Competitive Concerted and Stepwise Addition of Free Arylium Ions to Propane in the Gas Phase

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Labelled tolylium ions from the decay of ring-multitritiated toluene have been allowed to react with propane in the gas phase, at pressures ranging from 20 to 744 Torr, yielding isomeric propyltoluenes as the major addition products. The relative composition of the n- *versus* iso-propyltoluenes ($\sigma_p:\sigma_s$ 3.2—4.7) is found to depend appreciably upon the total pressure of the system and the presence of added bases (NH_3 or CH_3OH). Pressure and base effects on the isomeric distribution of both n- and iso-propyltoluenes are also investigated. The results are consistent with a reaction pattern involving preliminary formation of an electrostatic adduct, wherein fast hydride-ion transfer from a secondary C–H bond of C_3H_8 to the arylium ion takes place. The same mechanism does not seem operative when the first interaction occurs between the tolylium ions and a primary C–H bond of the substrate. The behaviour of isomeric tolylium ions towards propane is discussed and compared with related studies involving unsubstituted phenylium ions. A mechanistic model is proposed for both reactions, which accounts for the apparent discrepancy between the indiscriminate affinity of arylium ions for any kind of substrate and their 'abnormally' high site selectivities.

Owing to their thermodynamic instability and high reactivity, arylium ions are difficult to study in solution.[1] In contrast, singlet arylium ions are generated readily in the gas phase by ion-assisted dehalogenation reactions of halogenoarenes[2] or by spontaneous tritium decay in multitritiated aromatic precursors.[3] Irrespective of their formation, gaseous arylium ions appear to be extremely reactive electrophiles, attacking σ as well as π and non-bonding electrons with high efficiency.[2,4] The distinct affinity of arylium ions for n- and π-type basic sites of a given molecule and their tendency to insert efficiently into H–H and C–H bonds provides such unsaturated ionic species with both carbenium-like and a carbene-like character, deserving of further investigation.[2] Also noteworthy is the exceedingly high site selectivity of arylium ions, which markedly contrasts with their pronounced affinity for virtually every organic molecule.[4a–g] An outstanding example of such peculiar behaviour is provided by the site selectivity data for the attack of nuclear-decay-formed[3] phenylium ion (**1**) on propane in the gas phase [equation (1)].[4j] When generated by spontaneous β^- decay from 1,4-ditritiobenzene in the presence of 10—100 Torr propane, phenylium ion (**1**) displays a distinct preference for the σ_{C-H} bonds of the hydrocarbon (*ca.* 90%) over the σ_{C-C} bonds (*ca.* 10%). The site selectivity of the ion is even more significant for primary and secondary σ_{C-H} bonds in propane [equation (1)]. The relative proportions of n- and iso-propylbenzene recovered under the experimental conditions employed would suggest that phenylium ion (**1**) preferentially attacks the secondary σ_{C-H} bonds of the substrate rather than the primary ones. The measured primary:secondary σ_{C-H} bond reactivity ratio, denoted as $\sigma_p:\sigma_s$, is significantly lower than that expected on a statistical basis, *i.e.* $\sigma_p:\sigma_s$ 3.00, and appears to depend appreciably upon the total pressure of the decay system, *i.e.* $\sigma_p:\sigma_s$ 0.72 at 100 Torr and 0.25 at 10 Torr.

In order to explain such results, the reaction sequence (2) was proposed, involving non-selective attack of ion (**1**) at all propane σ_{C-H} bonds and subsequent unimolecular isomerization of the n-propyl group of the arenium intermediate (**2n**) to the isopropyl structure (**2i**) to an extent that increases at low pressures, namely at longer excited arenium ion lifetimes. However, independent radiolytic studies, carried out in the gas phase under conditions comparable with those of the decay experiments, failed to support the second isomerization step of sequence (2) since no evidence of side-chain isomerization was obtained for gaseous n-propylbenzene when submitted to protonation by very powerful Brönsted acids, such as H_3^+.[5]

An alternative explanation of the decay results implies attack of (**1**) at the σ_{C-H} bonds of propane to form the corresponding arenium intermediates (**2n** and **i**), which may subsequently undergo partial fragmentation, as shown in sequence (3). However, to account for the pressure effect on the experimental $\sigma_p:\sigma_s$ values, excited arenium intermediates (**2n**) are bound to collapse with a rate exceeding that of the isomeric intermediates (**2i**) ($k_p > k_s$), in spite of the well known higher propensity of isopropyl over n-propyl to undergo fragmentation.[6]

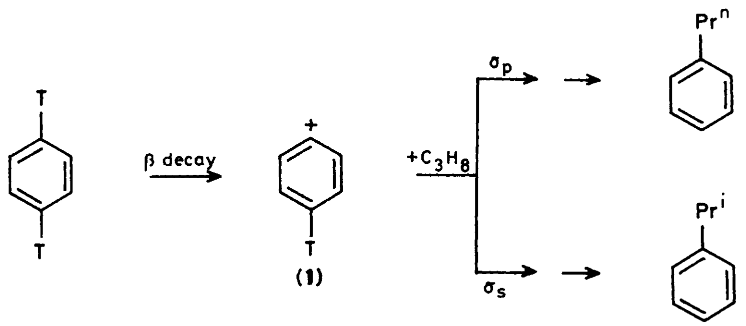
From the above considerations, it is evident that both mechanisms (2) and (3) are inadequate to describe the attack of phenylium ion on propane, which must therefore proceed *via* a more complex sequence.

