Aromatic Substitution in the Gas Phase. Part III.[1] Reaction of the D_2T^+ Ion with Gaseous Arenes. General Remarks on the Reactivity of Gaseous Brønsted Acids

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The results of a study of gas-phase triton transfer from D_2T^+ to benzene and toluene are reported. The electrophile, prepared from the γ-radiolysis of gaseous D_2 containing a tracer activity of DT, was allowed to react with the aromatic substrate, in the presence of oxygen as a radical scavanger. The relative reactivity of the arenes towards the electrophile, and the distribution of the tritium atoms in the labelled toluene formed were determined. The results are compared with those obtained with a stronger gaseous Brønsted acid, the helium tritiide ion, and the mechanism of gas-phase electrophilic attack is discussed. It is suggested that a model based on the formation of an electrostatic complex between the electrophile and the aromatic substrate can account for the main features of the gas-phase tritiodeprotonation.

In previous papers we have described the electrophilic attack of the gaseous Brønsted acid, the HeT^+ ion from the β-decay of molecular tritium, on gaseous aromatic substrates, including benzene, toluene, t-butylbenzene, halogenobenzenes, anisole, and ααα-trifluorotoluene.[1-3]

In order to broaden the scope of the investigation, we decided to examine the reactivity of similar electrophiles towards gaseous aromatic substrates. One of the simplest suitable reagents is the H_3^+ ion, whose properties have been well defined by extensive theoretical and experimental investigations,[4] and whose preparation can be conveniently carried out in the gas phase by a radiolytic technique introduced and developed to a high degree of sophistication by Ausloos and his co-workers.[5,6] Moreover, the reactions of H_3^+ with benzene, toluene, and the xylenes were the subject of a mass spectrometric study by Volpi and his co-workers,[7] whose data will help in elucidating the mechanisms of the corresponding processes occurring at ordinary pressure.

The use of H_3^+ in the study of aromatic substitution presents considerable practical difficulties. The use of D_3^+ is inadequate in that mass spectral techniques do not permit assignment of the position of the label in the products.

The analytical difficulties were overcome by the use of a radioactive reagent, the D_2T^+ ion, which was conveniently prepared from the γ-radiolysis of deuterium containing a tracer activity of DT. This allowed the application of the extremely precise radiometric techniques to the determination of the tritiated products and their substituted derivatives.

We report here on the reaction of the D_2T^+ ion with benzene and toluene, studied in the gas phase at 760 Torr and room temperature.

EXPERIMENTAL

Materials.—Deuterium was a research grade product from Fluka AG, (purity >99·8 mol %) and was passed through molecular sieve traps cooled to −196° for further purification. The deuterium tritiide was obtained from tritium (CEA, France) diluted with a large excess of deuterium and subjected to a Tesla discharge at reduced pressure. The isotopic composition was determined by gas-solid radiochromatography on an iron oxide–alumina column at −196°.[8]

Other chemicals were reagent grade and were used without further purification. [$^2H_8$]Toluene (purity >95%) was obtained from CEA, France.

Procedure.—Pyrex bulbs (1 l), outgassed and evacuated to 10^{-5} Torr, were filled to 760 Torr with deuterium, containing DT (85—125 mCi ml^{-1}), oxygen (*ca.* 1·5 Torr), and the aromatic substrate (*ca.* 10 mg). The samples were irradiated with ^{60}Co γ-rays at 25°, in a 220 Gammacell (Atomic Energy Canada Ltd.). After receiving a dose ranging from $2{\cdot}5 \times 10^{20}$ to $2{\cdot}5 \times 10^{21}$ eV mol^{-1} of deuterium at a rate of *ca.* 2×10^5 rad h^{-1}, the samples were analysed. The contents of the ampoules were added to a measured amount of the appropriate inactive substrate, cooled to −60°, and carefully evacuated with a Töepler pump to separate the gaseous product from the condensed arenes. Both liquid and gas were then subjected to a radio gas chromatographic analysis,[9] by use of a flow ionization chamber (100 ml) heated to 110° and connected to the outlet of a 116E Perkin-Elmer gas chromatograph. The analysis of the gas was carried out on a 5A molecular sieve column (4 m, 88°) and the liquid on a di-isodecyl phthalate column (3 m; 130°).

