J. Am. Chem. Soc. **1983**, *105*, 3783-3788

Mechanism of the Gas-Phase Reaction of the Benzene Radical Cation and Various Alkyl Iodides[†]

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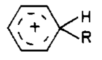
Abstract: The gas-phase reaction of the benzene radical cation with 2-iodoalkanes was explored by using tandem mass spectrometry (mass spectrometry/mass spectrometry) and pulsed ion cyclotron resonance spectrometry. The nature of the reaction products was determined from their collision-induced dissociation spectra. It was found that the benzene radical cation reacts with the 2-iodoalkanes under collisional stabilizing conditions to form an observable collision complex or intermediate. The intermediate undergoes reductive elimination of an iodine radical to yield a hydrocarbon cation of the "Wheland intermediate" type. Specifically, the product of the reaction of C_6H_6 radical cation and 2-iodopropane was shown to have the same CID spectrum and, thus, the same structure as protonated isopropylbenzene or isopropylated benzene. The reaction of $C_6H_6^{+\cdot}$ with 2-iodobutane similarly produces protonated isobutylbenzene or isobutylated benzene.

Introduction

The gas-phase reaction of the benzene radical cation with 2-alkyl iodides may represent a new route for the formation of Wheland-type intermediates (σ complexes) (I). Wheland intermediates have long been postulated as the intermediates in the Friedel–Crafts alkylation of benzene and possibly in the protonation of alkylbenzenes.[1] We report here evidence, from a study using a tandem mass spectrometer (MS/MS), for the formation of gas-phase Wheland intermediates, or similar structures differing in the site of protonation, where R = i-C_3H_7 and *sec*-C_4H_9.



I

In recent years, the nature of C_6H_6 radical cations has been of interest.[2-8] One specific area of research has been focused on the gas-phase reactions of the benzene radical cation with selected reagent neutrals.[2] For example, it was observed that ionized benzene exhibited a unique reaction with 2-iodopropane which other C_6H_6 radical cations do not show. Indeed, this reaction was so specific that if the iodine was replaced with a bromine or a chlorine or if the isopropyl group was changed to *n*-propyl, the reaction did not occur. When benzene and 2-iodopropane were mixed in an ion cyclotron resonance (ICR) spectrometer cell, they reacted and formed a single observable product which was determined to be $C_9H_{13}^+$ (m/z 121). The nature of this ion could only be speculated upon based on the ICR data since the collision complex could not be observed, and $C_9H_{13}^+$ underwent no fragmentations which precluded the use of isotopic labeling for structure determination. However, it was established by using double resonance experiments that the $C_9H_{13}^+$ arose through a reaction in which benzene, not the propyl ion, is the charged species (see eq 1 and 2). The rate of disappearance of the benzene ion

$$C_6H_6^{+\cdot} + 2\text{-}C_3H_7I \rightarrow C_9H_{13}^+ + I \tag{1}$$

$$C_3H_7^+ + C_6H_6 \not\rightarrow C_9H_{13}^+ \tag{2}$$

and the rate of appearance of the $C_9H_{13}^+$ were found to be identical within experimental error.

Previous workers have demonstrated the feasibility of determining the structures of ion–molecule reaction products from their collision-induced decomposition (CID) spectra.[9-11] We have recently refined the methodology to stabilize and investigate directly the products of gas-phase ion–molecule reactions.[12] By using a high-pressure or chemical ionization (CI) source, collisional stabilization of the intermediates could be achieved. We have made use of these capabilities to conduct a detailed study of the products of the gas-phase reaction of benzene with 2-iodopropane, and 2-iodobutane, and the results of that study are reported here. We have also determined the rate constants of the reactions of the benzene radical cation with a variety of iodoalkanes.

The tandem mass spectrometer used for these studies is a triple analyzer instrument which has been described previously.[13] The first spectrometer (MS-I) is a high-resolution, double-focusing instrument consisting of an electrostatic analyzer (ESA) followed by a magnet analyzer.[13] MS-I is used to separate the ion product under study from other ions formed in the source. Collisional activation takes place in a collision cell following MS-I and the CID spectrum is obtained by scanning MS-II, an ESA. The overall configuration of the spectrometer is designated EBE.

Experimental Section

All chemicals used in this study were purchased from various commercial sources, and their purity was checked by mass spectrometry and NMR. The benzene and the alkylbenzenes were used without further purification. The iodoalkanes were distilled prior to the NMR and mass spectral analyses. Good agreement between literature and experimental boiling points and spectra was achieved.

The experiments were carried out on a Kratos MS50 triple analyzer mass spectrometer which has been described elsewhere.[13] The standard Kratos CI source was used. Isobutane or methane as used as the reagent gas to generate $C_4H_9^+$ or CH_5^+ for protonation of the reference compounds at a total pressure of approximately 0.5 torr. Mixtures of benzene and the alkyl halides in a ratio of 100:1 and 10:1 (total pressure of 0.5 torr) were used to minimize the possible reaction of propyl and butyl cations with benzene. The same results were obtained with both mixtures.

Typical instrument conditions were: 6000 V accelerating voltage, 280 eV ionizing energy, 3000 mass resolution, and 150 °C source temperature.

CID spectra were obtained by adjusting the first electrostatic analyzer and the magnetic analyzer to pass ions of interest into the collision cell located in the third field-free region. Helium target gas was introduced into the collision cell until the precursor ion intensity was suppressed to

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[†] This paper is dedicated to the memory of Henry M. Rosenstock, an enthusiastic supporter of research on C_6H_6 radical cations.