We present here results for the same reaction using tolylium (**3**) instead of phenylium ions under similar experimental conditions [(equation (4)]. It is thereby hoped to provide a common reaction model for arylium ions with gaseous propane.

Experimental

Materials.—The preparation of toluene, containing at least two tritium atoms in the aromatic ring, was carried out according to an established procedure.[3c] The crude products, purified by preparative g.l.c., was diluted to a specific activity of 27.6 mCi mmol^{-1}. The intramolecular distribution of tritium, deduced from the decrease of the molar activity following substitution of the tritium atoms bound to different positions with inactive groups, was: α 0; *ortho* 33; *meta* 45; *para* 22%.

Growth of the Decay Products.—The procedure followed to prepare the gaseous samples were analogous to those described elsewhere.[4a] The gaseous systems were prepared by introducing



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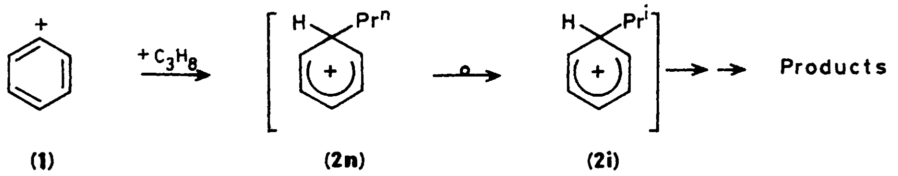

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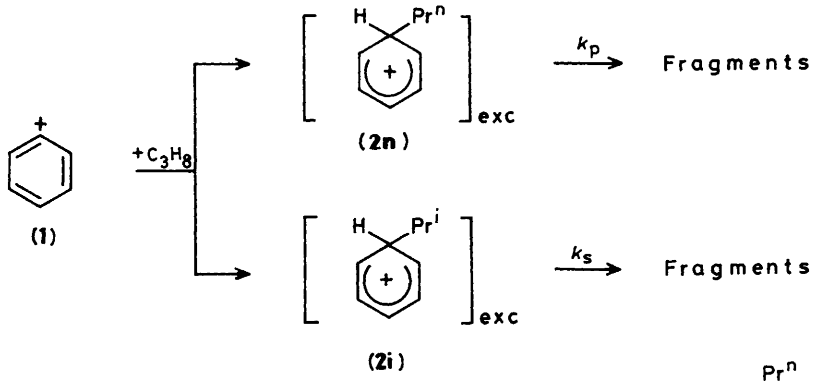

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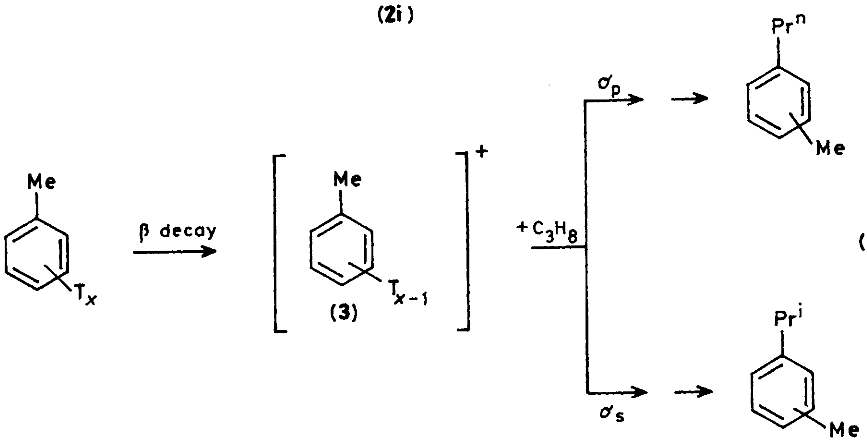


(4)

sealed glass capillaries containing *ca.* 1 mCi of ring-multitritiated toluene into Pyrex vessels (500 ml), equipped with a break-seal tip. The ampoules were then connected to a greaseless vacuum line and thoroughly degassed. Gaseous propane was then introduced, together with minor amounts of a nucleophilic additive (NH_3 or CH_3OH), when required, and of oxygen (4 torr), which was used as a scavenger of radical species conceivably formed by the passage of the energetic β-particle from the nuclear decay of multitritiated toluene through the gaseous mixture. The vessels were then sealed off and the tritiated toluene capillaries broken in order to allow complete mixing of the gaseous mixture. The vessels were stored in the dark at 25 °C for 10—12 months.

Radiochemical Analysis of Products.—The apparatus consisted of a C. Erba gas chromatograph, equipped with a hot-wire detector and connected to a internal flow proportional counter (80 ml; Berthold Laboratorium A.G.), heated at 160 °C. Helium was used as carrier gas, and the effluents were diluted with a precisely metered stream of methane, in order to obtain a 1 : 1 v/v mixture of the counting gas.

In most cases, the storage vessels were cooled at − 196 °C and opened, and their contents were diluted with known amounts of inactive carriers and subjected to radio-g.l.c. after thorough mixing. Control analyses, carried out by omitting the addition of carriers, gave the same results within experimental error.