In order to measure precisely the yields of tritiated benzene and toluene, and to obtain pure samples for the subsequent preparation of the toluene derivatives, the recovered arenes were subjected to rigorous purification by preparative g.l.c., using a specially modified [10] model 'C' C. Erba gas chromatograph and a di-isodecyl phthalate-modified Bentone 34 column (1·8 m, 65°). The purification was repeated until the radioactivity measurements (Nuclear Chicago Mark I liquid scintillation spectrometer) indicated that a constant value of the specific activity had been reached.

Preparation of Substituted Derivatives of Toluene.—The distribution of tritium in the labelled toluene was deter-

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

[2] F. Cacace and S. Caronna, *J. Amer. Chem. Soc.*, 1967, **89**, 6848.

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

[4] *Cf.* W. A. Chupka, M. E. Russel, and K. Refaey, *J. Chem. Phys.*, 1968, **48**, 1518, and references therein.

[5] P. Ausloos and S. G. Lias, *J. Chem. Phys.*, 1964, **40**, 3599.

[6] P. Ausloos, *Progr. Reaction Kinetics*, 1969, **5**, 113.

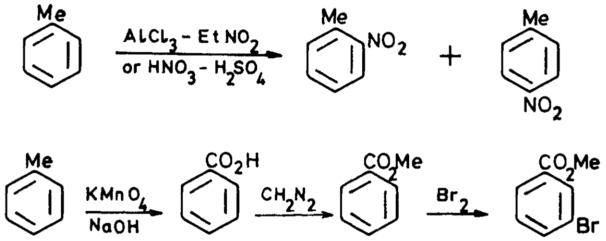
[7] V. Aquilanti, A. Giardini-Guidoni, and G. G. Volpi, *Trans. Faraday Soc.*, 1968, **64**, 3283.

[8] M. A. Smith and E. H. Carter, 'Tritium in the Physical and Biological Sciences,' IAEA, Vienna, 1962, vol. II, p. 21.

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

[10] B. Aliprandi, F. Cacace, and G. Ciranni, *Analyt. Chem.*, 1964, **36**, 2445.

mined by measuring the decrease of the molar radioactivity caused by replacement of hydrogen atoms by suitable inactive groups (Scheme 1).



SCHEME 1

The substituted derivatives were resolved and purified by preparative g.l.c., using a di-isodecyl phthalate-modified Bentone 34 column (1·8 m, 135°) for the nitrotoluenes; a di-isodecyl phthalate-modified Bentone 34 column (1 m; 140°) for methyl benzoate; and an Apiezon L column (2 m; 200°) for methyl *m*-bromobenzoate.

TABLE 1

Yields (%) of tritiated products from the attack of D_2T^+ ions on gaseous benzene and toluene

Composition of the system							Yields [a]	
DT (mCi l^{-1})	D_2 (Torr)	O_2 (Torr)	C_6H_6 (Torr)	C_7H_8 (Torr)	C_7D_8 (Torr)	Dose ($\times 10^{-21}$) (eV mol^{-1} of D_2)	[^{3}H]Toluene (%)	[^{3}H]Benzene (%)
125	760	1·5		1·86		0·25	83 [b]	Trace
105	760	1·5		1·86		2·5	76	0·12
92	760	1·5			1·86	1·4	66	Traces
85	760	1·5	1·2	0·30		2·5	$\frac{C_7H_7T}{C_7H_8} : \frac{C_6H_5T}{C_6H_6} = 1{\cdot}30$	
85	760	1·5	1·2	0·15		2·5	$\frac{C_7H_7T}{C_7H_8} : \frac{C_6H_5T}{C_6H_6} = 1{\cdot}34$	

[a] For the calculation of the yields, and the accuracy of the data, see text. [b] The standard deviation of the data is <10%.

