NO_2, we would expect E_a for HNO_2 addition to C_2H_4 to be the same as that for anti-Markovnikov addition to C_3H_6. (ΔC_p for the nitroethane reaction is also close to zero.) Taking E (decomposition) for the nitroethane as 43 ± 2 kcal/mole, we see that addition of HNO_2 to C_2H_4 has an activation energy of 27.5 ± 2 kcal/mole and that this is indeed the same as for anti-Markovnikov addition of HNO_2 to C_3H_6.

There are a number of problems raised by the present work that we are unable to resolve at the moment. We note that HNO_2 in the products reaches a maximum at about 50% decomposition and that the amount of HNO_2 produced is too small. Under our reaction conditions there is no rapid, homogeneous path for HNO_2 decomposition. The implication is that HNO_2 is removed by a wall reaction or else by the bimolecular route

$$2HNO_2 \rightleftarrows NO + NO_2 + H_2O$$

The small amounts of HNO_2 present in the products preclude establishment of this equilibrium by a bimolecular reaction having any activation energy. The equilibrium is known to be rapidly achieved at 298°K,[14] but all signs point to a surface-catalyzed reaction that should not be favored at our temperatures. A homogeneous reaction would have to have an activation energy of not more than 8 kcal/mole in order that it occur in our system. This, of course, is not unreasonable in view of the rapidity of attainment of the room-temperature equilibrium, but it must be considered speculative at the moment.

We note that alkyl nitrites may also decompose through a favorable six-center elimination of HNO_2 with a fairly low activation energy (perhaps only 40 kcal/mole less 5 kcal/mole ring strain), 35 kcal/mole. Evidently they do not decompose this way and we infer from the observed[15] Arrhenius parameters, $A = 10^{14.5}$ sec^{-1} and E = 38 kcal/mole, that it is the low A factor of the HNO_2 elimination process (say 10^{11} sec^{-1}) compared with the high A factor for the competing NO elimination which plays the decisive role in governing the path of the reaction.

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Chemical Ionization Mass Spectrometry. VII. Reactions of Benzene Ions with Benzene[1a]

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Contribution from the Esso Research and Engineering Company, Linden, New Jersey, and the Department of Chemistry, University of California, Los Angeles, California. Received May 31, 1967

Abstract: In the electron impact mass spectrum of benzene measured at pressures between 1 and 1000 μ, the predominant $C_6H_6^+$ ion does not react rapidly with benzene. Ionization of benzene by electron transfer to rare gas ions under chemical ionization conditions produces widely differing fragmentation patterns and thus permits clear-cut studies of specific fragment ions. Ionizing benzene with Xe^+ gives 94% $C_6H_6^+$ which again does not react rapidly with benzene. Using Ar^+, 14% $C_3H_3^+$, 30% $C_4H_4^+$, and 16% $C_6H_5^+$ are produced. Benzene does not react with $C_3H_3^+$; it electron transfers to $C_4H_4^+$, and both electron transfers to and condenses with $C_6H_5^+$ to give $C_6H_6^+$ and $C_{12}H_{11}^+$. Electron transfer from benzene to Ne^+ gives 37% $C_4H_3^+$ which can take an electron from benzene. Since $C_6H_6^+$ is unreactive and readily formed by electron transfer to benzene fragment ions, the radiation chemistry of benzene must be due mainly to free radicals.

To aid the understanding of the radiolysis and other high-energy chemistry of benzene, we have made positive ions from this aromatic hydrocarbon and studied their reactions with benzene molecules at pressures between 1 and 1000 μ. Barker[2a] and Hamill[2b] have briefly looked at secondary ions in a mass spectrometer containing benzene but only at pressures below 2 μ.

