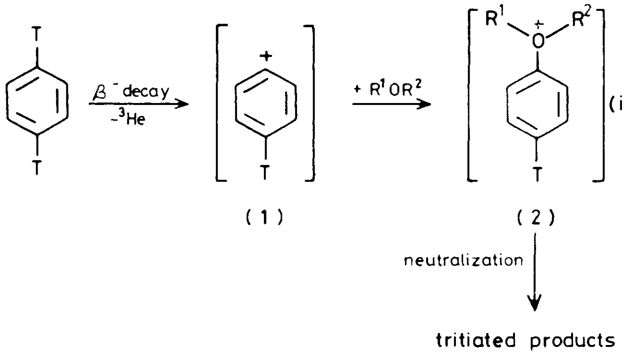
Arylation of Dialkyl Ethers by Gaseous Phenylium Ions. Formation and Behaviour of Dialkylphenyloxonium Ions in the Gas Phase

Simonetta Fornarini and Maurizio Speranza *
Istituto di Chimica Nucleare del C.N.R., 00016 Monterotondo Stazione, Rome, Italy

Tritiated phenylium ions, obtained in the gas phase from the spontaneous decay of 1,4-ditritiobenzene, have been allowed to react with dialkyl ethers (MeOPr^n, MeOPr^i, and Pr^{i}OPr^n) in the pressure range 20—400 Torr and in the presence of a thermal radical scavenger (O_2, 4 Torr). The effects of a gaseous base (NH_3, 4 Torr) on the reaction carried out at the highest pressure were also investigated. Singlet phenylium ion confirms its distinct affinity toward the *n*-centre of the substrate (*ca.* 80% for MeOPr), although significant insertion into the alkyl groups of Pr^{i}OPr^n is observed as well. The stability and reactivity features of the formed dialkylphenyloxonium ions, under the experimental conditions chosen, have been studied as well as their fragmentation and isomerization mechanisms. The behaviour of dialkylphenyloxonium ions in the gas state (20—400 Torr) is consistent with previous mechanistic hypotheses from mass spectrometric studies, carried out at much lower pressures (below 1 Torr).

Essential information on the tendency of gaseous phenylium ions to undergo unimolecular automerization as well as on their reactivity and selectivity towards a number of acceptors (MeX, where X = OH, F, Cl, and Br) was recently provided by nuclear-decay studies carried out in the gas phase, *i.e.* in a reaction environment entirely free from the complicating effects of solvation and ion pairing.[1] The relevant data are consistent with an exceedingly reactive phenylium ion with a distinct affinity for the *n*-electrons (the X centre) of the acceptor molecule.[2] This behaviour provides experimental support for theoretical calculations predicting a singlet-state electronic configuration for the ground-state phenylium ion (1).[3,4] From these data, however, it could not be decided whether the high site discrimination of cation (1) is restricted to simple molecules, such as MeX, or could be related to the specific nature of the ionic reactant.



R^1, R^2 = Me, Pr^i; Me, Pr^n; Pr^i, Pr^n

Our investigation has therefore been extended to ether-type substrates [R^{1}OR^2, equation (i)], where the mobile hydroxylic hydrogen, which provides an easy deprotonation channel for the ionic intermediates from the reaction of (1) with MeOH, is lacking, and where the number of σ-type sites in the molecule is progressively increased. We expected that ether-type substrates would also allow us to gain a direct insight into the stability of dialkylphenyloxonium ions (2) in the gas phase, provided that attack of (1) on the *n*-type centre (the ethereal oxygen) of the acceptor occurs as readily as in the case of MeX.

The ethers MeOPr^i, MeOPr^n, and Pr^{i}OPr^n are considered as suitable acceptors for phenylium ion (1). The different stabilities of primary and secondary propyl cations might be expected to lead to remarkable differences in both extent and mechanism of fragmentation of the dialkylphenyloxonium ion, and to influence the possibility of intramolecular isomerization to a ring-alkylated isomer.[5,6]

