Alkylation of benzene by alkyl cations. Stability of the *tert*-butyl benzenium ion

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Can. J. Chem. Downloaded from www.nrcresearchpress.com by 67.52.49.38 on 11/18/14 For personal use only. The kinetics and equilibria of the gas phase reaction [1] $tert-C_4H_9^+ + C_6H_6 = tert-C_4H_9C_6H_6^+$ were studied with a high ion source pressure pulsed electron beam mass spectrometer. Equilibria [1] could be observed in the temperature range 285–325 K. van't Hoff plots of the equilibrium constants led to $\Delta H_1^0 = -22\pm 2 \text{ kcal mol}^{-1}$ and $\Delta S_1^0 = -49\pm 5 \text{ cal K}^{-1} \text{ mol}^{-1}$. The rate constants at 305 K were $k_{1t} = 1.5 \times 10^{-28} \text{ molecules}^{-2} \text{ cm}^6 \text{ s}^{-1}$ and $k_{1r} = 2.9 \times 10^{-19} \text{ molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$. $tert-C_4H_9C_6H_6^+$ dissociates easily via [lr] not only because of the low dissociation energy $(-\Delta H_1^0)$ but also because of the unusually favorable entropy $(-\Delta S_1^0)$. The occurrence of transalkylation reactions: $tert-C_4H_9C_6H_6^+$ + alkylbenzene = $tert-C_4H_9$ alkylbenzene⁺ + benzene, was discovered in the present work.

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On a étudié la cinétique et l'équilibre de la réaction en phase gazeuse [1] $tert-C_4H_9^+ + C_6H_6 = tert-C_4H_9C_6H_6^+$ en faisant appel à un spectromètre de masse à faisceau d'électrons pulsés et ayant une source d'ions à haute pression. Les équilibres [1] peuvent être observés dans l'intervalle de température de 285–326 K. Les courbes de van't Hoff des constantes d'équilibre conduisent à $\Delta H_1^0 = 22 \pm 2$ kcal mol⁻¹ et à $\Delta S_1^0 = -49 \pm 5$ cal K⁻¹ mol⁻¹. Les constantes de vitesse à 305 K sont: $k_{1f} = 1,5 \times 10^{-28}$ molécules⁻² cm³ s⁻¹ et $k_{1r} = 2,9 \times 10^{19}$ molécules⁻¹ cm³ s⁻¹. L'ion $tert-C_4H_9C_6H_6^+$ se dissocie facilement via [Ir] non seulement parce que l'énergie de dissociation est faible ($-\Delta H_1^0$] mais également par suite d'une entropie exceptionnellement favorable ($-\Delta S_1^0$). Dans cette étude, on a découvert la manifestation des réactions de transalkylation: $tert-C_4H_9C_6H_6^+ +$ alkylbenzène = $tert-C_4H_9$ alkylbenzène⁺ + benzène.

[Traduit par le journal]

Introduction

The alkylation of benzene and other aromatic hydrocarbons by the electrophilic attack of alkyl cation intermediates is a classical condensed phase reaction. It is of interest in a very wide area. Thus it has played an important part in the development of the theory of carbonium ions in physical organic chemistry (1, 2) and, on the other end of the spectrum, it is an important industrial reaction for the production of alkyl benzenes. In the gas phase, the reactions are of analytical importance in chemical ionization mass spectrometry (3). Thus the often used reagent gases methane, propane, and isobutane produce $C_2H_5^+$, iso- $C_3H_7^+$, and tert-C₄H₉⁺ respectively, as reagent ions. These become involved in alkylation reactions when the unknown is benzene or some other aromatic compound.

The present work describes results obtained from measurement of the kinetics and equilibria of the gas phase reaction [1] with a high pressure mass spectrometer. Reaction [1] represents an associa-

[1]
$$tert-C_4H_9^+ + C_6H_6 \rightleftharpoons tert-C_4H_9 \cdot C_6H_6^+$$

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tion of a carbenium ion, i.e. a Lewis acid with a π Lewis base. Association reactions involving various alkyl cations and Lewis bases like H₂O, CO, RCl have been described in previous publications from this laboratory (4).

We believe that the present results are at least of partial interest to all areas mentioned above. They do represent also an addition to gas phase ion thermochemistry (5, 6).