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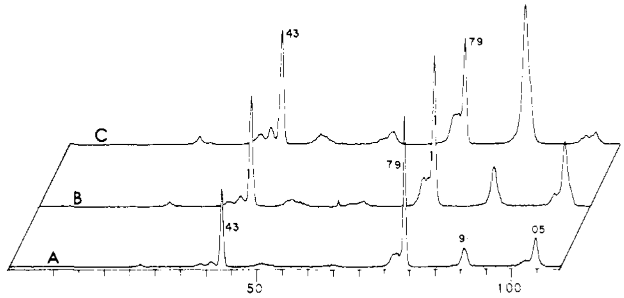


Figure 1. (A) CID spectrum of $C_9H_{13}^+$ from the reaction of ionized benzene and 2-iodopropane, (B) CID spectrum of protonated isopropylbenzene, and (C) CID spectrum of protonated *n*-propylbenzene.

75% of its original value. The second ESA was then scanned to obtain the CID spectrum.

To obtain the CID spectrum of the *m/z* 121 produced by consecutive decompositions, an MS/MS/MS technique[14] was used. *m/z* 248 ions were formed in the source and then accelerated out. Some ions then decomposed by CID in the first field-free region. The first ESA was adjusted to transmit the ions produced from the decomposition 248 to 121 and the magnet set to M_2^2/M_1. This passed those *m/z* 121 ions produced from *m/z* 248 in the first field-free region into the second collision cell (located in the third field-free region) where they collided with helium and their CID spectrum was obtained by scanning the second ESA.

$V^{1/2}/E$ linked scans[15] were used to achieve the necessary resolution to examine the products of hydrogen–deuterium exchange for the reactions using deuterated benzene. Scans of decompositions taking place in the first field-free region were produced by scanning the accelerating voltage and the two electrostatic sector voltages upward such that $V^{1/2}/E$ was a constant. The parent ion was observed at 4 kV, followed by the lower mass daughter ions which were focused as the acceleration voltage was scanned to higher values (up to 8 kV).

The CID spectra of ions desorbed by fast atom bombardment (FAB) were obtained using the FAB source supplied by Kratos. The sample of diphenyliodonium iodide salt was dissolved in Me_2SO and then mixed with glycerol. This solution was then applied to the FAB probe, and CID spectra were acquired as described previously.

The rate constant measurements were performed with an ion cyclotron resonance (ICR) mass spectrometer recently modified to operate in the pulsed mode.[16] The pulse sequence, including the delay time between ionization and analysis, was controlled by an Intel Model 8039 microprocessor and an interface of our own design and manufacture. Rates were obtained by monitoring the decay curves of the reactive species and then plotting $\ln I/I_0$ vs. t, where I_0 is the intensity at time = 0 and I is the intensity at some elapsed reaction time, t. Knowing the slope of $\ln I/I_0$ vs. t and the absolute pressures of the reactants (obtained from a Veeco RG1000 ionization gage which had been calibrated against a Datametrics Barocel electronic manometer, Model 1173), the rate constants were calculated from the equation k = slope/(pressure)(number density).

Results and Discussion

The first aim of this study was to determine if an observable collision complex or reaction intermediate was present under the conditions of a high-pressure CI source (P = 0.1 to 1.0 torr). For the reaction of benzene with 2-iodopropane, an intact collision complex was observed at *m/z* 248 which was not seen in the ICR experiments. The metastable spectrum of *m/z* 248 showed a single peak at *m/z* 121 indicating a single decomposition reaction to lose an iodine radical from the intact collision complex. This *m/z* 121 has an atomic composition of $C_9H_{13}^+$ (verified by peak matching using benzene molecular ion as reference) which is the expected composition for the "Wheland intermediate" formed in the Friedel–Crafts isopropylation of benzene.

The following strategy was employed to prove the structure of the intermediate $C_9H_{13}^+$. Since the Wheland intermediate cannot be directly synthesized and admitted into a mass spectrometer for study, a set of reference compounds was selected and then protonated in the CI source. These were then examined by taking their collision-induced dissociation spectra and the spectra compared to that of the reaction product. The reference compounds included isopropylbenzene, *n*-propylbenzene, 1,3,5-trimethylbenzene, and 1-ethyl-2-methylbenzene for the $C_9H_{13}^+$ system.

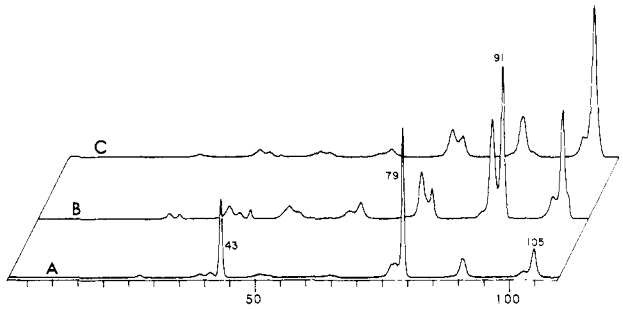


Figure 2. (A) CID spectrum of $C_9H_{13}^+$ from the reaction of ionized benzene and 2-iodopropane, (B) CID spectrum of protonated 1-ethyl-2-methylbenzene, and (C) CID spectrum of protonated 1,3,5-trimethylbenzene.

