Aromatic Substitutions by [$^3H_3$]Methyl Decay Ions. A Comparative Study of the Gas- and Liquid-phase Attack on Benzene and Toluene

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A nuclear technique based on the spontaneous decay of tritiated precursors that allows the generation of free carbonium ions of exactly the same nature in different environments, has been exploited in a comparative study of aromatic alkylation by CT_3^+ ions, both in the gas phase at various pressures and in the liquid phase. The differences between the reactivity pattern of the methyl cation in the two environments can be essentially reduced to the much greater efficiency of collisional stabilization in the condensed phase, allowing a larger fraction of the excited arenium ions, from the highly exoenergetic ($\Delta H^\circ < 335$ kJ mol^{-1}) attack of the CT_3^+ ions on benzene and toluene, to survive dissociation and/or isomerization. The mechanism of the major competitive processes promoted by CT_3^+ attack on arenes, *i.e.* methylation, tritiodemethylation, and methyldemethylation are discussed, and the substrate and positional selectivity of the CT_3^+ ions from the decay of CT_4 is compared with that of more conventional alkylating reagents.

CHARGED reagents obtained from the spontaneous β decay of tritiated precursors have been usefully applied since 1964 to the study of ionic reactions in a variety of organic systems.[1]

So far, the decay technique has been primarily exploited as a unique tool for introducing free, unsolvated cations of specified structure into any system of interest, to investigate their reactivity by the classical methods of physical organic chemistry, including in particular the isolation of the neutral end products, thus providing essential information on their chemical identity, isomeric composition, stereochemical configuration, *etc.*[2] Little attention has been paid in these studies to another unique, if less conspicuous feature of the decay technique, arising from the *nuclear* nature of the process responsible for the formation of the daughter ions, which is intrinsically independent of the specific environment where the decay of the tritiated parent occurs.

Therefore, *exactly the same* ionic reagent is obtained from the decay, irrespective of the physical state of the system investigated, the pressure or concentration of the substrate(s), the presence of a solvent, *etc.* Such unparalleled constancy of the nature of the reagent, over such a broad range of physical and chemical conditions, discloses the intriguing possibility of investigating the reactivity pattern of a given electrophile–substrate pair exclusively as a function of the variables which define the reaction environment.

The present paper describes the first comparative study of the reactivity of a decay ion, CT_3^+ from the decay of [$^3H_4$]methane, towards benzene and toluene, carried out in the gas phase at different pressures, and in the liquid phase.

The choice of the reaction was suggested in the first place by the potential value of this very simple aromatic substitution as a model for electrophilic alkylation in solution, where the unstable and extremely reactive

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[1] F. Cacace, Proceedings of the Conference on the Methods of Preparation and Storing Marked Molecules, Euratom, Bruxelles, 1964, p. 719.

[2] For a review, see F. Cacace, *Adv. Phys. Org. Chem.*, 1970, **8**, 79.

methyl cation, in contrast with other more stable carbonium ions, cannot be conveniently obtained in the free state. Furthermore, benzene and toluene are among the very few substrates whose reactivity towards another free cation, the HeT^+ ion from the decay of molecular tritium, had been investigated *in the liquid state*.[3]

Finally, the interaction of CT_3^+ decay ions with arenes has been studied by Nefedov and his co-workers in the gas phase at a single pressure.[4]

While their experimental conditions, in particular the high level of specific activity of the gaseous systems investigated, are far from ideal from a mechanistic standpoint since radiolytic processes cannot be excluded as a parasitic source of the tritiated products, the results of this early radiochemical study were regarded as a useful basis of comparison in an otherwise entirely unexplored area.

EXPERIMENTAL

Materials.—The preparation, purification, and isotopic analysis of the CT_4 sample used as a source of the decay ions has been described elsewhere.[5,6] The activity distribution, measured by radio g.l.c., corresponded to 60.4 ± 0.5% CT_4, 29.4% CHT_3, 8.1% CH_2T_2, and 2.0% CH_3T. The aromatic substrates, the solvents, and the products used as carriers or as standards in the g.l.c. analyses, were research grade chemicals from Merck, and were used without further purification.

Growth of Decay Products.—The gaseous samples were prepared with conventional vacuum techniques, introducing CT_4 (0.6 mCi), diluted with CH_4 to a specific activity of 0.22 Ci mmol^{-1}, into evacuated and carefully outgassed Pyrex vessels, containing a measured amount of the aromatic substrate(s), together with O_2, used as a radical scavenger. The vessels, closed with a mercury plug and sealed off, were stored in a thermostatic oven at 90 °C for 8—10 months. The liquid samples were prepared by dissolving tritiated methane into the carefully outgassed liquid substrate(s), at a typical specific activity of 0.3 mCi ml^{-1}. The samples were stored in the dark, at 22 °C, for 8—10 months in Pyrex vessels entirely filled with the liquid and equipped with a capillary arm closed by a mercury plug.