The identity of the radioactive products was established by

Table. Tritiated product distribution from the gas-phase reaction of isomeric tolylium ions with propane

System composition[a] (mole %)	Pressure (Torr)	Relative yields of products[b] (Activity, %)						σ_p/σ_s[c]	Absolute yields[d] (Activity, %)
		n-Propyltoluenes			Isopropyltoluenes				
		ortho	*meta*	*para*	*ortho*	*meta*	*para*		
C_3H_8 (100)	20	10.7(13)	68.4(83)	3.0(4)	3.9(22)	12.5(70)	1.4(8)	4.6	18
C_3H_8(83) + CH_3OH(17)	24	11.8(14)	65.7(80)	4.9(6)	4.0(23)	12.4(71)	1.1(6)	4.7	14[e]
C_3H_8(83) + NH_3(17)	24	11.8(14)	65.4(80)	4.8(6)	4.4(25)	12.1(67)	1.4(8)	4.6	29
C_3H_8(100)	100	12.4(16)	60.1(78)	4.1(6)	9.4(41)	11.2(48)	2.6(11)	3.3	27
C_3H_8(91) + NH_3(9)	110	12.5(16)	59.1(77)	5.1(7)	9.1(39)	11.4(49)	2.8(12)	3.3	29
C_3H_8(83) + NH_3(17)	120	14.4(19)	55.0(72)	6.8(9)	9.5(40)	10.7(45)	3.5(15)	3.2	31
C_3H_8(3) + He(97)	740	13.4(16)	62.6(77)	5.5(7)	4.0(22)	12.0(65)	2.5(13)	4.4	23
C_3H_8(3) + He(96) + NH_3(1)	744	14.6(18)	59.0(74)	6.4(8)	5.5(27)	11.7(59)	2.8(14)	4.0	24

[a] The systems contained *ca.* 1 mCi of ring-multitritiated toluenes (ring T distribution: 33% *ortho*, 45% *meta*, 22% *para*; specific activity: 27.6 mCi mmol^{-1}) and O_2 (4 Torr), used as a radical scavenger. The decay samples were stored in the dark, at room temperature, for 10—12 months. [b] Expressed as a percentage of the total activity of the aromatic fraction of the tritiated products. The figures in parentheses refer to the relative distribution of isomers in each propylated derivative. Standard deviation of data, *ca.* 10%. [c] n-Propyltoluenes: isopropyltoluenes yield ratio, see text. [d] Expressed as the percentage ratio of the total activity of the aromatic products to the activity originally contained in the nuclear-decay-formed tritiated tolylium ions. Part of the residual activity is contained in low boiling fragmentation products. [e] Tritiated isomeric methylanisoles (44% *ortho*, 46% *meta*, 10% *para*) are formed in *ca.* 9% absolute yield as well.

comparing their retention volumes with those of authentic samples on two different columns: (i) Bentone 34–SP 1200 5%:5% on 100—120 Supelcoport, 2 m, at temperatures ranging from 75 to 100 °C; (ii) SP 1000 1% on 80–100 Carbopack C, 2 m, 200 °C.

Results

The Table summarizes the experimental evidence, the relative and absolute yields of the tritiated aromatic products and the composition of the decay systems. Significant yields (18—31%) of tritiated aromatic products are formed from the gas-phase attack of isomeric tolylium ion (**3**) on the components of the decay mixtures. Further discussion is restricted to the labelled propyltoluenes, whose formation can be exclusively related to the attack of tritiated tolylium ions (**3**) on propane and to the stability of the ensuing ionic adducts, neglecting other labelled products (*e.g.* low boiling compounds, tritiotoluene, *etc.*) which account for most of the residual activity not reported in the Table.

The relative composition of the n- *versus* iso-propyltoluenes, expressed as $\sigma_p:\sigma_s$ (3.2–4.7), is found significantly to exceed that arising from attack of unsubstituted phenylium ion (**1**) on propane ($\sigma_p:\sigma_s$ 0.25—0.72) under comparable conditions [equation (1)].[4j] As the C_3H_8 pressure is increased, the $\sigma_p:\sigma_s$ ratio is found to decrease toward the value 3.0, expected on statistical grounds.

The *meta* isomers are the most abundant among the isomers of both n- and iso-propyltoluenes, produced by attack of (**3**) on propane (Table). Their relative yields are found to increase further at low pressure and in the absence of bases. However, the relative abundance of *m*-n-propyltoluene (72—83%) unexpectedly exceeds that of the corresponding isomer of iso-propyltoluene (45—71%) under all conditions, in spite of the fact that both classes of compounds derive from the same set of tolylium ion precursors.

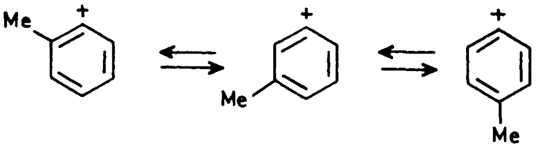
Discussion

The Reagent.—As extensively discussed previously,[3d] spontaneous β decay in ring-multitritiated toluenes leads to the formation of stable tolylium daughter ions (**3**), in their electronic ground-state singlet configuration with no recoil energy, for over 80% of the nuclear transitions. The remaining fraction (*ca.* 20%) of the transitions leads to the formation of highly excited daughter species (>20 eV), responsible for the formation of labelled fragmentation products.