In our study, positive ions were made from benzene by both electron impact and electron transfer to rare gas ions. Ion production by electron transfer has received much study but mainly in double mass spectrometers.[3] High-pressure mass spectrometer studies have been done, however, on electron transfer from ethylene to rare gas ions.[4]

Experimental Section

The Esso chemical physics mass spectrometer, which has been described elsewhere,[5] was used for this work. A determination of the ionic intensities as a function of source pressure at 210° was made for pure benzene using a previously described technique.[6] Ionization of benzene by electron transfer to rare gas ions was effected using chemical ionization techniques also described elsewhere.[5] Since chemical ionization experiments with methane at 170° were being done concurrently with the rare gas work, this lower temperature was used in the electron-transfer experiments.

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(1) (a) This research was supported in part by the Chemical Directorate of the U. S. Air Force Office of Scientific Research, Grant AF-AFOSR-245-65. (b) ESSO Research and Engineering Co. (c) University of California. (d) National Science Foundation Fellow

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(3) E. Lindholm, Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., 1966, p 4.

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(5) M. S. B. Munson and F. H. Field, *ibid.*, **88**, 2621 (1966).

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The absolute benzene pressure in these runs is subject to considerable uncertainty, but a relative accuracy of about 10% was achieved in duplicate runs.

The benzene used was Baker and Adamson reagent grade. Kr and Ne were Matheson research grade. Xe was Airco research grade, and Ar was Lif-o-gen research grade.

Results

In the electron impact mass spectrum of benzene taken at 1 μ (Table I), the predominant ion is $C_6H_6^+$ (57%), the next most abundant ions being only about 5% each. Some of the spectra taken at benzene pressures between 1 and 1000 μ, are shown in Table I. As benzene pressure increases to 11 μ, the $C_6H_6^+$ fraction increases to 0.69, accompanied by a corresponding decrease in the fragment ions. With further increase of benzene pressure to 118 μ, the $C_6H_6^+$ fraction falls to 0.58 and probable products of fragment ion condensations with benzene appear. This behavior suggests formation of electron-transfer complexes of fragment ions with benzene which would decompose giving $C_6H_6^+$ or could be stabilized to condensation products if the pressure was high enough to provide a third body. The fragment ions $C_4H_3^+$, $C_4H_4^+$, and $C_6H_5^+$ are studied separately later in this paper; each rapidly takes an electron from benzene, and $C_6H_5^+$ also condenses with benzene at high pressures. Increasing the benzene pressure to 585 μ produces no further change in $C_6H_6^+$ fraction and only minor changes in other ions. The only ion still gaining in intensity at 1000 μ of benzene is $C_7H_8^+$. Experiments discussed later suggest that this ion is formed by electron transfer to $C_6H_6^+$ from a *ca.* 0.1% toluene impurity rather than by reactions with benzene. These data clearly show that $C_6H_6^+$ does not react rapidly with benzene.

Table I. Fractions of Total Ions in Pure Benzene[b]

Ion	Source pressure, μ 1	11	45	118	335	585	1015
$C_3H_2^+$	0.042	0.006	...[c]	...	...	...	...
$C_3H_3^+$	0.050	0.038	0.034	0.032	0.030	0.030	0.030
$C_4H_2^+$	0.056	0.025	0.005	...	...	...	...
$C_4H_3^+$	0.054	0.047	0.022	0.002	...	...	...
$C_4H_4^+$	0.057	0.045	0.019	0.009	0.007	0.007	0.007
$C_5H_3^+$	...	0.015	0.019	0.014	0.012	0.012	0.011
$C_6H_4^+$	0.046	0.015	0.008	0.003	...	...	...
$C_6H_5^+$	0.096	0.053	0.034	0.009	...	...	...
$C_6H_6^+$ [a]	0.57	0.69	0.62	0.58	0.57	0.58	0.53
$C_6H_7^+$ [a]	...	0.002	0.036	0.045	0.048	0.051	0.063
$C_6H_8^+$	...	0.002	0.006	0.016	0.014	0.013	0.014
$C_7H_7^+$	...	0.001	0.010	0.012	0.009	0.007	0.007
$C_7H_8^+$	...	0.001	0.006	0.011	0.021	0.047	0.11
$C_8H_6^+$	...	...	0.011	0.011	0.008	...	0.004
$C_9H_7^+$	...	0.007	0.018	0.029	0.023	0.019	0.011
$C_{10}H_8^+$	...	0.004	0.026	0.033	0.026	0.022	0.019
$C_{10}H_9^+$	...	0.006	0.007	0.017	0.021	0.023	0.025
$C_{12}H_{10}^+$	...	...	0.018	0.033	0.032	0.027	0.021
$C_{12}H_{11}^+$	...	...	0.015	0.037	0.037	0.034	0.030
$C_{12}H_{12}^+$	...	...	0.004	0.014	0.024	0.030	0.036