Experimental

Materials.—The key substrate for the nuclear-decay experiments, 1,4-ditritiobenzene, was synthesized using a previously described procedure.[7] NH_3, O_2, CH_3F, and D_2 were obtained from Matheson Gas Products Inc.; their stated purity exceeded 99.9 mole %. Aldrich Chemical Co. and Fluka AG provided all the products used as g.l.c. standards or as components in the gas-phase experiments. Ether-type compounds, not available commercially, such as isomeric Alk$^1C_6H_4$OAlk^2 (Alk^1, Alk^2 = H, Pr^n; H, Pr^i; H, allyl; Me, Pr^n; Me, Pr^i; Pr^i, Me; Pr^i, Pr^n; *ortho*-allyl, Me), benzyl methyl ether, benzyl isopropyl ether, and isomeric methoxyphenylpropanes, were prepared by reaction of the sodium or potassium salt of the corresponding alcohol or phenol with the appropriate alkyl halide in acetone or alcoholic solvent, according to established procedures. Isomerization of allyl phenyl ether provided isomeric propenyl phenyl ethers.[8] β-Chlorophenetole was dehydrohalogenated to give phenyl vinyl ether.[9] All the products were purified by preparative g.l.c. on the following columns: (i) 5 m packed with 10% Apiezon L on 80—100 mesh Chromosorb W-DMCS, and (ii) 3 m packed with a 1 : 1 mixture of Bentone-34–di-isodecyl phthalate on 60—80 mesh Chromosorb W-AW. The identity of the synthesized products was established by conventional i.r. and n.m.r. spectroscopy.

Decay Experiments.—The decay samples were prepared by introducing sealed glass capillaries containing *ca.* 1 mCi of tritiated benzene (specific activity: 0.9 mCi μl^{-1}) into 300-ml Pyrex ampoules. The ampoules were then connected to a vacuum line and thoroughly de-gassed. The gaseous ethereal substrate was then introduced, together with minor amounts (at *ca.* 4 Torr) of oxygen, which was used as a scavenger of the radical species that could be formed by the passage of the β-particle from the nuclear decay of tritiated benzene through the gaseous mixture. The ampoules were finally sealed and the capillary tube containing the benzene broken with a glass hammer.

The decay products were allowed to accumulate for about a year in the dark and at room temperature. The ampoules were then opened under airtight conditions and their contents were collected by repeated washing with diethyl ether. Analysis of the recovered radioactive solutions was performed on a C. Erba Fractovap 4200 gas chromatograph equipped with a high-sensitivity hot-wire detector (model 450) coupled in series with a Berthold proportional counter tube, kept at 180 °C. The identity of the tritiated products was established by coincidence of the radiochemical peaks with the HWD signals from authentic reference compounds, on at least three different columns: (i) 2 m 25% Carbowax 4000 on 60—80 mesh Chromosorb W-DMCS, operated at 140 °C, (ii) 5 m 5% SP 1200/1.75% Bentone-34 on 100—120 mesh Supelcoport, operated at 120 °C, (iii) 4 m 20% tricresyl phosphate on 60—80 mesh Chromosorb W-AW, operated at 125 °C. About forty reference compounds were tested, including the ethers described in the previous section, arenes (*e.g.* propyl- and propenyl-benzenes), ketones (*e.g.* propiophenone), and a variety of benzocyclic compounds (*e.g.* indene, 2,3-dihydrobenzofuran, *etc.*).

Radiolytic Experiments.—The gaseous samples were prepared by introducing the required gaseous components (CH_3F 720 Torr, O_2 5 Torr, C_6H_5OPr 3 Torr) into 350-ml Pyrex bulbs by standard vacuum techniques. The samples were then irradiated in a 220 Gammacell (Atomic Energy Canada Ltd.) to a total dose of 3.2 Mrad (dose rate 1.07 Mrad h^{-1}) at 37 °C. The products were analysed by g.l.c. using a Perkin-Elmer Sigma 3 gas chromatograph, equipped with a flame ionization detector, on the following columns: (i) 5 m 5% SP 1200/1.75% Bentone-34 on 100—120 mesh Supelcoport, operated at 135 °C, (ii) 2 m Carbopack C, AW, operated at 200 °C. Individual calibration factors were used for the quantitative analysis of the products, the identity of which was confirmed by comparison of their retention volumes with those of authentic standards. Before irradiation of the gaseous samples, special care was taken to check the purity of their gaseous components with particular regard to the presence of the expected irradiation products.

Chemical Ionization (*CI*) *and Fourier Transform* (*FT-ICR*) *Mass Spectrometric Experiments.*—Phenylium-ion attack on the ethereal substrates was investigated by two different mass spectrometric approaches. In the source of a conventional VG Micromass 7070 mass spectrometer, phenylium ion was generated by D_2-CI of fluorobenzene in the presence of the ether. The total pressure in the source was kept around 1 Torr, while the D_2 : fluorobenzene : ether molar ratios ranged from $1 : 5 \times 10^{-4} : 1 \times 10^{-4}$ to $1 : 1 \times 10^{-4} : 5 \times 10^{-4}$.