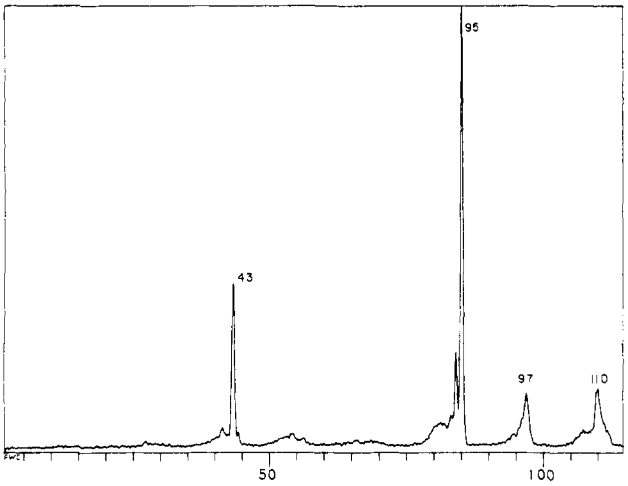


Figure 3. CID spectrum of $C_9D_6H_7^+$ from the reaction of benzene-d_6 and 2-iodopropane.

Structure of $C_9H_{13}^+$. The CID spectrum of the $C_9H_{13}^+$ produced in reactions of ionized benzene and 2-iodopropane (Figure 1A) shows four major peaks which may be attributed to the reactions given in eq 3–6. Several smaller and unresolved peaks

$$C_9H_{13}^+ \rightarrow C_8H_9^+ + CH_4 \qquad (3)$$

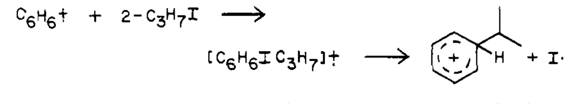
$$\rightarrow C_7H_7^+ + C_2H_6 \qquad (4)$$

$$\rightarrow C_6H_7^+ + C_3H_6 \qquad (5)$$

$$\rightarrow C_3H_7^+ + C_6H_6 \qquad (6)$$

were also observed on the low mass sides of the above peaks. These smaller peaks arise by losses of H and H_2 from the major ion.

A comparison of the CID spectra of the protonated reference compounds and that of the reaction product (see Figures 1 and 2) reveals that the reaction product has a ion structure different from that of protonated *n*-propylbenzene, 1,3,5-trimethylbenzene, or 1-ethyl-2-methylbenzene. However, the similarity of the CID spectrum of protonated isopropylbenzene and that of the reaction product is quite striking. Based on the similarity of the spectra, we postulate that the reaction product does indeed have the structure of a Wheland intermediate (see eq 7) or closely related



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species with the proton at another ring site. Certainly the carbon skeleton is as written in eq 7.

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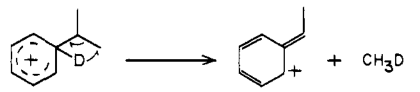
The ion–molecule reaction was also carried out using benzene-d_6 and 2-iodopropane to determine if any exchange of hydrogen atoms between the benzene ring and the side chain could be observed. A small amount was found (see Figure 3). The m/z 79 peak was shifted to m/z 85; also observed was a peak at m/z 84 corresponding to $C_6D_5H_2^+$. The peak at m/z 91 was shifted to m/z 97 and was the most intense peak in a poorly resolved cluster. The m/z 105 peak was also shifted, and the most intense peak of that cluster corresponded to m/z 110. No evidence was seen for exchange in the formation of the propyl cation at m/z 43.

In order to get a clearer picture of the H/D exchange process, the m/z 127 reaction product was examined by $V^{1/2}/E$ linked scans (see Experimental Section). The use of this linked scan yields spectra with better mass resolution than the CID spectra obtained by ESA scans. By examining the products of H/D exchange, we expect to gain insight into the fragmentation mechanisms and the nature of the bonding of the $C_9H_{13}^+$ reaction product (is it covalent or associative?). From the data obtained by linked scanning, it was determined that approximately 80% of the methane loss occurs as CH_3D. This can be explained by a deuterium transfer from the ring to one of the methyl groups of the isopropyl group followed by loss of CH_3D (eq 8).



(8)

It was also determined that no ethyl loss occurs from the reaction product. The ethane loss, arising from a rearrangement reaction, occurs as C_2H_6 (65%), C_2H_5D (20%), and $C_2H_4D_2$ plus $C_2H_3D_3$ (15%). It was also determined that m/z 85 ($C_6D_6H^+$) accounted for 80% of the propene loss in the system. The loss of benzene to give $C_3H_7^+$ could not be examined by the $V^{1/2}/E$ method because of the one-half mass limitation of the scan.

The results of the H/D exchange experiments are in accord with the structure of the $C_9H_{13}^+$. We observe that the reactions which require minimal rearrangement occur with minimal H/D exchange (i.e., loss of methane and C_3H_6), whereas more exchange is seen for the loss of ethane which can only occur through an extensive rearrangement process. We also conclude that the $C_9H_{13}^+$ is covalently bonded since we do observe H/D exchange prior to dissociation.