[a] Corrected for C^{13}. [b] Ions which never exceed 0.01 not listed. [c] Ions not present with enough intensity to measure.

To isolate the reactions of some of the ions in the electron-impact spectrum, we tried the more selective method of benzene ionization by electron transfer to rare gas ions. The cross sections for such unsymmetrical electron-transfer reactions are largest when there is a matching of energy levels between ion and molecule. For example, methane has no other one-electron ionization potentials (IP's) besides 12.99 ev[7] below several hundred electron volts,[8] and the cross section for electron transfer by methane to Ne^+ ions (recombination energy, RE = 21.6 ev)[3] is 0.013 of that for the same process with Kr^+ ions (RE = 14.0 ev).[9] Benzene has eight ionization potentials spread between 9 and 21 ev,[7] so electron transfer from various benzene orbitals to the rare gas ions used here should be rapid enough to occur under chemical ionization conditions. Indeed, for mixtures containing 1000 μ of rare gas and a few microns of benzene, electron impact produces mainly rare gas ions, yet only hydrocarbon ions were seen. Table II shows the recombination energies and fractions of rare gas ions which had not charge exchanged at about 0.6 μ benzene partial pressure. Because the absolute pressure of benzene in the system is only roughly known, no rate constant calculations are offered.

Table II. Fractions of Total Ions Which Are Rare Gas Ions in Mixtures of *ca.* 0.6 μ of Benzene and 1000 μ of Rare Gas

Rare gas	RE,[a] ev	$I_{\text{rare gas ions}}/I_{\text{total ions}}$
Ne	21.6	0.77
Ar	15.8	0.39
Kr	14.0	0.42
Xe	12.1	0.34

[a] Recombination energy of the singly charged ion as in ref 3.

Table III shows that the degree and type of fragmentation produced in the electron-transfer reaction varies with the recombination energy of the rare gas ion used. Almost no fragmentation results from the reaction of Xe^+ (RE = 12.1 ev) with benzene. Using Kr^+ (RE = 14.0 ev), the ions produced still include 78% $C_6H_6^+$. However, ionization with Ar^+ (RE = 15.8 ev) gives mainly the fragments $C_4H_4^+$ (relative intensity = 30%; AP = 15.8 ev),[10] $C_6H_5^+$ (16%; AP = 14.4 ev), and $C_3H_3^+$ (14%; AP = 16.2 ± 0.3 ev). The benzene–Ne^+ (RE = 21.6 ev) spectrum contains $C_3H_3^+$ (16%) and some new ions, mainly $C_4H_3^+$ (35%; AP = 18.4 ev) and two-carbon fragments.

The role here of doubly charged rare gas ions, whose highest recombination energies are above 19 ev,[3] is not clear. For example, in our mass spectrum of pure xenon at 1000 μ, Xe^{2+} comprises 20% of the ions and disappears along with Xe^+ as benzene is added. However, the resulting spectrum of benzene ions does not contain the fragments one might expect from acquisition by benzene of a 19-ev recombination energy. A similar result obtained by von Koch in allowing Xe^{2+} to react with methane[8] suggests the use of a lower recombination energy by electron transfer to give an excited state of

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(8) There are no other IP's near the 12.99-ev value[7] because the C–H bond electrons are identical. The next single electron IP is that of the carbon 1s electrons, which is near 285 ev [K. Siegbahn, *et al.*, *Nature*, 213, 70 (1967)].

(9) H. von Koch, *Arkiv Fysik*, **28**, 529 (1964).

(10) Appearance potential, AP, from F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957.