Because of its nuclear nature, the probability of decay of a tritium atom is independent of its position in a labelled molecule. On these grounds, it is presumed that the isomeric distribution of the nucleogenic tolylium ion reactant coincides with that of the tritium atoms in the ring-multitritiated toluene precursor, namely 33% *ortho*, 45% *meta*, and 22% *para*.

Nuclear decay in tritiated toluenes causes vibrational excitation in the daughter tolylium ion (**3**) due to relaxation from the regular hexagonal structure of the parent tritiated toluene precursor to the highly distorted one that, according to theoretical calculations, characterizes ground-state tolylium ions.[7]

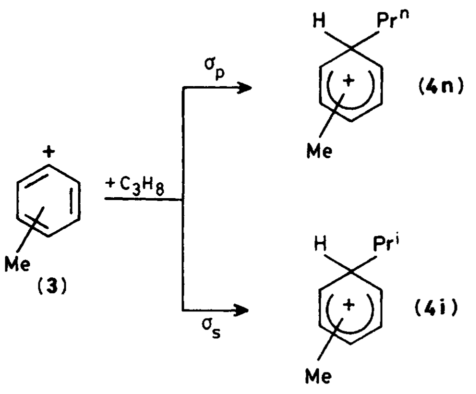
While specific data on the corresponding deformation energies are not available for isomeric tolylium ions, a reasonable estimate is represented by the value (32 kcal mol^{-1}) calculated for the correspondingly deformed phenylium ion, for which a similar structural relaxation is predicted.[8] In this view, 32 kcal mol^{-1} represents the excess of vibrational energy of the tolylium ions from the decay of tritiated toluene, following the relaxation of their regular hexagonal ring into the more stable deformed geometry.



(5)

(**3o**) (**3m**) (**3p**)

Owing to their excess of vibrational energy, isomeric tolylium ions (**3**) may undergo intramolecular 1,2-hydride shifts, according to sequence (5).[3,4a,b] The occurrence of the unimolecular isomerization (5) was demonstrated by trapping the isomeric nuclear-decay-formed species (**3**) after different delay times, using variable concentrations of a powerful nucleophile, such as CH_3OH.[3d] The dependence of the isomeric composition of tolylium ions upon their lifetime is shown in Figure 1. From the curves, it is possible to estimate the extent of intramolecular



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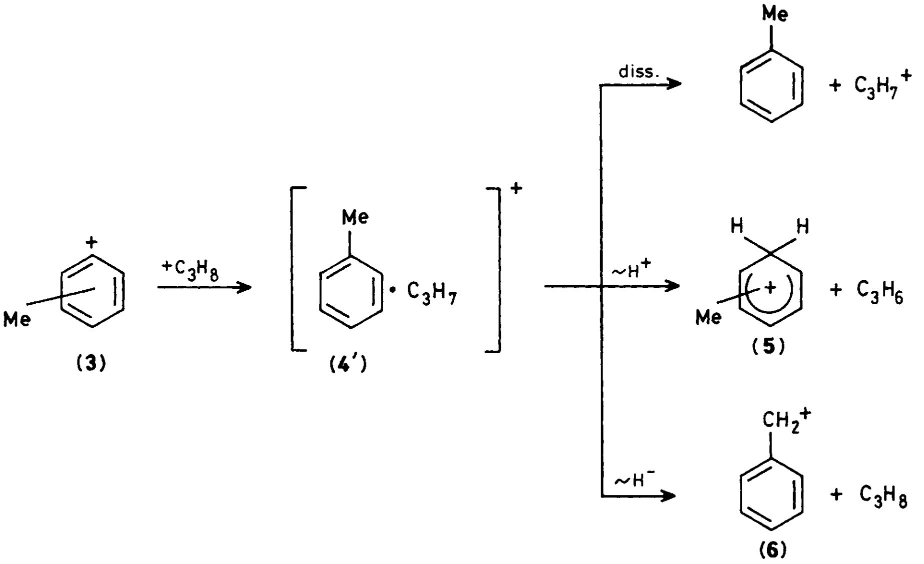

(7a)

(7b)

(7c)

isomerization of the initially formed isomeric tolylium ions (33% *ortho*; 45% *meta*; 22% *para*) in the average time interval between collisions in gaseous propane samples at 20 and 100 Torr. These are calculated according to the ADO model[9] to be 1.5×10^{-9} and 0.3×10^{-9} s, respectively. On these grounds, the isomeric composition of tolylium ions immediately before their attack on propane can be estimated to be 40% *ortho*, 45% *meta*, 15% *para* at 100 Torr, and 44% *ortho*, 45% *meta*, 11% *para* at 20 Torr propane.

Reaction in Gaseous Propane.—The difference between the calculated heats of formation of isomeric tolylium ions [ΔH°_f (*ortho*) 231.8; ΔH°_f (*meta*) 236.1; ΔH°_f (*para*) 236.6 kcal mol^{-1}][7] and the experimental values (ΔH°_f 253 ± 4 kcal mol^{-1}),[2e] obtained from H_2 chemical ionization mass spectra of the halogenotoluene precursors, raises some doubts that this latter method actually ends up with vibrationally ground-state tolylium ions. As mentioned in the previous section, the structure of the tolylium ions formed by the decay method may range from that of the toluene precursor to that of the corresponding vibrationally relaxed tolylium ion, and therefore the actual enthalpy of formation of isomeric tolylium ions (**3**) in the decay system may span from *ca.* 232—237 to *ca.* 260—270 kcal mol^{-1}.