The reaction of benzene with 1-iodopropane was also examined. It was previously shown that benzene and 1-iodopropane did not react to an observable extent in an ICR spectrometer.[2] In the high-pressure CI source employed in these experiments, no reaction intermediate ($C_9H_{13}I^+$) was observed; however, a m/z 121 was seen. The CID spectrum of the m/z 121 produced in the reactions of an ionized mixture of benzene and 1-iodopropane is identical with that from the reaction of benzene and 2-iodopropane. It is possible that the spectrum observed for the 1-iodopropane system is, in fact, due to the reaction of isopropyl cation, formed by dissociation of 1-iodopropane, with benzene. Supporting evidence for this suggestion comes from the CID spectrum of the product of propylation (using propane as the source of $C_3H_7^+$) of benzene in the high-pressure source (see eq 9). The spectrum is nearly identical with that for the 1-iodopropane system.

$$C_3H_8^{+\cdot} \xrightarrow{-H} C_3H_7^+ \xrightarrow{C_6H_6} [C_6H_6–C_3H_7^+]^* \xrightarrow{N} C_6H_6–C_3H_7^+ \tag{9}$$

The fact that the propylation of benzene produces $C_9H_{13}^+$ whose CID spectrum is almost identical with that from the reaction of benzene radical cation and 2-iodopropane raises the question of whether $C_9H_{13}^+$ is produced by loss of iodine radical from the collision complex or by the reaction of $C_3H_7^+$ from 2-iodopropane with benzene.

To obtain unequivocally the CID spectrum of $C_9H_{13}^+$ from the reaction of ionized benzene and 2-iodopropane, we made use of the ability of the triple analyzer mass spectrometer to examine consecutive reactions, a technique often referred to as MS/MS/MS.[14] The m/z 248 collision complex was formed in the high-pressure CI source and was then collisionally activated in the first collision cell to form m/z 121 ions which were transmitted to the second collision cell. The CID spectrum of the m/z 121 ions formed uniquely from m/z 248 was then taken by collisionally activating m/z 121 in the second collision cell and scanning the final ESA. The spectrum is nearly identical with that of $C_9H_{13}^+$ formed in the source (compare Figures 1 and 4). Based on the fact that the spectra of the $C_9H_{13}^+$ ions produced in the source, by the consecutive decompositions, and by propylation of benzene are the same, we have established that each process is yielding the same end product.

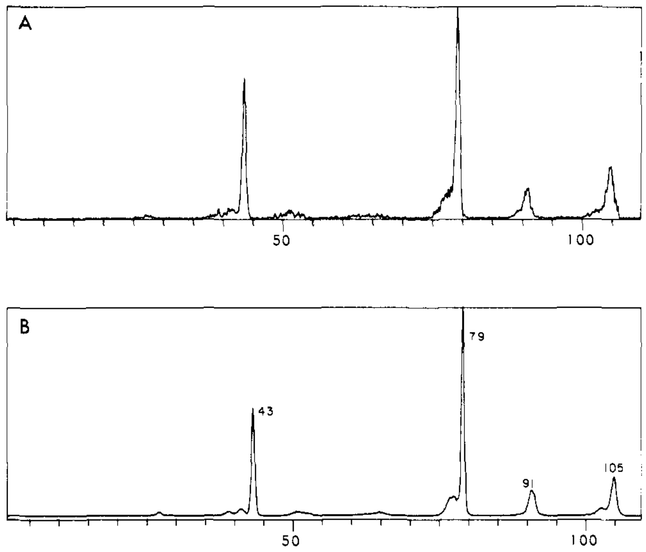


Figure 4. (A) CID spectrum of the $C_9H_{13}^+$ formed unequivocally by decompositions of $C_9H_{13}I^{+\cdot}$ and (B) CID of source formed $C_9H_{13}^+$.

We are also in a position to draw some conclusions concerning the relative efficiencies of the above reactions. While it is true that a $C_9H_{13}^+$ was produced in an ionized mixture of benzene and 1-iodopropane and in the reaction of $C_3H_7^+$ with benzene, its intensity was reduced compared to the $C_9H_{13}^+$ produced in the reaction of ionized benzene with 2-iodopropane when carried out under similar experimental conditions (ratio of m/z 43/78 the same). In fact, the abundances of the products produced in the 1-iodopropane experiment and the propylation of benzene were only 10% of that in the 2-iodopropane experiment. Therefore, we assign an upper limit of 10% contribution to the production of m/z 121 by direct propylation in the case of the 2-iodopropane system.

These results also indicate that $C_3H_7^+$ ions from propane and 1-iodopropane have the isopropyl structure in accord with a previous conclusion.[17] The different reactivities of furan and $C_3H_7^+$ ions formed from a variety of sources can be definitely attributed to an internal energy effect.[18]

Structure of the $C_9H_{13}I^+$ Intermediate. The nature of the intact intermediate or collision complex was also investigated in terms of its CID spectrum (see Figure 5). As can be seen, five peaks were observed which originate by the reactions shown in eq 10–14.

$$C_9H_{13}I^{+\cdot} \rightarrow C_6H_6I^+ + C_3H_7 \tag{10}$$

$$\rightarrow C_3H_7I^{+\cdot} + C_6H_6 \tag{11}$$

$$\rightarrow C_9H_{13}^+ + I \tag{12}$$

$$\rightarrow C_6H_6^{+\cdot} + C_3H_7I \tag{13}$$

$$\rightarrow C_3H_7^+ + C_6H_6I \tag{14}$$

Conclusions regarding the general nature of the bonding in the intermediate can be drawn based on the decomposition reactions observed. We postulate that the $C_9H_{13}I^+$ intermediate is a co-