Analysis of Products.—Two distinct procedures were followed for the analysis of tritiated products from the gaseous systems. Direct injection into the gas chromatograph of measured portions of the homogeneous gas samples was used essentially for estimating the absolute yields. In most cases, the sample was frozen to −196 °C, n-pentane was added, and the vessel content was thoroughly equilibrated by repeated freeze–thaw cycles. After removal of the undecayed CT_4, by outgassing and washing with excess of CH_4, measured portions of the n-pentane solution were subjected to g.l.c.

A similar procedure was adopted for the liquid systems, except that no solvents were required in this case.

A Hewlett–Packard model 7620 gas chromatograph was used, equipped with a hot-wire detector and a 12 m Bentone 38 (6% w/w)–DC 220 silicone oil (20% w/w) on Chromosorb W column, operated at 140 °C. The activity of the effluents was monitored with a 10 ml internal-flow proportional counter, heated at 150 °C. The tritiated products were identified from their retention volumes, compared with those of authentic samples under the same chromatographic conditions.

Degradation of Tritiated Toluene.—The tritium content in the methyl group of toluene was determined from the decrease of the molar activity caused by oxidation of C_7H_8 to benzoic acid. This procedure required rigorous purification of the arene, achieved, after addition of pure toluene as a carrier, by preparative g.l.c., using a 2 cm i.d., 3 m long Igepal CO 880 column at 85 °C, repeating the purification step until the molar activity reached a constant value.

Purified toluene was converted into methyl benzoate by oxidation to sodium benzoate with alkaline permanganate at 130 °C in a sealed tube, followed by methylation with $(CH_3)_2SO_4$ in alkaline solution. Methyl benzoate was isolated and purified by preparative g.l.c., using a 4 m Igepal CO 880 column at 85 °C. The activity of both purified toluene and methyl benzoate were measured with a Tri-Carb scintillation spectrometer from Packard Instrument Co.

RESULTS

The relative yields of the tritiated products from the attack of the CT_3^+ decay ions on benzene and toluene, and the isomeric composition of the xylenes formed are given in Table 1 for the gaseous systems, and in Table 2 for the liquid ones.

The absolute yields, defined by the ratio of the activity of the products to the total activity of the CT_3^+ ions formed within the system can be calculated from the initial activity and the isotopic composition of tritiated methane, the decay rate of tritium, the abundance (82%) of the methyl ions among the decay fragments, and the absolute counting efficiency of the detector employed.

These admittedly crude calculations show that the identified products account for *ca.* 50 ± 15% of the activity contained in the decay ions, without significant differences among the various gaseous and liquid systems investigated.

Furthermore, it has been observed that the total activity of the crude liquid arenes, after removal of the undecayed CT_4 and of other uncondensable gases, matches almost exactly the combined activity of the products identified by g.l.c., excluding the presence of other significant labelled products (*e.g.* dimers, polyphenyls, *etc.*), in the liquid, and suggesting that the activity balance must, instead, be provided by some gaseous species, most likely HT or partially tritiated methanes which are removed from the liquid, together with CT_4, by the outgassing procedure.

Finally, oxidation to benzoic acid of different samples of tritiated toluene from the gas-phase attack of CT_3^+ to C_7H_8 showed consistently, if rather unexpectedly, that the tritium atoms were almost exclusively (*ca.* 97%) contained in the methyl group, with only a minor fraction in the five ring positions.

DISCUSSION

Decay versus *Radiolysis as a Source of Tritiated Products.*—The experimental conditions chosen for the present study, in particular the low level of specific activity, ensure that the formation of the labelled products must be traced to the reactions of the tritiated

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[3] F. Cacace and S. Caronna, *J.C.S. Perkin II*, 1972, 1604.

[4] V. D. Nefedov, E. N. Sinotova, G. P. Akulov, and M. V. Korsakov, *Zhur. Org. Khim.*, 1970, **6**, 1214.

[5] F. Cacace and M. Schüller, *J. Labelled Compounds*, 1975, **11**, 313.

