Reactions of the Helium Tritiide Ion with Liquid Arenes

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The reactivity of the HeT^+ ion from the β-decay of molecular tritium to benzene and toluene has been investigated in the liquid phase. It is suggested that the tritiodeprotonation occurs *via* a mechanism based upon the exothermic triton transfer from HeT^+ to the arene, leading to the formation of an excited arylium ion followed by its collisional stabilization and by a thermoneutral proton transfer to another molecule of substrate. The attack of the HeT^+ reagent is characterized by the complete lack of substrate selectivity, as expected for an extremely reactive free cation carrying a net positive charge of unity. On the other hand, despite its extreme electrophilic character, the reagent retains a remarkable positional selectivity. The implications of these findings are discussed and the behaviour of the HeT^+ ion is compared with that of poorly solvated 'ionic' reagents, obtained with conventional techniques, towards the same substrates in non-polar solvents.

In the study of aromatic substitutions the nature of the electrophile is hardly defined *a priori*, and must rather be deduced from the kinetic and mechanistic details of the process. Even in the few cases where the 'ionic' character of the reagent appears firmly established, its more or less pronounced interactions with the counter-ion, the catalyst, and other bases contained in the system considerably complicate the interpretation of the results. It has been shown that a nuclear transformation, *i.e.* the β-decay of suitable tritiated precursors, provides a unique tool for producing *in situ* truly free ionic reagents of well defined structure, whose electrophilic reactivity has been extensively studied in the gas phase.[1] In particular, we have investigated the reactivity of the HeT^+ ion from the β-decay of molecular tritium with a variety of *gaseous* aromatic substrates,[2-4] and now extend the study to liquid systems, in particular to liquid benzene and toluene.

EXPERIMENTAL

Materials.—Tritium was purchased from CEA (France) and its purity, as determined by radio gas-solid chromatography,[5] was found to correspond to a minimum T_2 content of 94%. Benzene and toluene samples from Fluka AG were analysed by g.l.c. Oxygen and the other chemicals were commercial Research Grade products used without further purification.

Procedure.—Tritium (*ca.* 0·8 mCi) was introduced into carefully evacuated and outgassed Pyrex vials (5 ml), equipped with a long capillary arm closed by a fragile tip. Each vial was sealed off from the vacuum line and its capillary arm was introduced into a cylindrical vessel, containing at the bottom a layer of purified mercury, and filled with the appropriate aromatic substrate, which had been previously outgassed and partially saturated with O_2.

The fragile tip of the capillary arm was then broken under the level of the organic liquid which was consequently forced into the evacuated vial. When only a small bubble

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[1] F. Cacace, *Adv. Phys. Org. Chem.*, 1970, **8**, 79, and references therein.

[2] F. Cacace and S. Caronna, *J. Amer. Chem. Soc.*, 1967, **89**, 6818.

[3] F. Cacace and G. Perez, *J. Chem. Soc.* (*B*), 1971, 2086.

[4] F. Cacace, R. Cipollini, and G. Ciranni, *J. Chem. Soc.* (*B*), 1971, 2089.

[5] H. A. Smith and E. H. Carter, 'Tritium in the Physical and Biological Sciences,' I.A.E.A., Vienna, 1962, vol. I, p. 121.

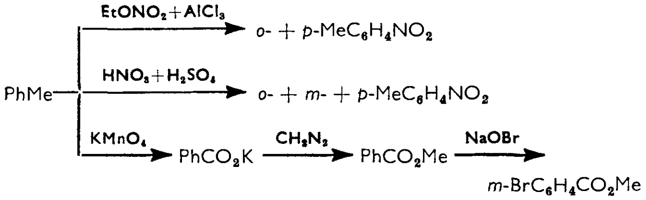
of gas was left at the top of the vial, the capillary arm was lowered further into the mercury.

After a few hours, the vial was entirely filled by the aromatic substrate, except for the lower portion of the capillary, where the mercury had risen, acting as a mobile seal. The vials were stored at room temperature for periods ranging from 122 to 401 days.