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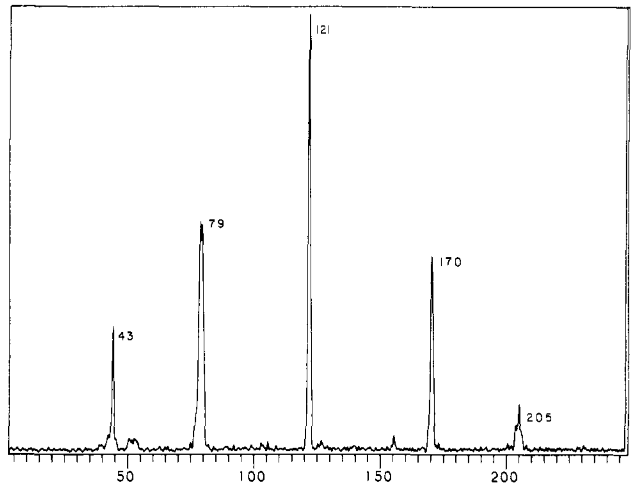


Figure 5. CID spectrum of the intact collision complex ($C_9H_{13}I^+$) from the reaction of ionized benzene and 2-iodopropane.

valently bonded complex for several reasons. McLuckey et al.[19] have shown that proton-bound species of the type A–H$^+$–B show only two peaks in their CID spectra corresponding to AH$^+$ and BH$^+$. It has also been shown that the same behavior is observed for silver-ion-bound species.[20] On the basis of these analogies, we conclude that the complex that we observe is not proton bound nor a weakly bound associative complex with iodine as the bridge.

We also examined the intermediate $C_9H_{13}I^+$ for evidence of hydrogen/deuterium exchange which would confirm covalent bonding. When the intact collision complex for the benzene-d_6 and 2-iodopropane reaction (*m/z* 254) was examined by CID, five peaks were observed (see eq 15–19). From the CID spectrum,

$$C_9H_7D_6I^{+\cdot} \rightarrow C_6D_6I^+ + C_3H_7 \quad (15)$$

$$\rightarrow C_3H_7I^{+\cdot} + C_6H_6 \quad (16)$$

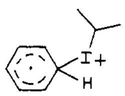
$$\rightarrow C_9H_7D_6^+ + I \quad (17)$$

$$\rightarrow C_6D_6^{+\cdot} + C_3H_7I \quad (18)$$

$$\rightarrow C_3H_7^+ + C_6D_6I \quad (19)$$

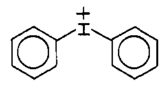
it was unclear if a small amount of exchange was taking place because of the width of the peaks and the poor signal-to-noise ratio of the spectrum. The measurements were repeated with improved S/N but were still inconclusive. Attempts were made to examine the *m/z* 254 ion by linked scans (see Experimental Section) in order to observe the exchange, but they were unsuccessful because of the low sensitivity of this method. Therefore, significant H/D exchange was not observed for the *m/z* 254 ion, but some exchange cannot be ruled out for the reasons mentioned above.

Because benzene is reacting as the charged species (proven by ICR double resonance), it is logical to expect that the large electron cloud of iodine would interact with the positive charge of the benzene to form an iodonium radical-cation intermediate having structure II. Indeed, we believe that the ability of the iodine to accommodate the positive charge of the incipient collision complex is the reason why the iodoalkanes react and the chloro- and bromoalkanes do not. The iodine is more polarizable than the bromine and chlorine and can better interact with the charged benzene. However, the proposed intermediate structure seems in conflict with the unimolecular and CID data which indicate a structure capable of a very facile iodine loss. The metastable spectrum of the $C_9H_{13}I^+$ intermediate shows that the most facile decomposition (in fact, the only detectable decomposition) is loss of an iodine radical to yield $C_9H_{13}^+$. This indicates that the correct structure must be amenable to a ready loss of iodine. Obviously, a rearrangement reaction is necessary if iodine is to be lost from structure II to yield the $C_9H_{13}^+$ product.



II

To investigate the propensity of iodonium ions to lose I, we obtained the CID spectrum of the diphenyliodonium ion (III)



III

produced from diphenyliodonium iodide. In order to investigate this compound, it was necessary to employ fast atom bombardment (FAB) mass spectrometry[21] to directly desorb the diphenyliodonium ion into the gas phase. The desorption was accomplished by bombarding the salt dissolved in a droplet of glycerol with a 6-kV beam of argon atoms. The CID spectrum showed three decomposition products, described in eq 20–22. It is apparent from the peak at *m/z* 154 that iodine is being extruded from the molecule is such a way as to yield an ion with the elemental composition of biphenyl. From this evidence we believe that the intermediate in the reaction of benzene and 2-iodopropane has a similar structure.

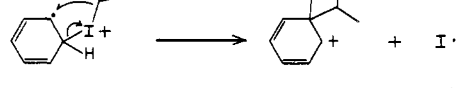
$$C_{12}H_{10}I^+ \rightarrow C_6H_5I^{+\cdot} + C_6H_5 \quad (20)$$

$$\rightarrow C_{12}H_{10}^{+\cdot} + I \quad (21)$$

$$\rightarrow C_6H_5^+ + C_6H_5I \quad (22)$$

We postulate that iodine elimination occurs via a process akin to the well-known reductive elimination reactions[22] of organometallic chemistry. In this type of reaction (eq 23) an organometallic complex undergoes elimination of a metal atom with a concomitant change in its oxidation state. A new bond is also formed between groups X and Y. One- and two-electron reductive eliminations are well established. In the benzene plus 2-iodopropane system, a three-electron reductive elimination is taking place. A two-electron reduction would form I$^+$ and a hydrocarbon radical. However, charge transfer from the I$^+$ to the hydrocarbon radical, an expected exothermic reaction, completes the reduction of iodine (see eq 24). For the diphenyliodonium ion, the charge transfer is exothermic by 2.2 eV. For the $C_9H_{13}^+$, the exothermicity would be even greater since the ionization potential for a hydrocarbon radical should be lower than that for a hydrocarbon neutral.

$$X{-}M{-}Y \rightleftharpoons M + X{-}Y \quad (23)$$



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Structure of $C_{10}H_{15}^+$. In an effort to explore the generality of the reaction of ionized benzene and iodoalkanes, the isomeric iodobutanes (1- and 2-iodobutane, 1-iodo-2-methylpropane, and 2-iodo-2-methylpropane) as well as iodoethane were examined for reactivity with ionized benzene.