[6] F. Cacace, G. Ciranni, and M. Schüller, *J. Amer. Chem. Soc.*, 1975, **97**, 4747.

decay ions, without any appreciable contribution from the radiolytic processes promoted by the β particles of tritium. In fact, even in the most critical cases, *i.e.* in gaseous arenes at low pressure, and under the unrealistically unfavourable assumptions that (i) CT_4 undergoes radiolysis with the enormous $G_{(-M)}$ value of 100 and, (ii) the activity of the radiolysed CT_4 molecules is quantitatively incorporated into aromatic end-products, the extremely low molar fraction of CT_4 makes radiolysis entirely negligible, as a source of tritiated products, in comparison with the reactions of the decay ions; the relative efficiency of the two labeling channels is calculated as below 1 : 10^3.

TABLE 1

Tritiated products from the attack of CT_3^+ decay ions on gaseous arenes

System composition [a] (Torr)			Relative yields of products [b] (%)				Composition of xylenes (%)			Apparent [c] k_T/k_B
C_6H_6	C_7H_8	O_2	Benzene	Toluene	Ethylbenzene	Xylenes	*ortho*	*meta*	*para*	
	36	1.2		55.7		44.3	19.5	68.5	12.0	
	350	2.4	2.2	39.6	0.7	57.5	26.1	56.4	17.5	
36	36	2.4	19.1	53.7	0.2	26.9	22.0	64.0	14.0	0.80
120	12	2.4	33.2	61.5	0.2	5.1	21.9	63.8	14.3	0.89
3.6	36	2.4	4.8	42.9	0.4	51.9	21.8	64.4	13.8	0.80

[a] All systems contained *ca.* 0.2 Torr CH_4, and a tracer concentration of CT_4. [b] Ratio of the activity of each product to the combined activity of all products identified. For the absolute yields, see the text. Each value is the average of several determinations, with a standard deviation of *ca.* 5%. [c] Apparent values, not corrected (see text).

TABLE 2

Tritiated products from the attack of CT_3^+ decay ions on liquid arenes

System composition (mol %)		Relative yields of products [a] (%)					Xylene composition (%)			k_T/k_B [c]
C_6H_6	C_7H_8	Benzene	Toluene	Ethylbenzene	Unknown [b]	Xylenes	*ortho*	*meta*	*para*	
	100		13.9	4.2	2.7	79.3	40.4	27.1	32.5	
	100		13.8	4.5	2.7	79.0	39.9	26.9	33.2	
50	50	8.0	36.0	1.5	1.5	53.0	39.1	27.0	33.9	2.19
10	90	2.0	18.4	2.8	2.1	74.7	39.9	26.8	33.3	2.35
90	10	14.1	69.6	0.3	0.6	15.9	38.4	27.0	34.6	2.39

[a] Reproducibility of the data is illustrated by comparison of the first two lines. [b] The elution volume of this product is close, if slightly lower, than that of ethylbenzene. [c] Apparent values, uncorrected (see text).

This view is supported by the observation that the combined activity of the tritiated products accounts for a reasonable 50% of the decay ion activity, both in the gaseous and in the liquid systems, despite the substantially different (30 : 1) level of specific activity that would undoubtedly cause a measurable change of the yields of tritiated products if radiolytic processes appreciably contributed to their formation.

Incidentally, the absence of radiolytic processes as a parasitic source of tritiated products can help explain the considerable discrepancies between the present results and those obtained by Nefedov and his co-workers for gaseous arenes at a single pressure,[4] at specific activity levels exceeding ours by a factor of at least 10^2.

The Reagent.—The decay-induced fragmentation pattern of CH_3T has been studied at low pressure with a specially built mass spectrometer by Snell and Pleasonton,[7] who reported the following abundances for the major decay ions: CH_3^+ 82.0%, CH_2^+ 4.9%, CH^+ 4.0%, C^+ 4.9%, H^+ 2.4%. These results are consistent with the conclusions of theoretical studies on the molecular excitation caused by the β decay of a constituent tritium atom,[2,8,9] showing that most of the primary daughter ions, $(CH_3{}^3He)^+$, are formed in their electronic ground state and dissociate immediately into ^3He and a methyl cation, while a 20% fraction receives large excitation energies that cause further extensive fragmentation. Given the peculiar distribution of excitation energy, either very large or negligible, the fragmentation pattern measured at 10^{-5} Torr can be reasonably assumed to describe the decay of tritiated methane in gases at much higher pressures, or even in liquid systems, since collisional deactivation can hardly affect the very fast decomposition of those daughter ions that are formed in very highly (up to 60 eV) excited states. For the same reason, isotopic effects can be reasonably disregarded in the dissociation of the decay ions, and the fragmentation pattern established for CH_3T can be reasonably extended to CT_4. From these assumptions, the activity distribution of the decay ions can be calculated as follows: CT_3^+ 82%, other reactive species, *i.e.* CT_2^+, CT_2, CT^+, T^+, T, HeT^+, $\leqslant$12%, molecular tritium 6%. These figures, and the experimental yields, show that CT_3^+ must represent the major source of the tritiated products identified, with only minor contributions from other reactive decay fragments.