Analysis of the Products.—The tritiated products were analysed by radio-g.l.c., as described previously.[2,6] The following columns were used: 5 Å molecular sieves (4 m; 90°) for the analysis of CH_3T; silica gel (6 m; 100°) for tritiated alkanes; di-isodecyl phthalate (20% on Celite; 3 m; 140°) for the arenes.

The purified samples of C_6H_5T and C_7H_7T required to determine with sufficient precision their yields, and to provide the starting material for the ensuing degradation of labelled toluene, were obtained from the crude reaction mixtures by preparative g.l.c., using a di-isodecylphthalate column (4 m; 110°). The purification step was repeated until a constant value of the specific activity of the sample was achieved, as measured with a Nuclear Chicago Mark I liquid scintillation spectrometer.

Preparation of Substituted Derivatives of Tritiated Toluene.—The tritium content in the different positions of labelled toluene was determined by a procedure based on the replacement of H by inactive substituents, followed by the measurement of the corresponding decrease of the molar activity. The reactions employed are shown in the Scheme.



SCHEME

It should be pointed out that the two different nitration procedures gave the same results within experimental error. The nitration of toluene in concentrated sulphuric acid does not exhibit a measurable isotope effect,[7] and was carried out under conditions excluding appreciable H–T exchange.

The purification of the reaction products was achieved by preparative g.l.c. using the following columns: Apiezon L grease (20% on Celite; 2 m) at 200° for methyl benzoate and at 210° for the methyl *m*-bromobenzoate; Bentone 34–di-isodecylphthalate (10 and 8% respectively on Chromosorb W; 3 m; 136°) for the isomeric nitrotoluenes.

RESULTS

The analysis of the reaction mixture shows that C_6H_5T and C_7H_7T are the only labelled products formed in measurable yields from the attack of the HeT^+ ion on the corresponding inactive substrate. In fact, despite a careful search, no other labelled compound could be identified in the radio-g.l.c. analysis of the products carried out on different columns.* This is corroborated by the observation that the absolute yields of C_6H_5T and C_7H_7T formed from the tritiodeprotonation of liquid benzene and toluene are nearly quantitative (Table 1).

The relative yields of C_6H_5T and C_7H_7T from the competition experiments, given in the last column of Table 1, and measured over a relative concentration range of almost two orders of magnitude depend exclusively on the concentration of each substrate, irrespective of its nature, showing the absolute lack of selectivity of the HeT^+ reagent towards benzene and toluene.

The positional selectivity of the HeT^+ attack on liquid toluene is reflected by the intramolecular tritium distribution illustrated in Table 2, whose data represent the average values of four separate determinations, carried out according to the different substitution procedures outlined in the Scheme.

TABLE 1

Yields of the products from the attack of HeT^+ on liquid arenes and their mixtures

Substrate [a]	Products	Yield (%) [b]	Ratio of yields
Benzene [b]	C_6H_5T	98 ± 10	
Toluene	C_7H_7T	105 ± 10	
Benzene + toluene (mol ratio 1 : 1)	C_6H_5T C_7H_7T		$\frac{C_6H_5T}{C_7H_7T} = 1{\cdot}01 \pm 0{\cdot}01$
Benzene + toluene (mol ratio 1 : 9)	C_6H_5T C_7H_7T		$\frac{C_6H_5T}{C_7H_7T} = 0{\cdot}111 \pm 0{\cdot}005$
Benzene + toluene (mol ratio 9 : 1)	C_6H_5T C_7H_7T		$\frac{C_6H_5T}{C_7H_7T} = 9{\cdot}02 \pm 0{\cdot}01$

[a] In addition to a tracer concentration of T_2, O_2 was dissolved in the liquid aromatics at the concentration of *ca.* 0·04 g l^{-1}, as determined by g.l.c. [b] Fraction of the activity of the HeT^+ ions formed in the system during the storage period isolated in each product. Corrections made for the abundance of the HeT^+ ions from the decay of T_2 (94·5%) and for the isotopic purity of T_2.

TABLE 2

Positional selectivity of the HeT^+ attack

Molecular positions	Each *ortho*	Each *meta*	*para*	Each α
Tritium content (%) [a]	22·9	8·6	32·4	1·5

[a] The standard deviation of the values, which represent the average values of four different degradation procedures, is *ca.* 2%.