Experimental

The measurements were made with the pulsed electron beam high ion source pressure mass spectrometer used in earlier work (4-6). Pulsing of the electron beam permits time resolved detection of the ions. The temperature of the ion source is controlled by means of heaters embedded in the ion source block. The usual procedure of flowing the gas mixture in and out of the ion source was employed. In the absence of such flow an enrichment of the heavier neutral components in the ion source is expected because of the effusive loss of gas through the ion source slits.

In a reaction mixture containing methane as major gas (3 to 4 Torr) and known low pressures of isobutane and benzene where p (isobutane) $\gg p$ (benzene), a sequence of reactions occurs. The dominant ionization is of methane and the final ions in methane are CH_s⁺ and C₂H_s⁺. In the presence of isobutane, reactions [2] and [3] convert CH_s⁺ and C₂H_s⁺ to C₄H₉⁺, which in turn reacts with benzene via the desired reaction [1].

$$[2] \quad CH_5^+ + iso-C_4H_{10} = CH_4 + C_4H_9^+ + H_2$$

[3] $C_2H_5^+ + iso-C_4H_{10} = C_2H_6 + C_4H_9^+$

At suitably high temperatures, reaction [1] becomes reversible which allows the determination of equilibrium [1].

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The ion-time dependence in a typical experiment leading to equilibrium is shown in Fig. 1. The equilibrium constants K_1 and their temperature dependence are displayed in Figs. 2 and 3. These results will be discussed in the next section. Here we wish to describe some observations which relate to the choice of concentrations used in the experiments. The data of Figs. 1-3 were obtained with methane 3 Torr, isobutane 1 Torr, and benzene in the 1 to 10 mTorr range. Initial experiments with much lower isobutane concentrations (e.g., isobutane 100 to 30 mTorr, benzene ~5 mTorr) led to anomalous results. A certain residual amount of $C_4H_9C_6H_6^+$ at equilibrium was observed to persist to much higher temperatures than could be expected from Fig. 3. For example, about 10% C₄H₉C₆H₆⁺ was still observed at 152°C. The corresponding $C_5H_9^+$ was 50%, which leads to an equilibrium constant " K_1 " = 25 (Torr⁻¹) (p(benzene) = 8 mTorr). The K_1 predicted from Fig. 3 for the same temperature is about four orders of magnitude smaller. Evidence cited below indicates that the residual $C_4H_9C_6H_6^+$ is not tert-butyl benzenium but the more stable isobutyl or sec-butyl benzenium, formed by the addition of the corresponding isomeric butyl cation to benzene.

Experiments at high temperature and low isobutane pressures showed that the residual $C_4H_9C_6H_6^+$ increased with benzene pressure but only up to a certain limiting concentration (~30%). Increase of the isobutane pressure led to a decrease of the residual butyl benzenium. Pressures above ~0.6 Torr isobutane caused the complete disappearance of the high temperature residual ion and these conditions led also to the normal equilibrium behavior at low temperatures (Figs. 1–3).



FIG. 1. Kinetics and equilibrium of reaction [1], $C_4H_9^+ + C_6H_6 = C_4H_9C_6H_6^+$. Reaction mixture employed: CH₄ 3 Torr, isobutane 1 Torr, benzene 4 mTorr, temperature 32°C. Rapid ion-molecule reactions in major gases methane and isobutane produce $C_4H_9^+$ as practically the only ion. $C_4H_9^+$ adds to benzene; however, reaction is reversible and reaches equilibrium after about 0.5 ms. Equilibrium constant $K_1 = 170 \text{ Torr}^{-1}$ from data in this figure. Approximate rate constants for the forward and reverse direction of the reaction can also be obtained from this figure.



FIG. 2. Invariance of equilibrium constant K_1 with pressure of benzene. Temperature 32°C.



FIG. 3. van't Hoff plot of equilibrium constant K_1 obtained from equilibria measurements as illustrated in Fig. 1. Slope and intercept lead to $\Delta H_1^0 = -22\pm 2 \text{ kcal mol}^{-1}$, $\Delta S_1^0 = 49\pm 5 \text{ cal } \text{K}^{-1} \text{ mol}^{-1}$ given in Table 1.