TABLE 2

Intramolecular distribution of tritium within the molecule of the labelled toluene

		Distribution (%)			
Substrate	Dose ($\times 10^{-21}$) (eV mol^{-1} of D_2)	$3 \times \alpha$	$2 \times o$	$2 \times m$	p
C_7H_8	0·25	4·5 ± 0·8	50·2 ± 4·6	18·6 ± 2·5	26·7 ± 2·5
C_7H_8	2·5	3·0 ± 0·8	50·6 ± 4·6	15·4 ± 2·4	31·0 ± 2·5
C_7D_8 [a]	2·5	4·0 ± 1·0	44·8 ± 4·0	30·6 ± 3·0	20·7 ± 2·0
C_7D_8 [b]	2·5	4·4 ± 1·0	42·8 ± 4·0	33·6 ± 4·0	19·9 ± 2·1

[a] Distribution determined by nitration with $C_2H_5NO_3$–$AlCl_3$. [b] Distribution determined by nitration with HNO_3–H_2SO_4.

Competition Experiments.—The relative reactivity of benzene and toluene towards the D_2T^+ electrophile was determined by irradiating gaseous samples of deuterium, containing the usual amounts of oxygen and DT, in the presence of a mixture of benzene and toluene of known molar ratio. The relative yields of the tritiated arenes were calculated from the ratio of the areas of the corresponding radiochemical peaks (di-isodecyl phthalate; 3 m; 120°).

RESULTS

The yields of tritiated benzene and toluene from attack of the D_2T^+ ion on the corresponding substrates are listed in Table 1. The yields are calculated from the dose absorbed by the deuterium gas, taking a $G_{H_3^+}$ value of 2·75,[11] and assuming a lack of isotope effects in the formation of the D_2T^+ ions.

In view of the approximate nature of the calculations, the figures listed in Table 1 should be regarded at best, as a rough estimate. Their consistency, measured by the standard deviation, is better than 10%.

The intramolecular distribution of tritium within the labelled toluene is given in Table 2, where the standard deviation of the data is included.

DISCUSSION

Formation of the Tritiated Products.—The electrophilic reagent is produced in the γ-radiolysis of deuterium gas containing a tracer concentration of deuterium tritiide by a well established [5,6] two-step mechanism [equations (1) and (2)].

$$X_2 \longrightarrow X_2^+ + e \quad (X = D \text{ or } T) \qquad (1)$$

$$X_2^+ + X_2 \longrightarrow X_3^+ + X \qquad (2)$$

The deuterium (or tritium) atoms formed together with the charged reagent from process (2) are effectively removed from the system by a low concentration of oxygen, a radical scavanger preferred in the present study to other frequently employed additives for its relative inertness towards hydrocarbon ions.[6]

The most noteworthy aspect of the results in Table 1 is that D_2T^+ attack on the aromatic substrates can be regarded essentially as a tritiodeprotonation, since [^{3}H]benzene and [^{3}H]toluene are the only products formed in significant yields from the corresponding inactive arenes.

We suggest that the first step of the tritiodeprotonation is exothermic triton transfer from D_2T^+ to the arene [equation (3)]. Using a value of *ca.* 4·5 eV for the

$$D_2T^+ + ArH \longrightarrow [ArHT]_{ex.}^+ + D_2 \qquad (3)$$

proton affinity of hydrogen [the most probable value

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[11] J. Weiss and W. Bernstein, *Radiation Res.*, 1957, **6**, 603.

among the rather uncertain data on the heat of formation of the (triangular) H_3^+ ion] the enthalpy change associated with reaction (3) can be evaluated at *ca.* 45 kcal mol^{-1} for benzene and -52 kcal mol^{-1} for toluene.[12,13]

The excited arylium ions can subsequently undergo collisional stabilization [equation (4)] followed by the

$$[\mathrm{ArHT}]_{\mathrm{ex.}}^+ + \mathrm{M} \longrightarrow \mathrm{ArHT}^+ + \mathrm{M}^* \qquad (4)$$

thermoneutral transfer of a proton to the inactive arene present in low concentration in the gaseous system [equation (5)].

$$C_7H_8T^+ + C_7H_8 \longrightarrow C_7H_7T + C_9H_9^+ \qquad (5)$$
$$\Delta H_5 \textit{ ca. } 0 \text{ kcal mol}^{-1}$$