While the mass spectrometric and the theoretical studies quoted above indicate that CT_3^+ is formed in its electronic ground state, they provide no evidence con-

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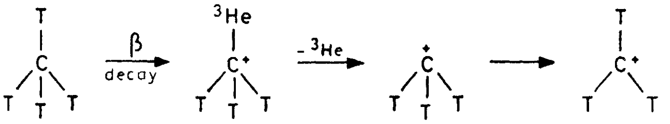
[7] A. H. Snell and F. Pleasonton, *J. Phys. Chem.*, 1958, **62**, 1377.

[8] M. Cantwell, *Phys. Rev.*, 1956, **101**, 1747.

[9] S. Ikuta, K. Okuno, K. Yoshihara, and T. Shiokawa, *Radiochem. Radioanalyt. Letters*, 1975, **23**, 213.

cerning the level of vibrational excitation associated with the relaxation from the tetrahedral structure typical of the CT_4 parent to the most stable trigonal geometry of the cation following the sudden nuclear event. In particular, no information is available concerning the fraction of energy carried away by the receding ^3He atom, *i.e.* the extent to which the relaxation of the organic system can be regarded as an adiabatic process.



Nevertheless, an upper limit for the vibrational excitation of the decay CT_3^+ ion can be deduced from theoretical results on the deformation energy of the planar methyl cation.

Indeed, in the (extreme) hypothesis that CT_3^+ is formed in a perfectly tetrahedral structure *via* an adiabatic process, with no energy released to ^3He, the calculation of Burdon *et al.*,[10] supporting earlier data of Williams *et al.*,[11] set an upper limit of *ca.* 134 kJ mol^{-1} to the vibrational excitation energy of the decay ion.

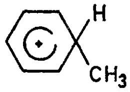
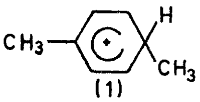
Energetics of CT_3^+ *Attack to Arenes.*—Several exoenergetic reaction channels are available to the CT_3^+ ion in its attack on the aromatic substrates, as illustrated in Table 3, thus providing approximate $\Delta H°$ values for several relevant processes. The enthalpy changes have been calculated from the $\Delta H_f°$ value of gaseous CH_3^+, which is appropriate for the gaseous systems and represents a rough approximation for the liquid-phase reactions, even considering the low degree of solvation of the electrophile.

Furthermore, no allowance is made for the excess of vibrational energy of the decay-formed CT_3^+ that could enhance (by up to 134 kJ mol^{-1}) the exothermicity of processes (1)—(7), and, more significantly, make protonation of arenes by CT_3^+ an energetically allowed process.

Owing to the exoenergetic character of processes (6) and (7), a preliminary question arises, concerning the charge state of the electrophile whose attack on the arenes actually leads to the alkylated products. It is conceivable, in fact, that CT_3^+ ions undergo charge exchange with the arenes, yielding CT_3 radicals, whose subsequent attack to the substrate(s) gives the observed alkylated products. Any significant contribution of this reaction pathway is however ruled out by the experimental observation that in the gaseous and in the liquid systems as well the yields of aromatic end products are independent of $[C_7H_8]$, which contrasts with the well documented ability of the methyl radicals to abstract a hydrogen atom from the side chain of toluene, giving quantitative yields of methane and benzyl radicals. This reaction, much exploited in the ' toluene carrier ' method to trap methyl radicals,[15] would in fact give higher yields of CT_3H, and correspondingly lower yields of alkylated aromatic products when the molar fraction of C_7H_8 is increased in the system. The experimental evidence fails entirely to support such a trend, and provides compelling, if indirect, evidence for the role of the CT_3^+ ion as an alkylating reagent.