Reactions [2] and [3] can produce not only *tert*- $C_4H_9^+$ but also another butyl isomer, $x-C_4H_9^+$. This isomer can either add to benzene giving the stable butyl benzenium by reaction [4] or be converted to *tert*- $C_4H_9^+$ by the hydride abstraction [5], reaction [5] being favored by a high isobutane to benzene ratio.

[4]
$$x-C_4H_9^+ + C_6H_6 = x-C_4H_9C_6H_6^+$$

[5] $x-C_4H_9^+ + iso-C_4H_8 = x-C_4H_{10} + tert-C_4H_9^+$

Experiments with $(CH_3)_3CD$ in methane showed that both CH_5^+ and $C_2H_5^+$ produced $C_4H_9^+$ and $C_4H_8D^+$. The $C_4H_8D^+/C_4H_9^+$ ratio observed for ethyl was approximately 2. The $C_4H_8D^+$ must be, at least initially, of the isobutyl structure. Evidence in the literature (9) suggests that the isobutyl cation is unstable (9a); however, the production of the unstable isobutyl was by electron impact (9b) and not the milder hydride abstraction occurring in the present work. The present work does not provide any evidence on the nature of the x-C_4H_9^+ except that it leads to an adduct that is more stable than $tert-C_4H_9C_6H_6^+$. $sec-C_4H_9^+$ will form a sufficiently stable benzenium ion to fit our experimental conditions. Thus, we observed that the $sec-C_3H_7C_6H_6^+$ is the elevated temperatures (150°C) at which the x-C_4H_9C_6H_6^+ was observed.

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Reaction	$-\Delta H^0$	$-\Delta S^{o}$		
[1] $tert-C_4H_9^+ + C_6H_6 = tert-C_4H_9 \cdot C_6H_6^+$	22±2 ^b	49±5 ^b		
	21.0 ± 1^{c}	46 ± 5^{d}		
$iso-C_{3}H_{7}^{+}+C_{6}H_{6}=iso-C_{3}H_{7}C_{6}H_{6}^{+}$	33.8 ± 1^{e}	34 ± 2^{e}		
$C_2H_5^+ + C_6H_6 = C_2H_5C_6H_6^+$	46.5±1 ^r	31.5 ± 2^{f}		
	Rate cor	istant ^o		
[1] $tert - C_4H_9^+ + C_6H_6 = tert - C_4H_9 \cdot C_6H_6^+$	$k_{1f} = 1.5 \times 10^{-28} \text{ mo}$ $k_{1r} = 2.9 \times 10^{-14} \text{ mo}$	$k_{\rm lf} = 1.5 \times 10^{-28} {\rm molecules}^{-2} {\rm cm}^6 {\rm s}^{-1}$ $k_{\rm lr} = 2.9 \times 10^{-14} {\rm molecules}^{-1} {\rm cm}^3 {\rm s}^{-1}$		
$[14] tert-C_4H_9C_6H_6 + CH_3C_6H_5 = tert-C_4H_9 \cdot CH_3C_6H_6 + C_6H_6$	$k_{14} \approx 10^{-11} \mathrm{molec}$	cules ⁻¹ cm ³ s ⁻¹		

Table 1	. '	Thermochemic	al	dataª	and	approximat	e i	ate	constan	its

^a Enthalpies in kcal/mol, entropies in cal mol⁻¹ K⁻¹ at 300 K, standard state 1 atm. ^b Present experimental work from van't Hoff plot in Fig. 3. Errors are estimated. ^c Evaluated from eq. [7] $\Delta PA = 1.5$ kcal/mol from McIver and co-workers (10, 11); ΔH ?: *tert*-butylbenzene = -7; benzene +19.8; isobutene -4.3 kcal/mol (13). ^a Estimated (statistical thermodynamics) see text. ^c From $\Delta H_{PT} = -10.1$ kcal/mol, $\Delta G_{PT} = -10.5$ kcal/mol (10-12); ΔH ?: C₃H₆ = 4.9 kcal/mol; isopropylbenzene = 0.9 kcal/mol; ΔG ?: C₃H₆ = 15 kcal/mol; isopropylbenzene = 32.7 kcal/mol (13, 14). ^a From $\Delta H_{PT} = -21.7$ kcal/mol, $\Delta G_{PT}^{a} = -21.3$ kcal/mol, based on ΔH ? (C₂H₅⁺) = 216 kcal/mol (10, 17); ΔH ? (ethylbenzene) = 7.1 kcal/mol, ΔG ?: C₁ H₆ are constants at 32°C. The rate constant k_H was assumed to be third order while k_H was assumed to be second order.