A minor fraction of the excited ions escape stabilization, and dissociate into simpler species, as indicated by the formation of C_6H_5T from toluene [equations (6) and (7)].

$$[C_7H_8T]_{\mathrm{ex.}}^+ \longrightarrow C_6H_4T^+ + CH_4 \qquad (6)$$
$$C_6H_4T^+ + C_7H_8 \longrightarrow C_6H_5T + C_7H_7^+ \qquad (7)$$
$$\Delta H_7 \textit{ ca. } -57 \text{ kcal mol}^{-1}$$

The technique employed to generate the electrophilic reagent requires the presence of a relatively large DT activity in the system, and therefore does not allow the detection of any tritiated hydrogen formed from the decomposition of excited ions, or from the Lewis acid reaction of the D_2T^+ ion whose occurrence cannot be therefore ruled out [equation (8)].

$$RC_6H_5 + D_2T^+ \longrightarrow RC_6H_4^+ + HT + D_2 \qquad (8)$$

The mechanism outlined in equations (3)—(7) is similar to those suggested for the reactions of the HeT^+ ion with gaseous arenes at atmospheric pressure.[1-3] Since, however, the exothermicity of triton transfer is higher by at least 65 kcal mol^{-1}, it is not surprising that the arylium ions formed from HeT^+ attack undergo a more extensive decomposition, as demonstrated, in the case of toluene, by the formation of CH_3T and C_6H_5T in 6 and 3·8% yield, respectively.

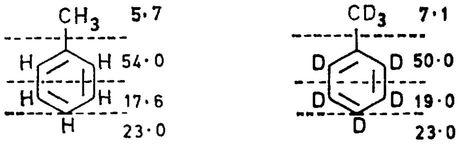
The occurrence of gaseous arylium ions, whose intermediacy plays a central role in the tritiodeprotonation, is independently supported by a number of mass spectrometric investigations. While unable to provide direct information on the chemical structure of the species involved, mass spectrometric techniques have demonstrated the formation and stabilization of $C_6H_7^+$ and $C_7H_9^+$ ions from the exothermic protonation of benzene and toluene by gaseous Brønsted acids, including H_3^+,[7] CH_5^+,$C_2H_5^+$,[14,15] and $C_3H_8^+$.[16] The results of Volpi *et al.*[7] are particularly relevant, since stable, long-lived $C_6H_6D^+$ and $C_7H_8D^+$ ions were observed as the major products from the gas-phase deuteron transfer from D_3^+ to C_6H_6 and to C_7H_8.

Despite the considerable exothermicity of process (3), it was found that the arylium ions were efficiently stabilized in the deuterium gas, as indicated by the small (*ca.* 20%) fraction of excited $C_7H_8D^+$ ions that was found to dissociate at the relatively low pressure of 0·8 Torr.

Furthermore, the major fragmentation products from D_3^+ attack on toluene at low pressure were the $C_7H_7^+$ and $C_6H_5^+$ ions, corresponding to the charged products from reactions (6)—(8).

Selectivity of the D_2T^+ *Attack.*—The data in Table 1 indicate that the D_2T^+ reagent exhibits a very low substrate selectivity, measured by a $k_T : k_B$ ratio of *ca.* 1·3. The result is in substantial agreement with the remarkably low substrate selectivity of the HeT^+ ions towards gaseous aromatic compounds,[1-3] and with the mass spectrometric results, whose main feature is that, within the precision of the experimental data (*ca.* 20%), the rate constants of proton transfer from H_3^+ to benzene and toluene are the same.

The intramolecular selectivity of D_2T^+ attack can be deduced, to a certain extent, from the distribution of tritium in the labelled products (Table 2). The tritium distribution is largely independent of the radiation dose received by the system, but depends considerably on the isotopic composition of the substrate. The data concerning the tritiodeprotonation of toluene show, in fact, a relatively pronounced intramolecular selectivity, characterized by a $p : \frac{1}{2}m$ ratio of *ca.* 3·4, as compared to *ca.* 2·5 measured in the gas-phase tritiodeprotonation of toluene and [$^2H_8$]toluene by the HeT^+ ion, whose labelled products gave the distributions shown in Scheme 2.