TABLE 3

Energetics of several relevant reactions of CT_3^+ with arenes

Process					$\Delta H°$/kJ mol^{-1}
CH_3^+ +	C_6H_6	$\longrightarrow$		(1)	−347 [a,12]
CH_3^+ +	$C_6H_5{-}CH_3$	$\longrightarrow$	 (1)	(2)	−372 [12]
CH_3^+ +	C_6H_6	$\longrightarrow$	$CH_4 + C_6H_5^+$	(3)	−126 [12a-c]
CH_3^+ +	$C_6H_5{-}CH_3$	$\longrightarrow$	$CH_4 + C_6H_5{-}CH_2^+$	(4)	−284 [12a-c]
CH_3^+ +	C_6H_6	$\longrightarrow$	$H_2 + C_6H_5{-}CH_2^+$	(5)	−243 [12a-c]
CH_3^+ +	C_6H_6	$\longrightarrow$	$CH_3 + C_6H_6^+$	(6)	−59 [12,13]
CH_3^+ +	C_7H_8	$\longrightarrow$	$CH_3 + C_7H_8^+$	(7)	−100 [12,13]
CH_3^+ +	C_6H_6	$\longrightarrow$	$CH_2 + C_6H_7^+$	(8)	*ca.* +67 [12d,14]

[a] See text.

Alkylation in the Liquid Phase.—In the discussion of

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[10] J. Burdon, D. W. Davies, and G. del Conde, *J.C.S. Perkin II*, 1976, 1193.

[11] J. E. Williams, jun., V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1971, **93**, 6867.

[12] Calculated from the $\Delta H_f°$ value for CH_3^+, 1 079 kJ mol^{-1}, given by (*a*) F. P. Lossing, ' Mass Spectrometry.' ed. C. A. McDowell, McGraw-Hill, New York, 1963; (*b*) M. Szwarc, *Chem. Rev.*, 1950, **47**, 75, taking into account the $\Delta H_f°$ value of gaseous toluene from (*c*) D. R. Stull, E. F. Westrum, jun., and G. C. Sinke, ' The Chemical Thermodynamics of Organic Compounds,' Wiley New York, 1969, and taking the PA of the *ipso* positions of toluene and *p*-xylene equal to that of benzene, given by (*d*) R. Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, 1976, **98**, 1320.

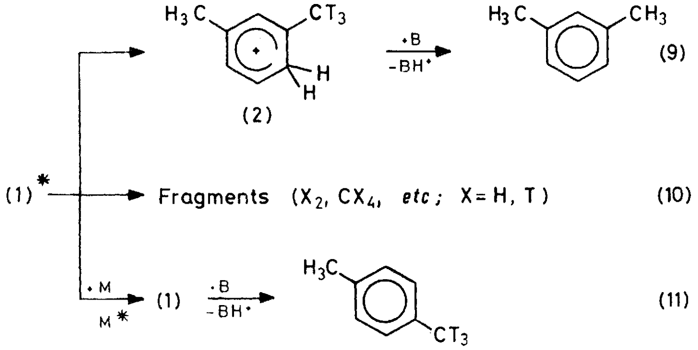
[13] From the ionization potential of benzene and toluene, *cf.* K. Watanabe, *J. Chem. Phys.*, 1957, **26**, 542.

[14] From the $H_f°$ of CH_2, 384 ± 4 kJ mol^{-1}; W. A. Chupka and C. Lifshitz, *J. Chem. Phys.*, 1969, **48**, 1109.

[15] J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465, *cf.* also ref. 12*b*.

CT_3^+ attack on arenes it is convenient to consider first the liquid-phase reaction, whose features appear to fit into the familiar picture of conventional solution-chemistry alkylation, displaying, in particular, considerable similarity with the substitution by highly reactive and poorly solvated electrophiles.

The evidence from the present study is in fact consistent with a straightforward reaction sequence, initiated by the highly exothermic attack of the alkyl cation to the substrate, yielding excited arenium ions, *e.g.* reaction (2), with CT_3^+ for CH_3^+, whose fragmentation and/or isomerization undergo effective competition by the fast collisional deactivation typical of the liquid environment.



Deprotonation of the stabilized arenium ions (1), or of their isomerization products, *e.g.* (2), by any base contained in the system, including the substrate(s) itself, provides a direct route to the alkylated products, whose yields amount to *ca.* 50%, the balance being provided by gaseous fragmentation products, most likely HT or variously tritiated methanes, formed either directly *via* processes such as (3)—(5), or from the dissociation (10) of excited arenium ions.

The efficiency of collisional stabilization in the liquid is apparent from the relatively low yields of products such as C_6H_5T from benzene and $C_6H_5CT_3$ from toluene, whose formation requires extensive isotopic scrambling and fragmentation, and which are considerably more abundant in the gas phase.