A mixture of methane (3 Torr) and isobutane (1 Torr) was used in the equilibria [1] determinations, rather than neat isobutane at 4 Torr, because an unknown trace impurity (probably C_4H_8) in the isobutane led to production of ions of mass 113 and 111. These were noticeable at long reaction times in runs undertaken below room temperature. Mass 113 is probably the $C_4H_9 \cdot C_4H_8^+$ while mass 111 results from dehydrogenation of mass 113.

Results and discussion

A typical experimental result is shown in Fig. 1. The reaction mixture produces $tert-C_4H_9^+$ as essentially the only ion some microseconds after the electron pulse.³ In the presence of a small concentration of benzene, reaction [1] is seen to occur. The reaction reaches equilibrium after

$$[1] \quad C_4H_9^+ + C_6H_6 \quad \stackrel{\text{lf}}{\underset{\text{lr}}{\leftrightarrow}} C_4H_9C_6H_6^+$$

about 0.7 ms. Runs with higher benzene concentration led to a shift of the equilibrium to the right as required by the equilibrium expression [6]. The ion intensity ratio from

[6]
$$K_1 = \frac{P(C_4H_9C_6H_6)^+}{P(C_4H_9^+)P(C_6H_6)}$$

runs as in Fig. 1, in the steady region, at long reaction times, was substituted into equation [6]. An example of the invariance of K_1 with changing benzene pressure is shown in Fig. 2. The results in Fig. 1 illustrate the clean reaction conditions that can be achieved by proper choice of the reaction mixture. The ions of interest, $C_4H_9^+$ and

 $C_4H_9C_6H_6^+$, represent almost 95% of the total ions observed during most of the reaction time. The reactions leading to $C_4H_9^+$ in the selected reaction mixture are described in the experimental section.

Raising the ion source temperature shifted the equilibrium to the left as expected for an exothermic reaction like [1]. The equilibrium constants K_1 determined at different temperatures are shown in the van't Hoff plot Fig. 3. The thermodynamic data ΔH_1^0 , ΔG_1^0 , and ΔS_1^0 obtained from the plot are given in Table 1. These results can be compared with calculated values obtained through eq. [7] and literature thermochemical data (10-14).

[7]
$$\Delta H_1 = \Delta H_{PT} - \Delta H_1^0 (iso-C_4H_8) + \Delta H_1^0 (C_4H_9C_6H_5) - \Delta H_1^0 (C_6H_6)$$

[8] $C_4H_9^+ + C_4H_9C_6H_5 = iso-C_4H_8 + C_4H_9C_6H_6^+$

$$\Delta H_8^0 = \Delta H_{PT}^0 = PA(iso-C_4H_8) - PA(C_4H_9C_4H_6)$$

 $\Delta H_{\rm PT}^0$ corresponds to the enthalpy for the proton transfer shown in eq. [8]. Analogous equations can be written also for ΔG_1^0 and ΔS_1^0 . The proton affinity of butylbenzene has been determined from proton transfer equilibria by McIver and co-workers (10). The proton affinity of isobutene also has been determined by proton transfer equilibria (7, 8, 11, 12). Since only the proton affinity difference is required in eq. [7], one needs only the relative proton affinities, i.e., there is no need to use an absolute PA scale. Heats of formation for the neutrals are also available (13). The $\Delta H^0 = -22 \text{ kcal/mol}$ obtained from the van't Hoff plot is seen to be in relatively good agreement with the value of -21 kcal/mol obtained via eq. [7].