As shown in Figure 2, several exothermic reaction channels are available to the tritiated tolylium ions in their attack on propane. Direct insertion (6) into a C–H bond of the hydrocarbon to give the corresponding *ipso*-protonated propyltoluenium intermediates (**4n** and **i**) is estimated to exceed 45 kcal mol^{-1} exothermicity.* Unless collisionally quenched, intermediates (**4n** and **i**), excited by the exothermicity of their formation process, may fragment to give toluene and $C_3H_7^+$ or, alternatively, protonated toluene and propene (C_3H_6).

The same fragmentation products, as well as others,† may conceivably arise from direct consecutive hydrogen transfers between (**3**) and propane, without necessarily involving the intermediacy of the excited σ-complex (**4n** and **i**) [equation (7)]. Irrespective of the actual fragmentation mechanism, Figure 2 shows that the fragmentation sequence (7a), if involving a ground-state species (**3**), is 2—7 kcal mol^{-1} exothermic, for isopropyl, and 10—15 kcal mol^{-1} endothermic, for n-propyl cation. The fragmentation sequence (7b) is instead exothermic for at least 11 kcal mol^{-1}.[11,12]

The fragmentation channels (7), except perhaps sequence (7c),[11] are all 'blind' reaction pathways, *i.e.* they cannot lead to

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* The lower limit of *ca.* 45 kcal mol^{-1} for the exothermicity of reaction (6) has been computed using the least favourable addition of *o*-tolylium ion (**3**) in its vibrational ground state (ΔH°_f 231.8 kcal mol^{-1}) to a primary C–H bond of propane. The heat of formation of the ensuing arenium intermediate (**4n**) has been estimated, taking the proton affinity of the position of *o*-n-propyltoluene bearing the n-propyl group as equal to that of the *ipso*-protonated *o*-xylene, *i.e.* *ca.* 190 kcal mol^{-1}.[10]

† Occurrence of the exothermic intermolecular isomerization channel (7c) (ΔH° −21 to −16 kcal mol^{-1}) is excluded, since no measurable amounts of tritiated benzyl methyl ether were recovered in the decay systems containing methanol.[11a] Other conceivable fragmentation paths, such as election transfer between tolylium ions and propane, are highly endothermic (ΔH° + 50 kcal mol^{-1}).[11b]

identifiable labelled products, other than the tritiated toluene precursor. Their occurrence may account for the activity loss observed in all decay systems. Irrespective of the nature of the intermediate adducts involved, either σ-bonded [equation (6)] or electrostatic [equation (7)] complexes, the extent of the fragmentation processes is expected to decrease at higher system pressure, and in the presence of bases, *i.e.* by increasing rapid quenching of the excited complexes involved. This expectation is verified by the experimental results (Table). Parallel to a generalized increase of the absolute yields of propyltoluenes at high pressures and in the presence of bases, a decrease of the relevant $\sigma_p:\sigma_s$ ratios to reach the statistical value of 3.0 is observed. This effect can be justified by the higher energy requirements involved in the fragmentation of the adducts (**4**) or (**4′**) with the n-propyl moiety with respect to these with the isopropyl structure. This makes the n-propylated adducts much less susceptible than the isopropylated ones to fragmentation, at equal internal excitation levels.

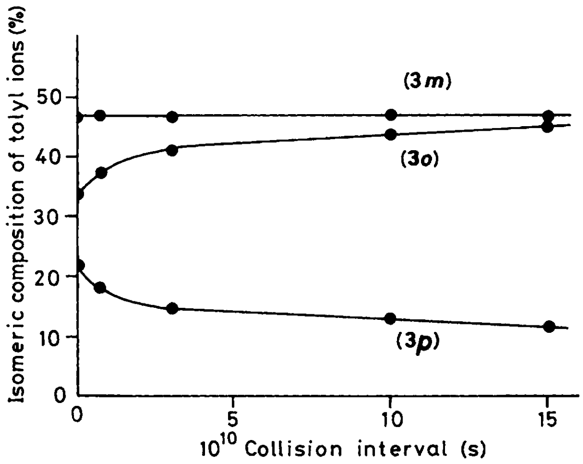


Figure 1. Dependence of the isomeric composition of methyl tolyl ether on the interval between collisions in gaseous methanol. The latter has been calculated according to the ADO model (ref. 9) for the different methanol pressure investigated

Direct information on the nature of the intermediate complexes, either the σ-intermediates (**4**) or the electrostatic adducts (**4′**), is available from analysis of the isomeric distribution of both n- and iso-propyltoluenes as a function of the composition of the decay systems (Table). Under all experimental conditions, the isomeric distribution of n- and iso-propyltoluenes diverges appreciably from that of their tolylium ion precursors at the corresponding pressures, in particular 40% *ortho*, 45% *meta*, 15% *para* at 100 Torr of propane, and 44% *ortho*, 45% *meta*, 11% *para* at 20 Torr of propane. In general, the relative abundance of the *m*-propyl toluenes exceeds that of the *m*-tolylium ion precursor (45%) by a factor which increases at low pressure and in the absence of bases, *i.e.* with increasing the excitation level and the lifetime of their parent ionic complexes. Of course, the reverse is true for *o*- and *p*-propyltoluenes, whose relative