The occurrence of fragmentation and isomerization undoubtedly complicates the evaluation of the substrate and positional selectivity of the electrophile. However, restricting the comparison to the alkylation channel, the present results indicate that CT_3^+, while quite unselective, is nevertheless capable of discriminating between benzene and toluene ($k_T : k_B$ *ca.* 2). The positional selectivity deduced from the isomeric composition of the xylenes must be regarded as a lower limit, owing to the occurrence of isomerization of a fraction of the initially formed *ortho-* and *para*-substituted intermediates to the *meta*-substituted arenium ion (2), that is thermodynamically the most stable, as discussed in the next section. Despite the isomerization processes, a limited, yet well measurable preference of the CT_3^+ cation for *ortho–para* attack is apparent from the isomeric composition of the xylenes, characterized by a *para* : 1/2 *meta* ratio of *ca.* 2.5.

Alkylation in the Gas-phase.—In contrast with the efficiency of collisional deactivation in the liquid, the gas-phase picture is dominated by extensive isomerization and fragmentation processes affecting the excited arenium ions from CT_3^+ attack. Such a trend is well documented by the occurrence of tritiodeprotonation of benzene, and of methyldemethylation of toluene. Furthermore, the relative reactivity of the arenes referred to the alkylation channel is inverted with respect to the liquid phase, as shown by an apparent $k_T : k_B$ ratio below unity (0.8—0.9), and the composition of the xylenes is also shifted in favour of the *meta*-isomer, which becomes by far the most abundant.

All such differences can be reasonably traced to the increased rate of fragmentation and isomerization processes occurring in the gas, where efficiency of the collisional stabilization is necessarily reduced with respect to the liquid environment. This is clearly demonstrated by the effects of the pressure on the products pattern. Thus, a tenfold decrease of the C_7H_8 pressure (from 350 to 36 Torr) raises the $C_6H_5CT_3$ yield from 40 to 56%, and the extent of *meta*-alkylation from 56 to 68%. No direct evidence is available concerning the specific nature of the processes responsible for the formation of C_6H_5T from benzene, and of $C_6H_5CT_3$ from toluene. The most direct route to C_6H_5T, *i.e.* the T^+ transfer (8) from CT_3^+ to C_6H_6 does not appear significant, even though it cannot be ruled out on purely energetic grounds, since intervention of vibrationally excited CT_3^+ ions could overcome the endothermicity of the process (8). However, it must be considered that if T^+ transfer from CT_3^+ to benzene is postulated as a significant source of C_5H_5T, the analogous and energetically less unfavourable, T^+ transfer to toluene should occur with comparable, if not greater efficiency, contrary to the experimental finding that little or no ring-tritiated toluene is formed. A more reasonable explanation [16] involves isotopic scrambling of the hydrogen atoms of the methyl group with those of the ring, *e.g.* reaction (12) as inferred by Blint [17] from the i.c.r. study of CD_3^+ attack on benzene, followed by triton transfer to another molecule of substrate [reaction (13)]. Formation of $C_6H_5CT_3$ from toluene is likely to represent one of the consequences of the extensive isomerization undergone in the gas phase, especially at low pressure, by the excited primary arenium ions, such as (1). Intramolecular H^+, and possibly methyl group shifts, *e.g.* reaction (14), can yield, *inter alia*, reactive species capable of alkylating, as well as protonating toluene [reaction (15)]. Other conceivable routes to $C_6H_5CT_3$ may involve fast, reversible dealkylation of the *ipso*-substituted arenium ion from the direct CT_3^+ attack