CH_3F-CI experiments were performed on isomeric C_6H_5OPr to gather information on the fragmentation mechanism of the corresponding methylphenyloxonium ions (2). A complete view of the ion chemistry of these systems was obtained by using a FT-ICR technique (Nicolet FT-MS 1000). The reactant ion $CH_3FCH_3^+$ was selected by triple resonance from the ionic plasma following electron impact (13 eV) and fast ion-molecule reactions in a CH_3F–C_6H_5OPr (20 : 1) mixture, introduced into the ion source of the spectrometer at a total pressure of *ca.* 2×10^{-6} Torr. Its reaction with C_6H_5OPr was studied in the decay time range 5—500 ms.

Results

Phenylation of Dialkyl Ethers.—When 1,4-ditritiobenzene is allowed to decay in the presence of a large excess of MeOPr^n, MeOPr^i, or Pr^{i}OPr^n, a variety of aromatic tritiated products are formed, the relative distribution of which is reported in Tables 1—3. Reaction conditions were chosen to span a factor of 20 in methyl propyl ether partial pressure (20—400 Torr), whereas in the Pr^{i}OPr^n experiments the lower volatility of the ether sets the upper limit at 50 Torr. A powerful base, such as NH_3 (4 Torr), was also introduced in the decay experiments carried out at the highest ether partial pressure. The overall absolute yield of tritiated products in Tables 1—3 is around 50%,* the remainder being accounted for by (i) low boiling fragmentation products, (ii) phenol, derived from traces of water in the decay system, and (iii) aniline, from direct addition of phenylium ion to NH_3 (when present). The identity of a few radioactive products is left undefined since it could not be safely assessed by comparison with authentic standard compounds. However, according to their retention volumes on the selected g.l.c. columns, these unknown products are most likely alkyl phenyl ethers or alkoxyphenylalkanes with unsaturation or branching in the alkyl chain.

Analysis of Tables 1—3 reveals that alkyl aryl ethers are invariably major products from the MeOPr decay systems, accounting for over 80% of the recovered tritiated products. This fraction becomes smaller in the reaction with Pr^{i}OPr^n, even allowing for the uncertainty associated with the relatively high abundance of unknown products (Table 3). The predominant product from the MeOPr systems is anisole, formation of which is invariably accompanied by minor yields of the corresponding phenyl propyl ether (Tables 1 and 2). Table 1 shows that the product distribution from the MeOPr^n decay runs is highly sensitive to the system composition. Increase in the ether pressure and addition of 1 mole % of ammonia to the gaseous sample lead to a substantial decrease of the relative yield of anisole (from 75% to 44%), which is counterbalanced by a significant increase of PhOPr^n (from 1 to 33%). Small amounts (0.5—3%) of PhOPr^i are also formed, which increase as the system pressure is lowered. In contrast, the relative yield of anisole from the MeOPr^i systems (76—80%, Table 2) appears substantially independent of the experimental conditions and much greater than the PhOPr^i counterpart (0—2%). This behaviour is paralled in the Pr^{i}OPr^n systems (Table 3), where PhOPr^i is absent despite the major formation of the PhOPr^n isomer (32—34%).

Formation of alkyl aryl ethers in the decay experiments is always accompanied by variable amounts of tritiated products apparently derived from the formal insertion of phenylium ion into the C–H ($Ph[CH_2]_3OMe$, $CH_3CHPhCH_2OMe$, and PhCH$_2$OPr^i) and C–C bonds ($PhCH_2OMe$) of the ethers. The isomeric propyl- and propenyl-benzenes must have the same origin, as must PhCOEt as well; however the formation of the latter implies a complex reaction mechanism.

In order to obtain independent information on the mechanism of formation of the decay products, the known reaction of D_3^+ ions with fluorobenzene to produce phenylium ions was exploited to examine their reaction pattern towards the chosen dialkyl ethers in the source of a conventional mass spectrometer.[10] The adduct between Ph^+ and the ether was not observed under the mass spectrometric conditions (source pressure: 1 Torr), nor was it expected, but low-intensity signals corresponding to the protonated masses of the neutral compounds recovered in the decay experiments were observed. The rather low abundance of these species can be attributed both to multiple fragmentation processes in the addition

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* The absolute yields, expressed as the ratio of total activity of the end products to the activity originally contained in the nuclear-decay-produced phenylium ion, can be calculated from the initial activity and the isotopic composition of the tritiated benzene sample, the decay rate of the tritium, the abundance (72%) of the phenylium ion among the decay fragments, and the absolute counting efficiency of the detector employed.