Immediately after the butylation, the proton may

³Since all subsequent discussion deals with $tert-C_4H_9$, the prefix tert will be omitted for brevity in all the subsequent text and formulas.

be expected to be in position 1, relative to the butyl group. The relative energies for different positions of the proton on the benzene ring should be similar to those in protonated toluene, for which Hehre and co-workers (15) have made STO-3G calculations. They found the following relative values 1(0); 2(-6.2); 3(-1.7); 4(-8.2), the numbers in brackets being the energies in kcal/mol. The proton affinity (10) of butylbenzene obtained from proton transfer equilibria should relate to the most stable position 4. The (approximate) agreement between ΔH_1 from the equilibria [1] and the calculated ΔH_1 from eq. [7] indicates that the proton in equilibria [1] was in the 2 or 4 position. One may expect considerable energy barrier(s) for the migration of the proton from the 1 to the 2 (and 4) position. The exothermicity of the butyl addition (proton in position 1) which should be around 12-15 kcal/mol is the only source that could provide the energy for the migration. Thus, we assume that the barriers are less than $\sim 15 \text{ kcal/mol}$ and the energy is provided by chemical activation.

Approximate rate constants k_{lf} and k_{lr} can be determined from runs like that shown in Fig. 1. These are shown in Table 1. It was assumed that the reaction is third order in the forward and second order in the reverse direction. The $k_{\rm lf} \approx 10^{-28} \, {\rm cm}^6$ molecules⁻² s⁻¹ is very small when compared to other third order association reactions involving polyatomic reactants and exothermicities in the 20 kcal/mol range. The low rate constant, however, is not so surprising when one considers that the primary product of [lf] contains the proton in position 1 and thus has a considerably lower exothermicity than 20 kcal/mol. Furthermore, the formation of the adduct is connected with unusually unfavorable entropy, as will be shown below.

Table 1 gives enthalpy changes for the alkylation of benzene by the isopropyl and ethyl cation. These were calculated from equations analogous to [7] and corresponding thermochemical data. As expected, a rapid increase of exothermicity is observed for the series $C_4H_9^+$, $sec-C_3H_7^+$, $C_2H_5^+$.

It is possible to calculate the entropy change of the alkylation reactions with an equation analogous to [7] but involving the corresponding entropy terms. The ΔS changes for the proton transfer reactions are small and are generally estimated from the rotational symmetry numbers. The entropies for the neutrals were taken from Stull *et al.* (14). The calculated entropies for iso-C₃H₇⁺ and C₂H₅⁺ alkylation are shown in Table 1. Unfortunately a value for S⁰ (C₄H₉·C₆H₅) is not available, so that ΔS_1^0 could not be evaluated from eq. [7]. An estimate of ΔS_1^0 can be made on the basis of equations for translational, rotational, and vibrational entropies from statistical mechanics. The translational and external rotation changes are easily evaluated and amount to $\Delta S_{tr}^{0} = -36.7$ and $\Delta S_{extrot}^0 = -15.2$. (All entropy values in cal K^{-1} mol⁻¹.) Space models indicate that the internal rotation of the butyl group relative to C_6H_6 in $C_4H_9C_6H_6^+$ may be restricted to a torsional oscillation. The same is true for the internal rotations of the methyl groups. Taking this into account, one obtains a $\Delta S_{int rot}^0 \approx -1.5$. The total $-\Delta S_1^0$, neglecting all vibrations, is 53.4. This value represents a maximum value for $-\Delta S_1^0$. Several soft vibrations created in the adduct $C_4H_9C_6H_6^+$ will reduce $-\Delta S_1^0$ by some 5-8 units, i.e. to the neighbourhood of $46 \operatorname{cal} \mathrm{K}^{-1} \operatorname{mol}^{-1}$. This is the estimated value given in Table 1.

The (absolute) entropy changes for the alkylation of benzene are seen to increase rapidly in the order $C_2H_5^+$, sec- $C_3H_7^+$, $C_4H_9^+$. The $-\Delta S^0$ value for butyl is unusually large, the largest we have ever measured. The entropy changes for many association reactions fall around 25 cal/degree mol. This is particularly true for clustering reactions, i.e. ion-solvent molecule association (7). The large entropy loss in reaction [1] must be attributed to the relatively large mass and large moments of inertia of both benzene and $C_4H_9^+$ and to the very restricted motions of the butyl group in the $C_4H_9C_6H_6^+$ ion. The very adverse entropy change for reaction [1] contributes significantly to the lack of stability of the $C_4H_9C_6H_6^+$ which was seen to thermally decompose (see Figs. 1 and 3) already below room temperature. Species with a dissociation energy of 22 kcal/mol $(-\Delta H_1)$ and more normal entropies remain stable to much higher temperatures.

