermal energies on benzene at an intermediate collision chamber pressure of around 1 μ. They found proton transfer to produce $C_6H_7^+$ was the major reaction observed although adducts $C_9H_{11}^+$ and $C_9H_{10}^+$ were detected as very minor products. Unfortunately $C_7H_7^+$ was not reported as a product in the tandem study. We are unable to suggest any ready explanation which would rationalize the two sets of data. It should be noted that the present results provide no information on the question whether $C_6H_7^+$ is a product from this interaction. The reason is that major contributions from other ions to this product obscure any contribution from $C_3H_5^+$. Consequently the definitive information provided here is that $C_7H_7^+$ is a product and that adduct ions are not produced in observable amounts at the observation times characteristic of our icr experiments.

The chemical ionization of cyclohexane and benzene are different from that of C_6 paraffins in that one product in each case dominates the product distribution. In *c*-C_6H_{12}, the (M − 1) ion constitutes around 76% of the CI product while the (M + 1) ion in benzene accounted for approximately 88%. Fragment ions are found only in cyclohexane and they are produced exclusively from CH_5^+. With benzene, the only other CI product detected other than $C_6H_7^+$ was the tropylium ion. Ejection results and benzene–3-bromopropene mixture experiments show that $C_3H_5^+$ reacts with C_6H_6 to give this ion. With both cyclohexane and benzene, only those species which are produced from exothermic and near-thermoneutral reactions are observed.

Conclusions

The application of icr techniques to chemical ioniza-

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

(20) L. I. Bone and J. H. Futrell, *J. Chem. Phys.*, **47**, 4366 (1967).

tion appears to be an important extension of icr mass spectroscopy. The icr CI products observed and their relative intensities agree well with the results from more conventional high source pressure techniques where comparisons are available. The minor discrepancies noted can be reconciled once the different experimental conditions of the two techniques are considered.

The use of the trapping field ejection makes it possible to investigate the mechanisms of chemical ionization. The utilization of this technique in CI of C_6 hydrocarbons with methane reagent distinguishes which of the major reagent ions, CH_5^+ and $C_2H_5^+$ in methane, are precursors to the various CI products. As an illustration, the work on the C_6 paraffins has shown that CH_5^+ leads exclusively to $C_5H_{11}^+$ while all the other fragments have varying but systematic degrees of contribution from both CH_5^+ and $C_2H_5^+$.

In the future, the use of isotopically labeled compounds could be used to study in more detail the mechanisms of CI reactions. Further, the use of different reagent gases and the CI study of other functional groups are natural extensions of this icr CI study.

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Emission Properties of Aromatic Amines in Solution. Phenoxazine System[1]

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Abstract: The absorption and emission properties of phenoxazine and 10-phenylphenoxazine in EPA and 3-methylpentane were investigated over a temperature range from 298 to 77°K. A PPP (SCF–MO–CI) calculation was used in conjunction with the absorption spectrum and polarization data to assign four electronic transitions in the region 27,000–40,000 cm^{-1}. The transitions of phenoxazine (C_{2v} symmetry) in order of increasing energy are $^1B_1 \leftarrow {}^1A_1$ (28,850 cm^{-1}), $^1B_1 \leftarrow {}^1A_1$ (31,970 cm^{-1}), $^1A_1 \leftarrow {}^1A_1$ (39,800 cm^{-1}), and $^1B_1 \leftarrow {}^1A_1$ ($\sim$42,000 cm^{-1}). The spectral appearance of the emission as well as the results of lifetime and quantum yield determinations can be explained on the basis of a change in geometry of the excited singlet and triplet states with respect to the planar ground state. The fact that phenoxazines exhibit in-plane phosphorescence polarization, whereas planar aromatic hydrocarbons are polarized out-of-plane, and the more effective spin–orbit coupling of the former, can also be attributed to such a geometry change.

Aromatic amines often exhibit unusual photochemistry such as photoionization *via* biphotonic absorption and dissociation processes with excited singlet states as the reactive intermediates.[2,3] For a clear understanding of the nature of these phenomena, it is necessary to examine the absorption spectra as well as the emission properties of these compounds. The present study deals with the emission characteristics of two such amines, phenoxazine (*cf.* Figure 1b) and 10-phenylphenoxazine in polar and nonpolar solvents.

In a recently published paper[3] we reported the results of a flash-photolytic study of phenoxazine (PH) which indicated a primary photolytic dissociation of an excited singlet state(s), leading to the neutral radical P·. Moreover, it was found that the observed photoionization process, which generates the monopositive cation, is consistent with a biphotonic mechanism in which the lowest triplet state acts as an intermediate. The emission spectrum of PH has also received some recent attention. In an attempt to elucidate the reactivity of heterocyclic systems, Mantsch and Dehler[4] have measured the polarized fluorescence excitation spectrum of PH using the photoselection method in a rigid ethanol glass. These workers found that all transitions below 45,000 cm^{-1} are polarized parallel with respect to the fluorescence, except for a transition around 40,000 cm^{-1} (barely discernible in absorption) which is negatively polarized. These results are in agreement with recent measurements by Lhoste and Merceille,[5] but only below 40,000 cm^{-1}.

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