SCHEME 2

Thus, taking into account only the data concerning toluene, the D_2T^+ reagent would be classified as an electrophile closely similar to the HeT^+ ion, and its slightly higher intramolecular selectivity could be satisfactorily traced to the considerably lower exothermicity of the triton transfer process (3). The situation is unfortunately more complicated, as indicated by the experiments with [$^2H_8$]toluene.

Evidence for Tritium Shifts within the Arylium Ion.—In contrast to the results obtained for the HeT^+ ion, a change in isotopic composition of the substrate significantly affects the tritium distribution in the product from the attack of D_2T^+ ions. The $p : \frac{1}{2}m$ ratio is *ca.* 1 in the tritiodeprotonation of [$^2H_8$]toluene.

We suggest that the difference in behaviour of the HeT^+ and D_2T^+ reagents, and the considerable decrease of the apparent selectivity of D_2T^+ in passing from toluene to [$^2H_8$]toluene, can be best rationalized by

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[12] R. E. Christoffersen, *J. Chem. Phys.*, 1964, **41**, 960.

[13] H. Conroy, *J. Chem. Phys.*, 1964, **41**, 1341.

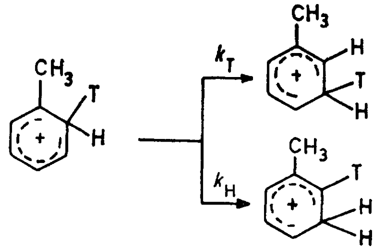
[14] J. L. Franklin, F. W. Lampe, and H. E. Lumpkin, *J. Amer. Chem. Soc.*, 1959, **81**, 3152.

[15] F. H. Field, *J. Amer. Chem. Soc.*, 1967, **89**, 5328.

[16] L. I. Bone and J. H. Futrell, *J. Chem. Phys.*, 1967, **47**, 4366.

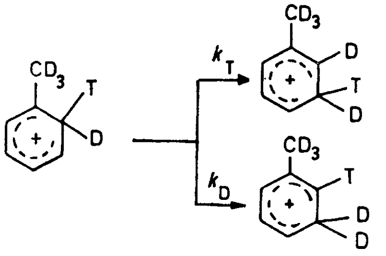
postulating secondary, intramolecular processes that measurably affect the original distribution of tritium within the excited intermediate from the electrophilic reaction. Whereas the arylium ions formed from HeT^+ attack in the pure, gaseous substrate at 760 Torr, can be immediately quenched by reaction (4), and have little chance of undergoing intramolecular rearrangements, the lifetime of the arylium ions from D_2T^+ attack must be much longer, owing to the substantially lower concentration of the quenching reagent, *i.e.* the inactive toluene.

Under these circumstances, $1 \longrightarrow 2$ proton shifts, similar to those frequently observed in solution,[17] are likely to affect the excited intermediate, causing the migration of either hydrogen or tritium, according to the competitive processes (9a) and (9b). The competition between the corresponding processes in $[^2H_8]$-toluene [processes (10a) and (10b)] must clearly shift in favour of tritium migration, since the $k_H : k_T$ ratio is likely to exceed the $k_D : k_T$ ratio. As a consequence, it is reasonable to assume a more extensive randomization of tritium within the deuteriated arylium ion, leading to more pronounced flattening of the distribution of tritium within the product.



(9a)

(9b)

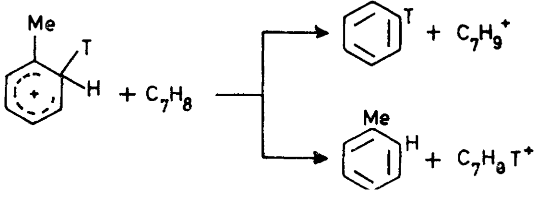


(10a)

(10b)

An alternative explanation would involve the transfer of a triton, rather than a proton, from the arylium ion to the inactive toluene in the quenching step [reactions (11a) and (11b)].

It is conceivable that replacement of hydrogen by deuterium in the substrate would increase the significance of reaction (11b), which involves an additional step in the formation of the labelled toluene and is therefore likely to cause a decrease of the overall positional selectivity.