In superacid solution Olah *et al.* (1*c*) have observed, by ¹Hmr, that the protonated butylbenzene is stable at -78° C. However, "warming of the solution leads to immediate cleavage of the butyl group" i.e. the reverse of reaction [1]. From this description, it appears that the cleavage is considerably more facile in solution than in the gas phase. This difference probably is largely due to solvation effects, in particular the better solvation of the butyl cation when compared to the butyl benzenium ion.

The facile decomposition of $C_4H_9C_6H_6^+$ is obviously responsible for protolysis being the almost exclusive reaction in the mass spectral chemical ionization of butylbenzene (3) with strong Brönsted acids like CH_5^+ and $C_2H_5^+$. But even after the most gentle protonation, thermal decomposition by [lr] will occur at the 100°C temperature commonly used in C.I. ion sources. McIver and Can. J. Chem. Downloaded from www.mrcresearchpress.com by 67.52.49.38 on 11/18/14 For personal use only. SEN SHARMA ET AL.





co-workers (10) were able to measure proton transfer equilibria involving butylbenzene only because, at the low pressures used in the ICR apparatus, the thermal activation required for [lr] is very much slower than the proton transfer reactions.

Some experiments were made in order to determine the fate of $C_4H_9C_6H_6^+$ produced by protonation of butylbenzene. The time dependence of the ions observed in two such experiments is shown in Figs. 4 and 5. A mixture of methane (1.6 Torr) with traces of butylbenzene (0.7 mTorr) was used in Fig. 4.

The proton transfer from the methane ions CH_5^+ and $C_2H_5^+$ is strongly exothermic and results in almost complete protolysis of the butylbenzene. The $C_4H_9^+$ created by the protolysis is seen

[9]
$$CH_{5}^{+}(or C_{2}H_{5}^{+}) + C_{4}H_{9}C_{6}H_{5} = [C_{4}H_{9}C_{6}H_{6}^{+}]^{*} + CH_{4}(or C_{2}H_{4})$$

$$= [C_{4}H_{6}C_{6}H_{6}^{+}]^{*} \longrightarrow C_{4}H_{6}^{+} + C_{6}H_{6}$$

to alkylate the butylbenzene in reaction [10] which is analogous to [1]. In comparing Figs. 1 and 4, which are for experiments at the same

[10] $C_4H_9^+ + C_4H_9C_6H_5 = (C_4H_9)_2C_6H_5^+$

temperature, it becomes immediately obvious that the equilibrium constant K_{10} is much larger than K_1 , i.e. $K_1 \approx \ge 1.7 \times 10^2$ while $K_{10} \ge 3 \times 10^4$ (Torr⁻¹). This is an expected result. It has long been known, from condensed media experiments, that the stability of benzenium ions (cyclohexadienyl cations) increases as the number of alkyl substituents is increased (1, 2). This is due to the greater stabilization of the charge in the benzenium ions by the multiple alkyl substituents. A well-known consequence of this effect is the reduced synthetic utility of Friedel-Crafts alkylations, i.e. the difficulty in stopping the reaction at the single alkylation stage. The product of reaction [10] is most likely the most stable isomer, i.e. the *meta* dibutylbenzenium shown in structure **I**.



Not all of the protonated butylbenzene formed by reaction [9] suffers immediate dissociation; a small

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FIG. 5. Time dependence of major ions observed with reaction mixture: CH_4 1 Torr, toluene 10 mTorr, *tert*-butylbenzene 0.5 mTorr. CH_5^+ and $C_2H_5^+$ rapidly protonate toluene. The protonated toluene proton transfers to butylbenzene [11] $CH_3C_6H_6^+ + C_4H_9C_6H_5^+ = CH_3C_6H_5 + C_4H_9C_6H_6^+$. Reaction [11] comes near equilibrium for longer reaction times. Some of the $C_4H_9C_6H_6^+$ decomposes to $C_4H_9^+$ by [lr]. The final major product $(CH_3)(C_4H_9)C_6H_5^+$ is formed by the addition of $C_4H_9^+$ to toluene [12] and also by the direct reaction [14], $C_4H_9C_6H_6^+ + CH_3C_6H_5 = (C_4H_9)(CH_3)C_6H_5^+ + C_6H_6$.

fraction becomes thermalized (see Fig. 4) and then gradually disappears by reactions [lr] and [15] to be discussed below.