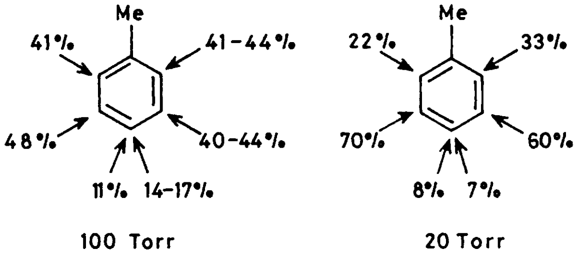


Figure 3. Isomeric distribution of isopropyltoluenes from attack of tolylium ion (**3**) on propane (left side) and attack of isopropyl ion on toluene (right side) in gaseous propane at 20—100 Torr

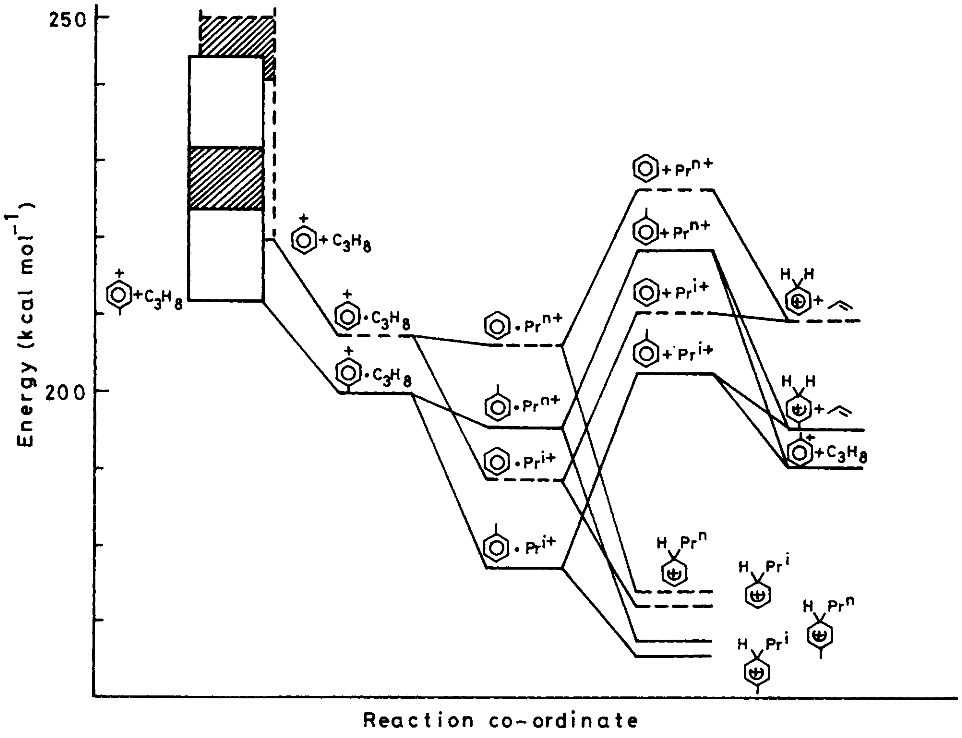
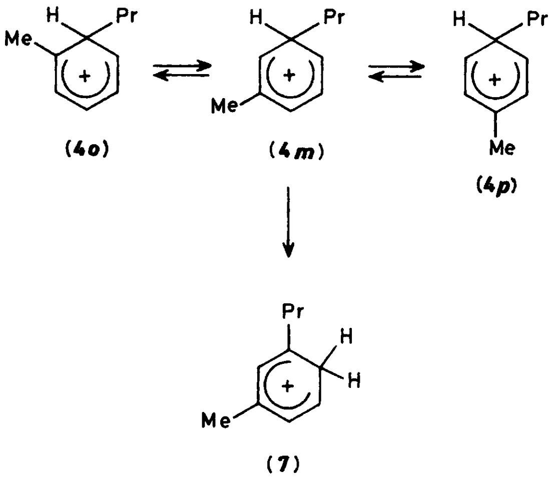


Figure 2. Energetics of several relevant ion–molecule reactions involved in arylium-ion attack on propane. Thermochemical data taken from S. G. Lias, J. F. Liebman, and R. D. Levin, *J. Phys. Chem. Ref. Data*, 1984, **13**, 695. Energy levels of the electrostatic adducts calculated following the procedure described in refs. 16 and 17



(8)