An analogous reaction was observed for benzene and 2-iodobutane, and a product $C_{10}H_{15}^+$ was observed (see eq 25). No $C_{10}H_{15}^+$ reaction products were found for the other iodobutanes,

$$C_6H_6^{+\cdot} + 2\text{-}C_4H_9I \rightarrow [C_{10}H_{15}I]^{+\cdot} \rightarrow C_{10}H_{15}^+ + I \quad (25)$$

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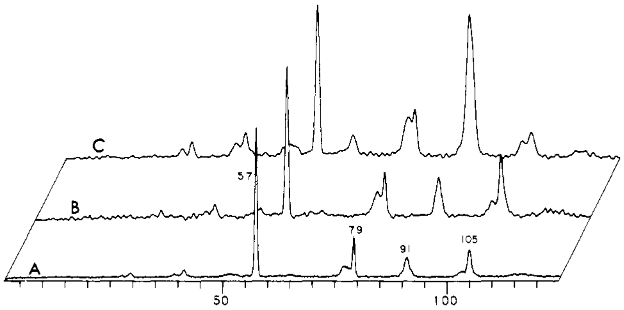

Figure 6. (A) CID spectrum of the $C_{10}H_{15}^+$ from the reaction of ionized benzene and 2-iodobutane, (B) CID spectrum of protonated *sec*-butylbenzene, and (C) CID spectrum of protonated *n*-butylbenzene.

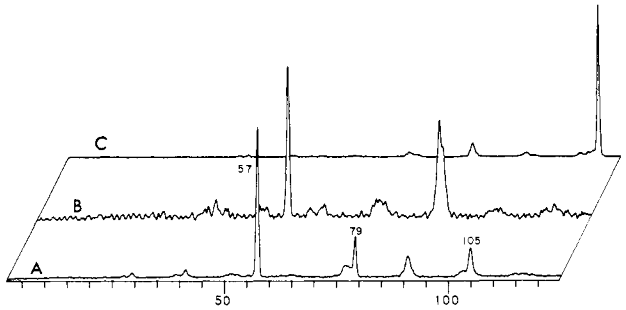

Figure 7. (A) CID spectrum of the $C_{10}H_{15}^+$ from the reaction of ionized benzene and 2-iodobutane, (B) CID spectrum of protonated isobutylbenzene, and (C) CID spectrum of protonated *tert*-butylbenzene.

and no $C_8H_{11}^+$ was detected for iodoethane. Under the conditions employed in the ICR experiments, no intact collision complex was observed. This is understandable since the adduct ion experiences no stabilizing collisions, and the only way it can lose excess internal energy, released as the exothermicity of the reaction, is by decomposition.

The same strategy employed in the $C_9H_{13}^+$ study (protonation of reference compounds followed by acquisition of CID spectra) was followed in the study of the structure of $C_{10}H_{15}^+$. The reference compounds for the $C_{10}H_{15}^+$ system included *n*-butylbenzene, *sec*-butylbenzene, isobutylbenzene, and *tert*-butylbenzene. The CID spectrum of the $C_{10}H_{15}^+$ produced in the reaction of benzene and 2-iodobutane (see Figure 6) shows four major peaks (similar to those observed for $C_9H_{13}^+$) as described in eq 26–29. The CID

$$C_{10}H_{15}^+ \rightarrow C_8H_9^+ + C_2H_6 \quad (26)$$

$$\rightarrow C_7H_7^+ + C_3H_8 \quad (27)$$

$$\rightarrow C_6H_7^+ + C_4H_8 \quad (28)$$

$$\rightarrow C_4H_9^+ + C_6H_6 \quad (29)$$

spectra of the protonated reference compounds are shown in Figures 6 and 7. It is readily apparent from the spectra that the reaction product has an ion structure different from that of protonated *n*-butylbenzene, isobutylbenzene, or *tert*-butylbenzene. However, based on the similarity of the spectrum of the reaction product and that of protonated *sec*-butylbenzene, we conclude that the reaction product has the same carbon skeleton as protonated *sec*-butylbenzene.

Although we know that at least a portion of the $C_{10}H_{15}^+$ was produced by loss of iodine from the intact collision complex, it is also possible that a reaction between butyl cation and neutral benzene was taking place even though a large excess of benzene was employed to give excess reactant $C_6H_6^{+\cdot}$ for the ion–molecule reaction. To check this possibility, the $C_4H_9^+$ ions from *n*-butane and benzene were allowed to react and the spectra compared with that of the butylated benzene from the reaction of ionized benzene and 2-iodobutane. It was observed that the CID spectrum of the $C_{10}H_{15}^+$ ion from the reaction of the $C_4H_9^+$ was identical with that from the reaction of ionized benzene and 2-iodobutane. The butane was then removed and 2-iodobutane added. For reaction with the same amounts of neutral benzene and under the same pressure conditions, the reaction with neutral 2-iodobutane gave *m/z* 135 which was 10 times more abundant than that from the reaction of neutral benzene and the $C_4H_9^+$ ion from the butane.