Table III. Fractions of Total Hydrocarbon Ions Made from Benzene by Electron Impact and Electron Transfer to Inert Gas Ions

Ion	Electron impact[b]	1000 μ Xe, ~0.2 μ C_6H_6	1000 μ Kr, ~0.3 μ C_6H_6	1000 μ Ar, ~0.6 μ C_6H_6	1000 μ Ne, ~0.6 μ C_6H_6
$C_2H_2^+$	0.015	...	0.013	0.010	0.091
$C_2H_3^+$	0.013	...	0.005	0.002	0.086
C_3H^+	0.017	...	...	0.005	0.015
$C_3H_2^+$	0.023	...	0.013	0.007	0.030
$C_3H_3^+$	0.057	0.007	0.028	0.14	0.16
$C_4H_2^+$	0.068	0.011	0.016	0.029	0.081
$C_4H_3^+$	0.079	0.022	0.013	0.004	0.37[a]
$C_4H_4^+$	0.081	0.011	0.028	0.30	0.033[a]
$C_5H_3^+$	0.012	0.005	...	0.030	0.004
$C_6H_4^+$	0.027	...	0.023	0.031	0.002
$C_6H_5^+$	0.059	...	0.075	0.16	0.005
$C_6H_6^+$ [a]	0.46	0.94	0.78	0.20	0.016

[a] Corrected for C^{13} [b] From the API Catalog of Mass Spectral Data, Serial 250.

Xe^+. It is of some interest, although perhaps not surprising, that Xe^{2+} ions are quite stable in Xe with respect to disproportionation to give two Xe^+ ions.

Ionization of benzene by electron transfer to xenon ions produces $C_6H_6^+$ as about 94% of hydrocarbon ions (Table III). As the partial pressure of benzene increases to 440 μ (Table IV), the $C_6H_6^+$ fraction decreases to 0.85 while the $C_{12}H_{12}^+$ fraction rises to 0.09. The observed diminution of $C_6H_6^+$ corresponds to a rate constant (k) of 7 × 10^{-12} cc/molecule sec for reaction 1.

$$C_6H_6^+ + C_6H_6 \longrightarrow C_{12}H_{12}^+ \tag{1}$$

The lack of significant $C_{12}H_{12}^+$ production above 500 μ in the pure benzene system suggests that the $C_6H_6^+$ in reaction 1 needs to be in an excited state as it would be when made from Xe^+ ion. We have no evidence about what excited state of $C_6H_6^+$ may be involved here, but two higher IP's of benzene[7] are below the Xe^+ recombination energy. The small observed rate constant for reaction 1 does not mean, of course, that the excited $C_6H_6^+$ possibly involved here is unreactive; rapid de-excitation would make the rate constant for the loss of $C_6H_6^+$ less than that for the actual reaction of the excited ion with benzene.

Table IV. Fractions of Total Hydrocarbon Ions from Benzene in 1000 μ of Xe[b]

Ion	Benzene pressure, μ ~0.2	~60	~160	~440
$C_6H_6^+$ [a]	0.94	0.94	0.89	0.85
$C_6H_7^+$ [a]	...	0.009	0.024	0.040
$C_{12}H_{12}^+$	...	0.008	0.033	0.091

[a] Corrected for C^{13}. [b] Ions which never exceed 0.02 not listed.

Having established that at least ground-state $C_6H_6^+$ does not react rapidly with benzene, we briefly investigated possible reactions with other molecules. In a system containing 950 μ of xenon, 160 μ of benzene, and about 6 μ of toluene (IP = 8.82 ev),[10] 85% of the $C_6H_6^+$ made from Xe^+ and benzenee ntered reaction 2

$$C_6H_6^+ + C_6H_5CH_3 \longrightarrow C_7H_8^+ + C_6H_6 \tag{2}$$

to give $C_7H_8^+$. This ion, which will have at most 0.4 ev excitation energy if formed from ground-state $C_6H_6^+$, reacted no further with benzene, and this result provides some additional support for the suggestion that $C_{12}H_{12}^+$ formation (reaction 1) results from excited $C_6H_6^+$. Reaction 2 occurring with the 0.1% toluene in the "pure" benzene experiments can account for the $C_7H_8^+$ ion seen at high pressures (Table I).