(11a)

(11b)

Since, however, the tritonation of $[^2H_8]$toluene by HeT^+ ions did not produce a change in the intramolecular tritium distribution, we are inclined to believe that the differences in the apparent selectivity of D_2T^+ in its reaction with toluene and $[^2H_8]$toluene are likely to arise from fast intramolecular $1 \longrightarrow 2$ tritium shifts which occur during the relatively long life time of the tritiated arylium ions.

Whereas it is hard to deduce from the available data the extent of randomization, and to assess how closely the tritium distribution in the gaseous arylium ion approaches the equilibrium value, the present results nevertheless show conclusively that the determination of the tritium content in the various ring positions of the final product can provide only a lower limit for the intramolecular selectivity of the reagent, as suggested in earlier reports.[2,3]

A Model for the Gas-phase Attack of D_2T^+ *and* HeT^+ *Ions.*—The present results confirm those obtained for the closely related HeT^+ ion, as the positional selectivity of the reagent considerably exceeds its substrate selectivity. Thus, any rationale of the gas-phase selectivity of the Brønsted acids, HeT^+ and D_2T^+ should provide a reasonable, explanation for two significant experimental data, *i.e.*, the lack of correlation between the intramolecular selectivity (Table 3) and the substrate selectivity, and the relative reactivity of the different substrates towards the electrophiles (Table 4) which show that, with the exception of αα-trifluorotoluene, all the

TABLE 3

Distribution of tritium in the products of gas-phase tritiodeprotonation

Substrate	Reagent	Ref.	Distribution (%)			
			2 × *o*	2 × *m*	*p*	3 × α
C_6H_5F	HeT^+	2	53·6	32·2	14·2	
C_6H_5Cl	HeT^+	2	45·8	31·6	21·5	
C_6H_5Br	HeT^+	2	37·4	38·6	23·8	
$C_6H_5{\cdot}CH_3$	HeT^+	1	54·0	17·6	23·0	5·7
$C_6H_5{\cdot}CH_3$	D_2T^+	This work	50·6	15·4	31·0	3·0
$C_6D_5{\cdot}CD_3$	HeT^+	1	50·0	19·0	23·0	7·1
$C_6H_5{\cdot}CF_3$	HeT^+	3	29·2	58·4	11·4	
$C_6H_5{\cdot}O{\cdot}CH_3$	HeT^+	3	49·6	33·6	16·7	<0·2

TABLE 4

Gas-phase competition of aromatic substrates towards HeT^+ and D_2T^+

Substrate	Reagent	Ref.	Approx. yield relative to benzene
$C_6H_5{\cdot}CF_3$	HeT^+	3	0·8
C_6H_6			1·0
C_6H_5F	HeT^+	2	1·2
$C_6H_5{\cdot}CH_3$	HeT^+	1	1·5
$C_6H_5{\cdot}CH_3$	D_2T^+	This work	1·3
C_6H_5Cl	HeT^+	2	1·6
C_6H_5Br	HeT^+	3	2·0
$C_6H_5{\cdot}CN$	HeT^+	3	2·2
$C_6H_5{\cdot}O{\cdot}CH_3$	HeT^+	3	3·0

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[17] *Cf.* D. M. Brouwer, E. L. Mackor, and C. Maclean, ' Carbonium Ions,' eds. G. A. Olah and P. Von Schleyer, Wiley–Interscience, New York, 1970, vol. II, p. 882.

substrates studied react faster than benzene, irrespective of the nature of the substituent.

It is tentatively suggested that the attractive electrostatic forces between the attacking ion and a polar and/or polarizable molecule allow the trapping of the positive ion in long-lived complex, whose stability is ensured either by classical Langevin spiralling or, more likely, by the multiple reflection mechanism recently suggested by Dugan and Magee,[18] and by Dugan and Rice.[19]

The formation of the complex, determined by long-range electrostatic interactions, is envisaged as not requiring activation energy. The attractive force which causes the formation of the complex, and therefore determines the ability of a given substrate to trap the HeT^+ and D_2T^+ ions in competition with others, is the sum of two terms, describing the interaction between the ion and, respectively, the permanent and the induced dipole of the molecule.* Their relative contributions depend on many parameters in addition to the permanent dipole moment and the electronic polarizability of the neutral molecule, and include its moment of inertia and rotational energy, which are determined in turn by the temperature of the system.