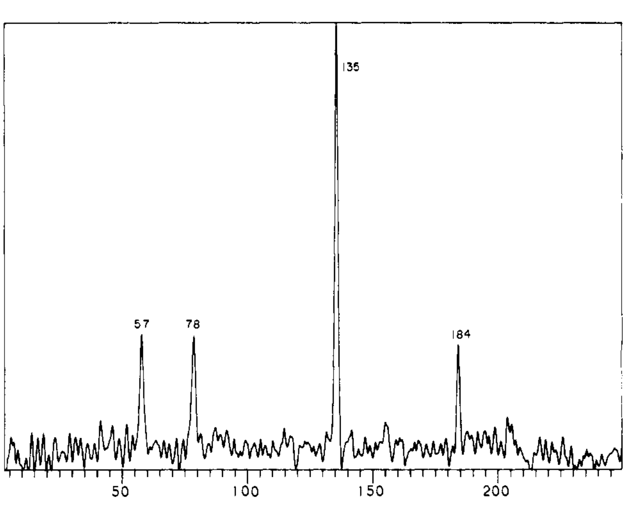

Figure 8. CID spectrum of the intact collision complex ($C_{10}H_{15}I^+$) from the reaction of ionized benzene and 2-iodobutane.

The reaction with 1-iodobutane was also investigated. A *m/z* 135 was observed, but it was only 10% as intense as that produced in the reaction of the benzene radical cation and 2-iodobutane. ICR data show no detectable reaction of benzene radical cation with 1-iodobutane to give $C_{10}H_{15}^+$ (vide infra). Taking this fact into account as well as the information concerning the reaction of the $C_4H_9^+$ from butane with benzene, we conclude that the *m/z* 135 observed arises from the reaction of butyl cation produced from fragmenting 1-iodobutane and with neutral benzene. This idea is supported by the lack of a collision complex at *m/z* 262. These observations more firmly establish that less than 10% of the $C_{10}H_{15}^+$ produced in the mixture of benzene and 2-iodobutane originates by direct butylation of benzene by $C_4H_9^+$.

These results also indicate that the $C_4H_9^+$ ions from *n*-butane and 1-iodobutane have the *sec*-butyl structure in accord with previous ICR[23] and solution studies.[24]

The benzene-d_6/2-iodobutane reaction product (*m/z* 141) was also examined by $V^{1/2}/E$ linked scans to sort out the H/D exchange reactions taking place. Four clusters of peaks were observed representing losses of one, two, three, and four carbon-containing fragments. It was determined that exchange was indeed taking place.

Methane is the exclusive one-carbon neutral fragment loss: 70% as CD_3H and 30% as CD_2H_2. Both ethyl and ethane are lost as two-carbon fragments with ethane loss predominant. Approximately 90% of the ethyl is lost as C_2H_5 and the remainder as C_2H_4D. For the ethane loss, 75% is lost as C_2H_5D and 25% as C_2H_6. For C3 fragments, both propyl and propane losses occur with loss of propane major. Ninety percent of the propyl is lost as C_3H_7 and the remainder is C_3H_6D. For the propane loss, 59% is C_3H_8, 27% C_3H_7D, and 14% $C_3H_6D_2$ (a ratio of approximately 4:2:1). For C4 fragments, only butene is lost: 60% C_4H_8 and 20% C_4H_7D. The remainder includes $C_4H_6D_2$, $C_4H_5D_3$, and $C_4H_4D_4$ (8, 6, and 7%, respectively).

The results of the H/D exchanges are in agreement with the proposed structure of the $C_{10}H_{15}^+$ product. The conclusions arrived at for the $C_9H_{13}^+$ also apply in this case. We again observe that reactions of the intermediate which require minimal rearrangement occur with minimal H/D exchange.

Structure of the $C_{10}H_{15}I^+$ Intermediate. The intact collision complex (*m/z* 262) could be stabilized by collision and observed. The collision complex was examined by studying its metastable and collision-induced dissociation spectra. The metastable spectrum showed a single peak at *m/z* 135 corresponding to loss

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Table I. Experimental Rate Constants for the Reaction of Neutral Iodoalkanes with the Benzene Radical Cation[a]

reaction system	k (cm^3 mol^{-1} s^{-1})	reaction system	k (cm^3 mol^{-1} s^{-1})
$C_6H_6^{+\cdot} + C_2H_5I$	$<10^{-11}$	$C_6H_6^{+\cdot} + 2\text{-}C_4H_9I$	2.0×10^{-9}
$C_6H_6^{+\cdot} + 1\text{-}C_3H_7I$	$<10^{-11}$	$C_6H_6^{+\cdot} + i\text{-}C_4H_9I$	$<10^{-10}$
$C_6H_6^{+\cdot} + 2\text{-}C_3H_7I$	1.3×10^{-9}	$C_6H_6^{+\cdot} + t\text{-}C_4H_9I$	$<10^{-10}$
$C_6H_6^{+\cdot} + 1\text{-}C_4H_9I$	$<10^{-10}$		

[a] To produce *m/z* 121 or *m/z* 135.