The reactions of $C_4H_4^+$, $C_6H_5^+$, and $C_3H_3^+$ with benzene were studied using the Ar–benzene system. In Table V the relative intensities of the major ions seen are listed as a function of benzene partial pressure. The disappearance of $C_4H_4^+$ is matched only by the appearance of $C_6H_6^+$; thus electron-transfer reaction 3, which is 13 kcal/mole exothermic,[10] is occurring. The diminution of $C_4H_4^+$ intensity with increasing benzene

$$C_4H_4^+ + C_6H_6 \longrightarrow C_6H_6^+ + C_4H_4 \tag{3}$$

pressure corresponds to a rate constant of about 5 × 10^{-9} cc/molecule sec for reaction 3.

Table V. Fractions of Total Hydrocarbon Ions from Benzene in 1000 μ of Ar[b]

Ion	Benzene pressure, μ ~0.6	~3	~10	~220
$C_3H_3^+$	0.14	0.14	0.13	0.10
$C_4H_4^+$	0.30	0.17	0.058	0.022
$C_6H_5^+$	0.16	0.10	0.037	0.017
$C_6H_6^+$ [a]	0.20	0.42	0.55	0.60
$C_6H_7^+$ [a]	...	0.003	0.005	0.030
$C_{12}H_{11}^+$	...	0.039	0.074	0.076
$C_{12}H_{12}^+$	...	0.005	0.010	0.035

[a] Corrected for C^{13}. [b] Ions which never exceed 0.03 not listed.

$C_3H_3^+$ made from Ar^+ and benzene is unreactive. Its apparent decrease at 220 μ of benzene may be due to a contribution from direct ionization of benzene by electron impact, which gives a lower yield of the ion (Table I). $C_6H_5^+$ seen in Table V both adds to benzene to form $C_{12}H_{11}^+$ (reaction 4) and takes a benzene electron to give $C_6H_6^+$ (reaction 5). The condensation product is seen

$$C_6H_5^+ + C_6H_6 \longrightarrow C_{12}H_{11}^+ \tag{4}$$

$$C_6H_5^+ + C_6H_6 \longrightarrow C_6H_6^+ + C_6H_5 \tag{5}$$

at low benzene partial pressure here, but there is always 1000 μ of argon present for collisional stabilization. The diminution of $C_6H_5^+$ exhibits about the same rate constant as reaction 3, and at our pressure the ion is about equally partitioned between reactions 4 and 5. Reaction 5 is about thermoneutral,[10] and the observance of reaction 4 sets $\Delta H_f(C_{12}H_{11}^+) < 302$ kcal/mole.

In Table VI the major ions in the benzene–neon system are listed as a function of benzene partial pressure. A fairly firm conclusion that can be drawn from the data

Table VI. Fractions of Total Hydrocarbon Ions from Benzene in 1000 μ of Ne[b]

Ion	Benzene pressure, μ ~0.6	~3	~10	~16	~240
$C_2H_2^+$	0.091	0.050	0.014	...	...
$C_2H_3^+$	0.086	0.080	0.014	...	...
$C_3H_3^+$	0.16	0.24	0.34	0.33	0.29
$C_4H_2^+$	0.081	0.040	0.008	0.003	...
$C_4H_3^+$	0.35	0.35	0.11	0.039	...
$C_4H_4^+$	0.056	0.053	0.042	0.045	0.039
$C_6H_6^+$ [a]	0.015[c]	0.096[c]	0.31	0.39	0.52
$C_6H_7^+$ [a]	...	0.025[c]	0.070	0.069	0.057

[a] Corrected for C^{13}. [b] Ions which never exceed 0.03 not listed. [c] Doublet.

is that $C_4H_3^+$ undergoes electron-transfer reaction 6 to

$$C_4H_3^+ + C_6H_6 \longrightarrow C_6H_6^+ + C_4H_3 \qquad (6)$$

give $C_6H_6^+$. Although $C_4H_3^+$ is a potential proton-transfer agent, the electron-transfer reaction is apparently faster.