DISCUSSION

The Reagent.—The decay of one of the constituent atoms in a T_2 molecule leads to the formation of a daughter HeT^+ ion in nearly quantitative (>94%) yield [equation (1)]. The unique property of the ionic reagent

$$T_2 \xrightarrow[\beta\text{-decay}]{} HeT^+ + \beta^- \qquad (1)$$

formed *in situ* from the β-decay of molecular tritium dissolved in a liquid substrate is the lack of a negatively charged counterion associated with the decay ion. In fact, as the necessary charge balance is provided by a remote, negative β particle, the HeT^+ reagent can be regarded as a truly free molecular ion, carrying a net positive charge equal to unity. In addition, it is relevant to point out that a high fraction of the HeT^+ ions is formed from process (1) in the ground state, and their kinetic energy distribution is essentially thermal,

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* However, owing to the large excess of undecayed T_2, any HT formed would probably escape detection.

[6] F. Cacace, *Nucleonics*, 1961, **19** (5), 45.

[7] J. F. Eastham, J. L. Bloomer, and F. M. Hudson, *Tetrahedron*, 1962, **18**, 653.

as indicated by theoretical calculations and mass spectrometric studies.[1] Finally, the structure and the energetics of the reagent are unusually well defined, as a result of extensive calculations[8] and photo-ionization studies[9] concerning the related HeH^+ molecular ion. In particular, the heat of formation of the HeT^+ ion is *ca.* 320 kcal mol^{-1}.

Tritiodeprotonation.—The HeT^+ ion undergoes an exothermic triton transfer to the liquid aromatic substrate [equation (2)] followed by the collisional de-

$$RC_6H_5 + HeT^+ \longrightarrow [RC_6H_5T]^+_{exc.} + He \qquad (2)$$

activation of the excited arylium ion [equation (3)] and

$$[RC_6H_5T]^+_{exc.} + M \longrightarrow RC_6H_5T^+ + M^* \qquad (3)$$

by the transfer of a proton to any base contained in the system, possibly to another molecule of substrate according to the thermoneutral process (4) which leads to the formation of the tritiated arene.

$$RC_6H_5T^+ + RC_6H_5 \longrightarrow RC_6H_4T + RC_6H_6^+ \qquad (4)$$

A comparison of the data in Table 1 with the product distribution observed in the gas phase at 760 Torr indicates a considerable increase of the yield of C_7H_7T, from *ca.* 60% in the gas to 100% in the liquid, reflecting the higher efficiency of collisional stabilization in the condensed phase. The lack of fragmentation products (CH_3T, C_6H_5T) from the attack of HeT^+ on liquid toluene is a further indication that essentially no excited arylium ions decompose in liquid toluene, despite the large exothermicity of reaction (2), calculated as *ca.* -102 kcal mol^{-1} for R = H and -110 kcal mol^{-1} for R = Me.[10,11]

Selectivity of the HeT^+ *Reagent.*—The results of the competition experiments outlined in Table 1, and the intramolecular distribution of tritium within the labelled toluene given in Table 2, provide an interesting picture of the selectivity of HeT^+ attack on liquid arenes.

In fact, while no substrate selectivity of the HeT^+ has been observed in the liquid phase, as the reagent fails to discriminate between benzene and toluene, its positional selectivity, whose lower limit can be deduced from the intramolecular distribution of tritium in the toluene formed, is relatively high.

The contrast between the substrate and the positional selectivity of the reagent seems to rule out any mechanism in which the individual positions of the aromatic ring compete for the electrophile in the rate-determining step, and suggests the rate-determining formation of some kind of electrophile–substrate 'adduct' or 'encounter pair', kinetically if not structurally analogous to the π complexes long postulated by Olah,[12-15] followed by a step (formation of σ complexes) leading to the orientation of the substituent.