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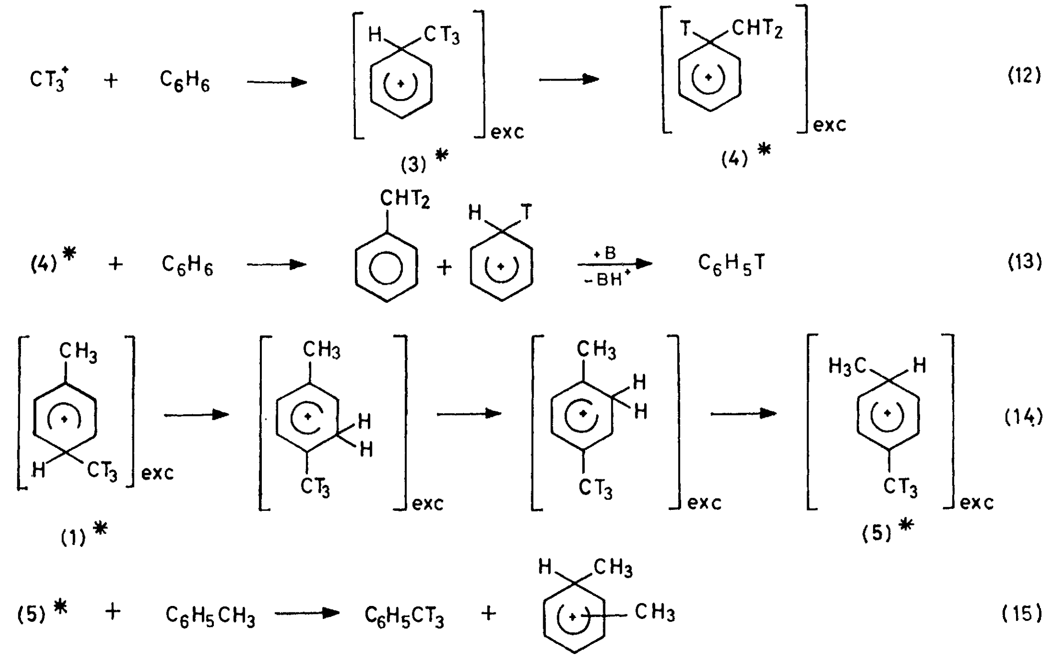
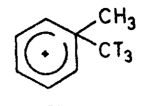
[16] A number of other mechanisms are conceivable, for instance ring expansion of (3) to a dihydrotropylium structure which would lead to H–T scrambling, *cf.* (*a*) D. H. Williams and G. Hvistendahl, *J. Amer. Chem. Soc.*, 1974, **96**, 6753, or the attack of $C_6H_5CT_2^+$ ions from (5) to C_6H_6, leading to formation of C_6H_5T by a process analogous to that reported by (*b*) J. Shen, R. C. Dunbar, and G. A. Olah, *ibid.*, p. 6228.

[17] R. J. Blint, Ph.D. Thesis, California Institute of Technology, 1972, *cf.* J. L. Beauchamp in ' Interactions between Ions and Molecules,' ed. P. Ausloos, Plenum Press, New York, 1975, p. 441.



to the ring carbon bearing the methyl group, or intramolecular CH_3^+ transfer from (6) to other substrate molecules. In any case, degradation of the labelled toluene formed indicates that very little tritium activity is present at the ring positions, suggesting that transfer and migration of the entire methyl group must be fast in comparison with the isotopic scrambling processes, such as (12), affecting the hydrogen atoms of the methyl group and those of the ring. This result is consistent with the fact that activation energy for intramolecular methyl shifts, measured in acidic solution[18,19] and calculated with the CNDO/2-FK method,[20] amounts to only a fraction of the excitation energy of the primary arenium ions (1)*, and is also consistent with the results of a study on the gas-phase attack of the strong Brønsted acid HeT^+ on the xylenes, giving tritiated toluene *via* tritiodemethylation in yields comparable with those of the isomerized xylenes.[21]



(6)

Gas-phase Positional Selectivity and Stability of Isomeric Dimethylbenzenium Ions.—The predominance of *meta*-substitution in the gaseous systems is to be traced to extensive isomerization of the primary arenium ions, as shown, *inter alia*, by its pressure dependence. There is no *a priori* reason why CT_3^+ attack on toluene should not lead, in the gas as well in the liquid, to kinetically predominant *ortho*/*para* substitution. On the other hand, it is known from experimental measurements in solution[18,19] and from theoretical calculations[20,22] that the *meta*-substituted species (2) is the most stable among isomeric dimethylbenzenium ions. Consequently, the population of primary arenium ions, excited by the exothermicity of (2) well above activation energy for intramolecular proton and methyl shifts, tends towards an equilibrium isomeric composition characterized by a predominance of (2), the extent of conversion depending on the time available for intramolecular isomerization before a deactivating collision takes place. This accounts for the prevalent *ortho*/*para* orientation in liquid-phase alkylation, where efficient collisional deactivation helps to preserve, at least in part, the initial, kinetically controlled composition of the primary arenium ions, and for the observed pressure dependence of the isomeric composition of xylenes. The present results provide experimental support to the theoretical calculations concerning the stability of isomeric, gaseous dimethylbenzenium ions, whose relative energy increases in the order (2) < (1) < (6), with a separation of *ca.* 84 kJ mol^{-1} between adjacent pairs of isomers according to Heidrich and his co-workers.[20,23]

Conclusions.—The nature of the charged reagent formed by β decay in the site formerly occupied by a CT_4 molecule in a very short time on the chemical reactivity scale * is essentially the same in the gaseous and in the

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* The time required by a 5.6 keV β particle to reach 100 Å from the decayed molecule is very short, $<10^{-15}$ s. As no C–He bond exists within the primary decay ion $[^3He-CH_3]^+$,[24] dissociation into a free methyl ion can be expected to occur in a time comparable with the period of a bond vibration, roughly 10^{-14} s.