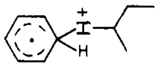
of an iodine radical. The CID spectrum (Figure 8) shows four peaks (see eq 30–33). These decompositions (which are similar to those of the $C_9H_{13}I^+$ collision complex) enable us to conclude that the $C_{10}H_{15}I^+$ collision complex is a covalently bound iodonium radical cation of structure IV.

$$C_{10}H_{15}I^{+\cdot} \rightarrow C_4H_9I^{+\cdot} + C_6H_6 \qquad (30)$$

$$\rightarrow C_{10}H_{15}^+ + I \qquad (31)$$

$$\rightarrow C_6H_6^{+\cdot} + C_4H_9I \qquad (32)$$

$$\rightarrow C_4H_9^+ + C_6H_6I \qquad (33)$$



IV

Rate Constant Measurements. The rate constant for the reaction of benzene with 2-iodopropane was determined previously[2] in this laboratory from data taken on a ICR spectrometer equipped with a three-section drift cell. The observation time of that experiment was restricted to less than 10 ms which limited us to observation of no more than approximately 15% of the reaction. The rate constant for the reaction has been redetermined for several reasons. (1) We wished to check the accuracy of the original measurement by using a pulsed ICR, a more accepted method. (2) We wished to examine some of the other iodoalkanes to see if we could observe reactions which would have been too slow to observe with the drift cell system. (3) Finally, we wished to determine the rate constants for the reactions of benzene radical cation and various iodobutanes which have not been determined to date.

The following compounds were examined for reactivity with the benzene radical cation: iodoethane, 1-iodopropane, 2-iodopropane, 1-iodobutane, 2-iodobutane, 1-iodo-2-methylpropane, and 2-iodo-2-methylpropane (see Table I). We found that iodoethane and 1-iodopropane are unreactive with the benzene radical cation. For 2-iodo-2-methylpropane, we observed a decrease in the benzene signal with time, but no reaction products corresponding to Wheland intermediates were formed. However, the intensities of the 2-iodo-2-methylpropane molecular ion and its fragment $C_4H_9^+$ increased at longer times. Thus, we conclude that benzene is charge exchanging with the 2-iodo-2-methylpropane. Similar results were obtained for 1-iodobutane and 1-iodo-2-methylpropane. This is consistent with the fact that the charge exchange reactions are exothermic (benzene has a higher ionization potential than that of the iodobutanes).[25] Iodine elimination only occurred for 2-iodopropane and 2-iodobutane intermediates.

Table II. Comparison of Experimental and Theoretical Rate Constants for the Reaction of Ionized Benzene and 2-Iodobutane

k (cm^3 mol^{-1} s^{-1})	source of rate constant	k (cm^3 mol^{-1} s^{-1})	source of rate constant
2.0×10^{-9}	exp	1.7×10^{-9}	ADO[28]
3.8×10^{-9}	LDO[27]	1.2×10^{-9}	Langevin[26]

In the previous study, a rate constant of 1.2×10^{-9} cm^3 mol^{-1} s^{-1} was obtained at an ionizing energy of 15 eV for the reaction of benzene with 2-iodopropane to give $C_9H_{13}^+$. The precision and accuracy of the measurement are ±10 and ±20%, respectively. Using the pulsed ICR, we obtained a rate constant of 1.3×10^{-9} cm^3 mol^{-1} s^{-1} for this reaction with a precision of ±10%. The rate constant for the reaction with 2-iodobutane is 2.0×10^{-9} cm^3 mol^{-1} s^{-1}.

A comparison of the experimental rate constant for the 2-iodobutane reaction with theoretical collision rate constants calculated using Langevin,[26] locked dipole orientation (LDO),[27] and average dipole orientation (ADO)[28] theories is given in Table II (see ref 2 for a similar comparison for the 2-iodopropane reaction). As can be seen, the Langevin calculated rate constant is less than the experimental value. This is expected since Langevin theory neglects the permanent dipole of 2-iodobutane. On the other hand, the LDO theory gives a value greater than the experimental value because of an overestimate of the dipole effect. The ADO theory gives the best agreement.

Conclusions

We have obtained data which permit us to assign the structures of the $C_9H_{13}^+$ and the $C_{10}H_{15}^+$ ions produced in the reactions of ionized benzene with 2-iodopropane and with 2-iodobutane, respectively, as protonated alkylbenzenes which initially exist as Wheland intermediates. We infer that these products arise via formation of an intermediate radical cation which has an iodonium site and which undergoes a three-electron reductive elimination to form the Wheland intermediates (structures II and IV and eq 24) or similar structures differing only in the location of the proton. We have also shown that the complementary techniques of ion cyclotron resonance spectrometry and tandem mass spectrometry (mass spectrometry/mass spectrometry) represent powerful means for investigating ion–molecule reactions.

These gas-phase reactions may also serve as guideposts for the design of solution reactions. Investigations are underway elsewhere to explore this chemistry initiated electrochemically in solution.[29]

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE-8008008) and by the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (Grant No. CHE-8211164).

Registry No. $C_6H_6^{+\cdot}$, 34504-50-2; C_2H_5I, 75-03-6; 1-C_3H_7I, 107-08-4; 2-C_3H_7I, 75-30-9; 1-C_4H_9I, 542-69-8; 2-C_4H_9I, 513-48-4; *i*-C_4H_9I, 513-38-2; *t*-C_4H_9I, 558-17-8; protonated *n*-propylbenzene, 85442-71-3; protonated isopropylbenzene, 83875-74-5; protonated 1-ethyl-2-methylbenzene, 85442-70-2; protonated 1,3,5-trimethylbenzene, 85442-72-4; protonated *sec*-butylbenzene, 85479-30-7; protonated *n*-butylbenzene, 85442-73-5; protonated isobutylbenzene, 85442-74-6; protonated *tert*-butylbenzene, 83927-54-2.

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