Two extreme cases can be visualized, corresponding, respectively, to highly polar substrates, such as benzonitrile which has a large permanent moment, and whose ion–molecule interaction is dominated by the ion–dipole term, and to substrates having no permanent moment, whose interaction is determined exclusively by the ion-induced dipole term.

Substrates belonging to the first group should more readily capture the gaseous electrophile, irrespective of the sign of the dipole.

Once the HeT^+ (or D_2T^+) ion is trapped within the ' electrostatic cage ', the ion–molecule separation decreases in such a way as to allow the transfer of the triton to the various reaction centres of the substrate.

In contrast with the initial formation of the electrostatic complex, we suggest that the transfer of the triton to a given position of the substrate requires a well defined activation energy, essentially determined by the electron density at the reaction site, which depends, in turn, on dipole and polarizability factors similar to the inductive and mesomeric effects invoked to explain the positional selectivity in the conventional aromatic substitutions.

In the case of an unreactive collision with a particular reaction centre, the electrophile may remain trapped within the electrostatic complex and be available for subsequent collisions. This model can qualitatively explain the behaviour of the HeT^+ and D_2T^+ reagents, and especially their unique selectivity.

Substrates characterized by a strong permanent dipole should successfully compete with benzene, even in those cases (halogenobenzenes, benzonitrile) where the negative end of the dipole points away from the ring (causing a strong deactivaction in solution). On the other hand, the effects of a high electronic polarizability on the possibility of capture are clearly demonstrated in the case of anisole and especially of toluene, whose relatively small permanent dipoles do not appear to justify the higher reactivity relative to benzene.

Finally, since the competition of the various reaction centres within the electrostatic complex is regulated by factors similar to inductive and mesomeric effects, it is not surprising that the HeT^+ and D_2T^+ ions exhibit a measurable intramolecular selectivity, analogous to, if considerably lower than, the selectivity of conventional electrophiles in solution.

The formation of an electrostatic complex postulated in our model is equivalent, from a purely kinetic standpoint, to the preliminary formation of a complex invoked by Olah to account for the lack of correlation between the positional and the substrate selectivity of strong electrophiles in solution. Indeed, ' π-complexes ' have been suggested as possible reaction intermediates in mass spectrometric [7] and radiolytic [20] studies on ion-molecule reactions in the gas phase. Since, however, the formation of π-complexes in the first step of the gaseous reaction can hardly explain the observed reactivity order, we are inclined to believe that the formation of a long-lived reagent–substrate complex, whose stability is ensured by long range electrostatic forces, is the step which regulates the competition of different substrates for the gaseous Brønsted acids.

[1/1169 *Received, July 8th*, 1971]

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* The attractive terms of the interaction potential between a neutral molecule, with a permanent dipole μ and an electronic polarizability α, and a positive ion of unit charge are given [18] by $-V = \mu e \cos\gamma/4\pi\varepsilon_0 r^2 + \alpha e^2/8\pi\varepsilon_0 r^4$ where r is the distance and γ the angle between the dipole (negative end) and the separation vector. As the molecule rotates, γ continuously changes during the interaction time, and a precise evaluation of the relative weights of the two attractive terms becomes rather difficult. However, if the assumption that the dipole is capable of continuously adjusting itself to the minimum electrostatic energy orientation as the collision proceeds (' adiabatic ' hypothesis) gives only an upper limit to the capture cross section, there is evidence that for strongly polar molecules the mean value of $\cos\gamma$ is positive and large at significant interaction distances.[19]

[18] J. V. Dugan and J. L. Magee, *J. Chem. Phys.*, 1967, **47**, 3103.

[19] J. V. Dugan and J. H. Rice, NASA Report TN D-5407, 1970.

[20] S. Takamuku, K. Iseda, and H. Sakurai, *J. Amer. Chem. Soc.*, 1971, **93**, 2420.