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liquid phase. In both environments the CT_3^+ cation is absolutely free, lacking a counterion and having its positive charge neutralized by a far removed electron. Moreover, although one could argue that the only unsolvated carbonium ions are to be found in the dilute gas state, the CT_3^+ ion from the decay is as unsolvated as conceivable for a charged species in a condensed phase. In fact, owing to the very high collision frequency with the molecules of the liquid substrate, and to the proven ability of the methyl cation to react at a rate approaching collision frequency even with weak nucleophiles, its attack on benzene and toluene is likely to occur within a much shorter time than required for the formation of an organized solvation sphere that requires, *inter alia*, rotational relaxation of dipolar molecules in the field of the cation. The unparalleled constancy of the nature of the reagent over an extended range of physical conditions affords the unusual possibility of evaluating its reactivity pattern in different media exclusively as a function of the reaction environment. For the specific case investigated, in order to rationalize the observed differences between the liquid and the gaseous systems, no other factors are necessary, except for the greatly enhanced efficiency of collisional stabilization that allows a much larger fraction of the excited arenium ions from (2) to survive isomerization and/or fragmentation. To our knowledge, in the search to substantiate the long postulated[25] role of carbonium ions in Friedel–Crafts alkylation, the present study provides the first data concerning a reagent whose +1 net charge, and lack of a counterion, are positively established in the liquid phase. Consequently, a comparison of CT_3^+ reactivity with that of a few typical representatives of the vast collection of polarized molecules, polarized complexes, ion-pairs, 'incipient' or 'hot' carbonium ions (in the solution chemistry sense) employed as reagents in conventional aromatic alkylation is of interest, and is concisely illustrated in Table 4.

TABLE 4

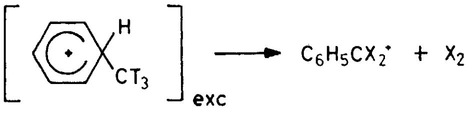
Substrate and positional selectivity of typical methylating reagents

Reagent		k_T/k_B	Isomeric composition of products (%)			Reference
			ortho	*meta*	*para*	
$CH_3Br + GaBr_3$	Arenes	5	63	11	25	26
$CH_3Br + Al_2Br_6$	Arenes	3.6	53	17	30	27
$CH_3I + Al_2Br_6$	Arenes	4.6	48	12	40	27
$CH_3NH_2 + NOPF_6$	Nitromethane	1.8—2.0	42	21	37	28
$CH_3NH_2 + NOPF_6$	Acetonitrile		41	21	38	28
$RNH_2 + HCl + RONO$ [a]	Arenes	1.8	40	27	33	29
N-Nitroso-*N*-alkylamine [a]	Arenes	1.8	40	26	34	29
CT_3^+		2.2—2.4	40	27	33	Present work

[a] R = Pr^i, heterogeneous reaction.

Significantly, the substrate and positional selectivities of the free CT_3^+ cation appear extremely close to those measured in the solution chemistry experiments where intervention of poorly solvated cationic reagents appears more likely, owing to the specific way of generating the reagent, *e.g.* diazotization in aprotic media, and/or to the greater stability of the carbonium ion involved, *e.g.* Pr^{i+}, included for comparison purposes in Table 4. On the other hand, the reactivity of CT_3^+ is appreciably different from that observed in methylation by conventional Friedel–Crafts reagents, which involves, as shown by Brown and his co-workers,[26,27] displacement by the arenes of the polarized complexes formed by the methyl halides with metallic salts.

Finally, it should be noted that the gas-phase methylation by CT_3^+ ions provides some interesting pieces of evidence concerning the preferred fragmentation pattern of those excited arenium ions that escape collisional stabilization in the pressure range investigated. Thus, in contrast with the unexpected efficiency of the tritiodemethylation and methyldemethylation channels, no evidence could be obtained for the occurrence of the expected dissociation into benzyl ions, *e.g.* reaction (16),



(16)

observed at much lower pressures.[17] The benzyl ions formed should in fact react with the aromatic substrate, yielding, *inter alia*, diphenylmethane derivatives;[30] these have not been isolated among the products. The unexpectedly low efficiency of (16) can possibly be traced to its high activation energy which adds to the considerable endothermicity of the process.[16a]

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