Discussion

Calculations on the $C_6H_6^+$ ion indicate that its ground state has a uniform charge density on all six carbons,[11] and this gives the ion a very low energy (ΔH_f = 233 kcal/mole).[10] Forming a chemical bond with the ion at the expense of the uniform charge distribution gives no decrease in energy, at least in the case of $C_6H_7^+$ (ΔH_f = 235 kcal/mole).[12]

Besides being of low energy, $C_6H_6^+$ ion is very stable. Our work with benzene–Kr^+ or the appearance potential data show that about 5 ev more than the minimum ionization energy is needed to begin fragmentation of the ion. Although something is known about the stability of the ions formed from various benzene energy levels,[7] we do not know whether our destructive electron-transfer process is making benzene ions in repulsive states or too high vibrational levels of bonding states.

Our findings that $C_6H_6^+$ is unreactive and rapidly formed by electron transfer to benzene fragment ions are useful in interpreting the results of benzene radiolysis. Since little ionic chemistry will occur, free radicals will have to produce the observed products, and experimental results conform with this view. The over-all reaction observed in benzene radiolysis can be largely explained by the reactions of H atoms and phenyl radicals.[13]

The use of electron transfer to rare gas ions as a technique for producing new fragmentation patterns of additive molecules under chemical ionization conditions has been illustrated here. Because of the high pressure in the ion source, the rare gas ions should be near thermal energy, a situation unattainable in beam experiments. The high total pressure also permits the cascading of ionization (*e.g.*, the Xe–benzene–toluene experiment), and the study of reactions of resulting hydrocarbon ions with the parent molecule or additives is in principle possible. Thus some new chemical ionization techniques have been demonstrated in studying the reactions of benzene ions.

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The Binding of Quaternary Ammonium Ions by Polystyrenesulfonic Acid Type Cation Exchangers[1]

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Abstract: A thermodynamic study was made of the binding of quaternary *n*-alkylammonium ions by cross-linked polystyrenesulfonic acid type cation exchangers. Calorimetric measurements of the exchange reactions with sodium ion at 25° showed that the enthalpy and entropy changes were negative for the preferential binding of tetramethyl- and tetraethylammonium ions by lightly cross-linked sodium-form exchanger, but, with tetra-*n*-propyl- and tetra-*n*-butylammonium ions, heat was absorbed and the entropy increased markedly. The increase in the preferential uptake with the size of the tetra-*n*-alkylammonium ion therefore was determined by the entropy increase in the exchange reaction (*i.e.*, hydrophobic bonding). The selective uptake of Me_4N^+ ion decreased with increasing exchanger cross-linking, and with nominal 8% DVB exchanger the Na^+ ion was preferred for all compositions. The heat of exchange became progressively less negative, and with the most highly cross-linked preparation heat was absorbed when Me_4N^+ replaced the Na^+ ion, but the entropy change remained constant. The decrease in the binding of Me_4N^+ ion with increased cross-linking was attributed to the increase in enthalpy of the molecular network of the ion exchanger when it expanded to accommodate the large organic cation. A comparison of the enthalpy with the free energy of swelling showed that the entropy also increased, which is contradictory to the hypothesis that ion exchangers are rubber-like gels. The more highly cross-linked polystyrenesulfonate exchangers behaved as if they were in a glass-like state (*i.e.*, a rubber below its gel point).

The ion-exchange reactions of quaternary *n*-alkylammonium ions, R_4N^+, in aqueous solution with singly charged cations on polyelectrolytes appear to be unusual in a number of respects.[2-8] In reactions with alkali metal ions on lightly cross-linked polystyrenesulfonic acid (PSSA) exchangers the binding of R_4N^+ increases with ion size,[3] but with lightly cross-linked polymethacrylic acid (PMA) a *decrease* with increasing size is observed.[7] However, with both strong-acid and

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