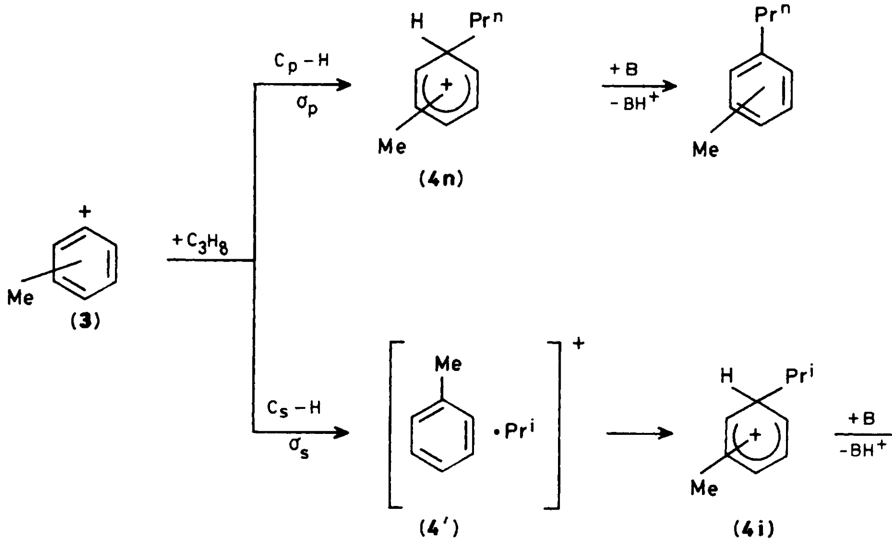
abundances are in general lower than those of the corresponding tolylium ion precursor. These findings are consistent with the eventual formation of σ-bonded *ipso*-propylated toluenium isomers (**4**) from their corresponding tolylium parent (**3**). Isomers (**4**) subsequently undergo partial equilibration in favour of the thermodynamically most stable isomer (**7**) [equation (8)].[13]

Closer inspection of the Table, however, reveals that, under the same experimental conditions, the relative abundance of the *meta* isomer of n-propyltoluene (72—83%) invariably exceeds that of the corresponding isomer of isopropyltoluene (45—71%). This result would imply that the overall rate of the isomerization process (8), involving n-propyl-group shifts, is substantially higher than that involving iso-propyl-group transfer, in spite of the more pronounced migratory aptitude of the isopropyl moiety with respect to n-propyl in arenium ions.[13d] This apparent discrepancy can be readily settled if a comparison is made between the isomeric distribution of the isopropyltoluenes of the Table and that arising from gas-phase attack of radiolytically formed isopropyl cations on toluene, under the same experimental conditions (Figure 3).[13,14]

The agreement between the isomeric distributions in Figure 3 appears very good, if allowance is made for the different reaction enthalpies involved in the two sets of experiments [$\Delta\Delta H° = \Delta H°(\text{decay}) - \Delta H°(\text{radiolysis})$ -7 kcal mol^{-1}] (Figure 2), which favour more extensive isomerization and, therefore, *meta* formation in the decay runs. This suggests that both reactions proceed by a common intermediate, *i.e.* (**4′**). Occurrence of an electrostatic intermediate, similar to (**4′**), in the formation of isomeric n-propyltoluenes from attack of (**3**) on propane can be safely excluded on the grounds that, contrary to the experimental evidence (Table), it would give rise to an isomeric distribution of n-propyltoluenes close to that of isopropyltoluenes.*

In this connection, it might be argued that an electrostatic complex (**4′**) between toluene and n-propyl ion is initially formed in the attack of (**3**) on propane, wherein the n-propyl moiety subsequently isomerizes to isopropyl before collapsing to a σ-bonded intermediate (**4**). However, the extent of such internal isomerization is expected to increase and, therefore, the experimental $\sigma_p:\sigma_s$ ratio to decrease at low pressure and in the absence of bases, in contrast to the experimental evidence (Table).†

On these grounds, it is proposed that indiscriminate tolylium-ion attack on propane induces a complex reaction pattern (9), involving the direct formation of a classical σ-bonded arenium ion (**4n**) [equation (9a)] or, alternatively, the preliminary formation of electrostatic adduct (**4′**), which eventually collapses to the corresponding σ-intermediate (**4i**) [equation (9b)].



(9a)

(9b)

The nature of the C–H bond of propane, either primary or secondary, undergoing the initial attack of tolylium ions determines which channel is predominant, either (9a or b), respectively. In fact, the entropically favoured preliminary formation of an electrostatic adduct (**4′**) between toluene and n-propyl cation from hydride transfer between the primary carbon of propane and (**3**) is energetically less favoured than that of the corresponding adduct (**4′**) with isopropyl from interaction between (**3**) and the secondary C–H bond of the hydrocarbon (Figure 2).

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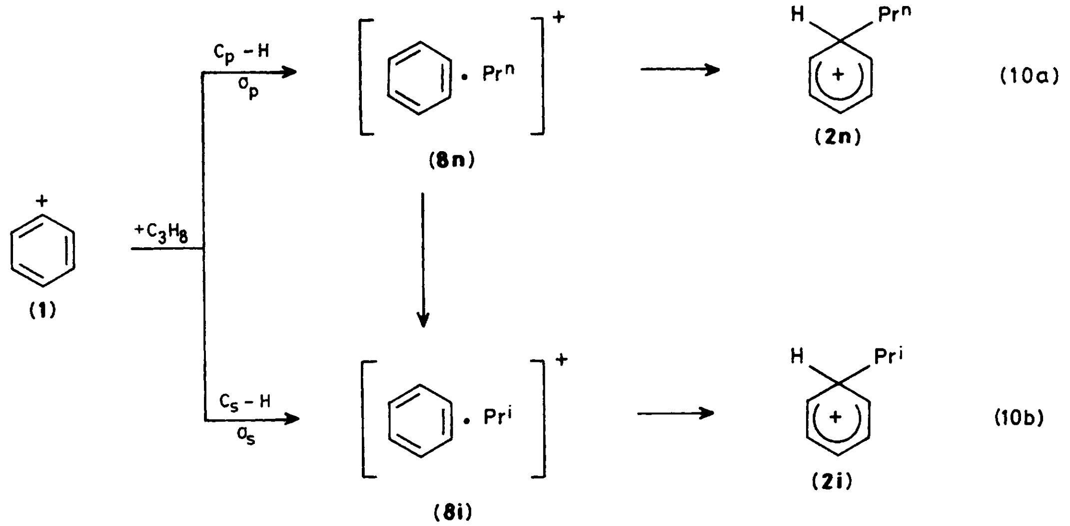
* As a matter of fact, the intermediacy of the electrostatic adduct (**4′**) in the formation of n-propyltoluenes from tolylium-ion attack on propane would result in an isomeric distribution of products where the relative proportion of the *meta* isomer is even *lower* than that for the *meta* isomer of iso-propyltoluene (see ref. 13*d*).