The substantially higher reactivity of the HeT^+ ion when compared to the most powerful conventional electrophiles used in the study of aromatic substitutions is illustrated by the fast and quantitative tritonation of gaseous methane at 760 Torr and 25 °C,[16] in contrast with the very limited extent of the $NO_2^+PF_6^-$ attack on the same substrate, giving very low (0·1%) yields of CH_3NO_2 in CH_2Cl_2–sulpholan solutions.[17]

In view of its intrinsic molecular properties, and taking into account the extreme reactivity displayed towards inert substrates, the HeT^+ ion represents, in our opinion, the best available approximation to the 'ultimate electrophilic species', the hypothetical reagent entirely insensitive to differences in the reactivity of the organic substrate.[18]

Indeed, the lack of substrate selectivity supports the hypothesis of an indiscriminate attack on benzene and toluene, occurring at the 'encounter rate'[18] of the reagent with the aromatic molecules in the liquid phase.

If the extreme electrophilic character of the reagent and the indiscriminate nature of its attack on the different substrates are taken into account, the observation of positional selectivity is of interest. The results of the present study demonstrate, for a simple reaction involving a cation whose free nature is established *a priori*, that the ability to discriminate among the individual ring positions is retained even by a most active electrophile, attacking the substrate at the 'encounter rate' and displaying no substrate selectivity.

None of the criticisms based on the incomplete mixing of the reagents, raised in connection with Olah's work,[19,20] apply to the competition experiments involving the HeT^+ ion, which is generated from extremely dilute solutions of molecular tritium in the liquid aromatic mixture. Moreover, the positional selectivity of the free, unsolvated HeT^+ cation, which has selectivity similar to the other strong electrophiles listed in Table 3, seems to represent a distinctive feature of the reagents having pronounced 'ionic' character.

Selectivity of HeT^+ *in the Gas Phase.*—The positional selectivity of HeT^+ is not significantly different when the reaction is carried out in the gas phase at 760 Torr[2] or in the liquid phase, in agreement with the intramolecular nature of the step leading to orientation of the substituent postulated by the reaction model outlined in the preced-

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TABLE 3

Isomers formed from the attack of ' ionic ' reagents on toluene

Reagent	Catalyst	Solvent	Yield (%) of isomers			Ref.
			ortho	*meta*	*para*	
CH_3F	SbF_5	SO_2FCl at −78°	54	18	28	21
C_2H_5F	SbF_5	SO_2FCl at −78°	39	19	41	21
C_2H_5F	BF_3	*a*	46·2	28·7	25·1	22
C_2H_5F	BF_3	CH_3NO_2	43·8	24·2	32·0	22
i-C_3H_7F	BF_3	n-C_6H_{14}	45·6	21·0	33·4	23
i-C_3H_7F	BF_3	cyclo-C_6H_{12}	45·1	21·5	33·4	23
i-C_3H_7F	BF_3	CH_3NO_2	43·2	22·3	34·5	23
n-$C_3H_7NH_2$ + HOAc + RONO		*a*	40	26	34	24
i-$C_3H_7NH_2$ + HCl + RONO		*a*	40	26	34	24
N-Nitroso-*N*-isopropylamide		*a*	40	25	35	24
i-C_3H_7Br	$AlCl_3$	*b*	46	20	34	25
HeT^+		*a*	45·8	17·2	32·4	This work

[a] Excess of aromatic solvent. [b] Heterogeneous reaction.

ing sections. On the other hand, it appears that the HeT^+ ion[2] and other gaseous electrophiles such as D_2T^+,[26] H_3^+,[27] and $^{80}Br^+$,[28] exhibit a small but measurable selectivity in their reactions with gaseous substrates, attacking preferentially the molecules characterized by a permanent dipole moment.

As the effect does not depend on the sign of the dipole, and even deactivated molecules with electron-withdrawing groups appear to react faster than benzene, the mechanism must be entirely different and unrelated to the mechanisms regulating competition in the liquid phase.

It has been suggested[26,28] that the substrate selectivity of HeT^+ and other electrophiles in their gas-phase reactions is simply determined by electrostatic factors, *i.e.* by the differences existing in the cross sections of the various substrates for the capture of the gaseous positive poles.

We thank Professor E. Baciocchi for discussions and Mr. N. Pepe for experimental assistance.

[2/794 *Received, 7th April,* 1972]

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