The ion-time profiles shown in Fig. 5 were obtained with a gas mixture of the major gas methane (1 Torr) with toluene (10 mTorr) and butylbenzene (0.5 mTorr). For these conditions, proton transfer from CH_5^+ and $C_2H_5^+$ to toluene is rapid. The protonated toluene proton transfers to the butylbenzene by reaction [11]. Since the proton affinities of

[11] $CH_3C_6H_6^+ + C_4H_9C_6H_5 = CH_3C_6H_5 + C_4H_9C_6H_6^+$

toluene and butylbenzene are close, reaction [11] reaches equilibrium after ~100 µs. This is demonstrated by the essentially constant ratio $[C_4H_9C_6H_6^+]/[CH_3C_6H_6^+]\approx 3$ at longer reaction times. This ratio taken together with the concentration ratio of the neutrals, [toluene]/[butylbenzene] = 20, leads to K_{11} ≈ 60 and $\Delta G_{11}^0 = -2.5$ kcal/mol in good agreement with McIver's (10) value of -2.3 kcal/mol. The butylbenzenium ion formed via (11) disappears gradually and is replaced by the two ions $(CH_3)(C_4H_9)C_6H_5^+$ and $(C_4H_9)_2C_6H_5^+$. These products can be created by reactions [12] and [13], the association of $C_4H_9^+$ with toluene and butylbenzene. The butyl⁺ is formed by the thermal

[12] $C_4H_9^+ + CH_3C_6H_5 = C_4H_9CH_3C_6H_5^+$ [13] $C_4H_9^+ + C_4H_9C_6H_5 = (C_4H_9)_2C_6H_5^+$

decomposition of the C₄H₉C₆H₆⁺, i.e. reaction [lr]. Reactions [lr], [12], and [13] undoubtedly occur, evidence for this is the small, near steady state concentration of $C_4H_9^+$ observed in Fig. 5 over the whole duration of the $C_4H_9C_6H_6^+$ ion. This is consistent with $C_4H_9^+$ being produced by [lr] and disappearing by [12] and [13]. (A "burst" of $C_4H_9^+$ at short reaction times is due to protolysis of butylbenzene by CH_5^+ and $C_2H_5^+$.) Comparing the rate of $C_4H_9C_6H_6^+$ disappearance with the expected rate due to reaction [lr] (the rate constant $k_{\rm lr}$ was determined from Fig. 1) one finds that the observed rate in Fig. 5 and other similar runs is much faster. Furthermore this rate was found to increase as the concentration of toluene and butylbenzene was increased. This is very strong evidence that reactions [14] and [15] are also occurring. The rate constants k_{14} and k_{15} could be estimated to be around

- [14] $C_4H_9C_6H_6^+ + CH_3C_6H_5 = C_4H_9CH_3C_6H_5^+ + C_6H_6$
- [15] $C_4H_9C_6H_6^+ + tert C_4H_9C_6H_5 = (C_3H_9)_2C_6H_5^+ + C_6H_6$

 $k_{14} \approx k_{15} \approx 10^{-11}$ molecules⁻¹ cm³ s⁻¹ which is two orders of magnitude lower than the orbiting collision rates. Reactions [14] and [15] probably proceed via the intermediate shown in structure II (for toluene). While the positive charge in II is formally on the benzene ring, in actual fact a considerable fraction of the charge will be also on the butyl group. After all, in the dissociation [lr] all the charge ends up on the butyl group. Thus, one can visualize the butyl group involved in an electrophilic attack as in **II**. Reactions [14] and [15] via the complex II probably have no counterpart in solution where solvent assistance of the dissociation [lr] favors very much the route [lr] followed by alkylations [12] and [13]. Also, solvation of the $C_4H_9C_6H_6^+$ ion probably reduces the electrophilicity of the C_4H_9 group and thus its tendency to form an activated complex like II. Reactions [14], [15], and the intermediate II are somewhat analogous to the alkylation reactions of benzenes by alkyl chloronium ions observed in solution and recently also in the gas phase (16) (see structure III). The gas



phase chloronium ion reactions were found to proceed with rate constants much lower than the orbiting rates (16); i.e., the alkylations by butyl benzenium (II) and alkylchloronium (III) are both relatively slow reactions.

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