† It should also be noted that occurrence of internal isomerization of n- to iso-propyl in (**4′**) would imply a very peculiar affinity of tolylium ion for primary C–H bonds of propane over secondary ones, in order to account for the experimental $\sigma_p:\sigma_s$ ratios invariably exceeding the statistical value 3.0.



Comparison with Related Phenylation Results.—On the basis of the general reaction pattern (9), involving indiscriminate attack of tolylium ion (**3**) at the primary and secondary C–H bonds of propane, it is possible to provide a plausible explanation for the discrepancy between the high reactivity of phenylium ion (**1**) and its exceedingly high site selectivity between the primary and secondary C–H bonds of propane ($\sigma_p:\sigma_s$ 0.72 100 Torr; 0.25 10 Torr).[1j] From the $\sigma_p:\sigma_s$ ratios, indiscriminate attack of phenylium ion (**1**) on propane leads invariably to the formation of the electrostatic adducts (**8**), irrespective of the characteristics of the C–H involved [equation (10)]. Electrostatically bound n-propyl ion in (**8n**) is able to isomerize to the isopropyl structure (**8i**), before collapsing to a σ-bonded intermediate (**2**), as shown by the distinct decrease of the $\sigma_p:\sigma_s$ values with propane pressure. It is concluded that the apparent site discrimination in the attack of (**1**) on propane may arise from extensive propyl group isomerization within the electrostatic adducts originated from indiscriminate hydride-ion transfer between (**1**) and propane.

The only difference between the tolylium ion reaction pattern (9) and the phenylium ion reaction network (10) resides in the occurrence of the electrostatic adduct (**8n**) in channel (10a), which is prevented in the corresponding pathway (9a) involving (**3**). No straightforward reasons for such a difference can be at present advanced, unless referred to energetic constraints. Considerable uncertainty is attached to the actual heat of formation of ground-state tolylium ion and to the vibrational excitation levels of nucleogenic arylium ions (Figure 2). The actual excess energy of the arylium ions may be relevant to the occurrence of electrostatic or σ-bonded adducts, as shown in Figure 2. For instance, if the most well established heats of formation are taken for nucleogenic phenylium (ΔH°_f 270 kcal mol^{-1})[15] and tolylium ions (ΔH°_f 253 $\pm$ 4 kcal mol^{-1})[2e] (dashed regions in Figure 2), the difference of behaviour of (**3**) and (**1**) towards propane can be easily accounted for by a different minimum number of quenching collisions to prevent formation and isomerization of an n-propyl moiety in the electrostatic adduct between (**3**) [or (**1**)] and C_3H_8.

Conclusions.—The present results remove the anomaly represented by the 'abnormal' site selectivity of arylium ions in their efficient gas-phase attack on simple hydrocarbons. From a detailed analysis of the pressure and base effects upon the isomeric distribution of the addition products, it is shown that first interaction between the arylium (phenylium or tolylium) ion and propane leads to the formation of an electrostatic complex, wherein a rapid entropically favoured hydride-ion transfer takes place, if thermochemically allowed. An arene–propyl ion adduct is formed, wherein extensive isomerization of the propyl moiety occurs, before collapsing to a σ-bonded intermediate. If, instead, the first hydride-ion transfer is prevented by unfavourable energy requirements, such as in the abstraction of a primary hydrogen of C_3H_8 by tolylium ions, insertion of the unsaturated ion at a given C–H bond takes place to yield directly the corresponding σ-bonded intermediate.

Interplay between such reaction pathways is significantly influenced by the nature of both the arylium ion and the alkane substrate and leads to a product distribution barely related to the actual site selectivity of the electrophile.

Exothermic as well as quasi-resonant group isomerization in ion–molecule collison complexes are by no means novel reaction pathways, in the gas phase.[16] Their common mechanism, however, normally proceeds *via* a preliminary proton transfer between the ionic electrophile and the neutral molecule. In the present case involving unsaturated ionic species, group isomerization of the propyl moiety within the collision complex is instead promoted by a preliminary hydride-ion transfer from the different C–H bonds of the neutral molecule (*i.e.* the primary and secondary bonds of propane) to the unsaturated ionic electrophile.

Extensive isomerization is found to occur in ion–molecule complexes involved in unimolecular fragmentations of gaseous cations as well. It may lead to profound structural reorganization of the cationic species before fragmentation.[17] This evidence as well as those presented in the present paper and in others[4j,16] spell a word of caution against stuctural analysis of ionic species formed in the source of a mass spectrometer by conventional electron impact or chemical ionization procedures, without a detailed mechanistic study of all the possible isomerization channels conceivably opened within the time interval between the formation of the ion and its structural assay.

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