Table 1. Tritiated product distribution from gas-phase attack of phenylium ions on $MeOPr^n$

System composition[a]		Relative yields of products[b] (%)										
					$Pr^iC_6H_4OMe$			PhCH= CHMe				
$MeOPr^n$ (Torr)	NH_3 (Torr)	PhOMe	$PhOPr^i$	$PhOPr^n$	*ortho*	*meta*	*para*	*trans*	$PhCH_2$-OMe	PhCH(Me)-CH_2OMe	$Ph[CH_2]_3OMe$	Unknowns
400	4	44	0.5	33	2	0.5		5	2		12	1
400		48	1	24	3	1	1	5	1	1	10	5
20		75	3	1	1	2		8	2			8

[a] All gaseous systems contain O_2 (4 Torr) and tritiated benzene (*ca.* 1 mCi). [b] Expressed as a percentage of the total activity of the recovered aromatic products; standard deviation of data, *ca.* 10%.

Table 2. Tritiated product distribution from gas-phase attack of phenylium ions on $MeOPr^i$

System composition[a]		Relative yields of products[b] (%)							
				$Pr^iC_6H_4OMe$			PhCH=CHMe		
$MeOPr^i$ (Torr)	NH_3 (Torr)	PhOMe	$PhOPr^i$	*ortho*	*meta*	*para*	*trans*	$PhCH_2OPr^i$	Unknowns
400	4	76	1	2	1	1	13	3	3
180		80	2	2	2	1	12	1	
20		76			2		16		6

[a] See footnote *a*, Table 1. [b] See footnote *b*, Table 1.

Table 3. Tritiated product distribution from gas-phase attack of phenylium ions on Pr^iOPr^n

System composition[a]		Relative yields of products[b] (%)						
Pr^iOPr^n (Torr)	NH_3 (Torr)	PhOEt	$PhOPr^n$	PhCH=CHMe *trans*	$PhPr^i$	$PhPr^n$	PhCOEt	Unknowns
50	4	12	34	30		2		22
20		4	32	2	3	3	8	48

[a] See footnote *a*, Table 1. [b] See footnote *b*, Table 1.

Table 4. Relative product yields from the gas-phase methylation of isomeric ethers PhOPr by radiolytically formed ions $CH_3FCH_3^+$

	Relative yields of products[b] (%)						Absolute yields of products[a] (G_M value)[d]
		MeC_6H_4OPr					
Substrate[a]	PhOMe	*ortho*	*meta*	*para*	$Pr^iC_6H_4OMe$	MeC_6H_4OH	
$PhOPr^i$	65	23	2	7	3	N.d.[c]	2.8
$PhOPr^n$	71	20	2	6	2	N.d.[c]	2.5

[a] System composition MeF (720 Torr), O_2 (5 Torr), PhOPr (3 Torr); dose 3.2 Mrad (dose rate 1.07 Mrad h^{-1}). [b] Standard deviation of data *ca.* 10%. [c] Below detection limit ($G_M \leqslant 1 \times 10^{-4}$). [d] The number of molecules produced per 100 eV of absorbed energy; standard deviation of data *ca.* 10%.

complexes * and to efficient competitive addition of the Ph^+ reactant to the D_2 bulk gas yielding the $C_6H_5D_2^+$ species.[10]

Methylation of Propyl Phenyl Ethers.—An independent route to gaseous methylpropyloxonium ions is provided by methylation of the appropriate propyl phenyl ether with $CH_3FCH_3^+$ ions, generated in the gas phase by γ-radiolysis of CH_3F.[11] The relevant results are reported in Table 4. Predominant formation of anisole among the products (65—71%) confirms the distinct tendency of $CH_3FCH_3^+$ to attack the oxygen atom of the aromatic ether, rather than its π system. Limited ring methylation is, however, observed (28—32%), which follows the typical *ortho-para* distribution of classical electrophilic aromatic substitutions [$o : m : p$ 72 : 6 : 22 ($MeC_6H_4OPr^i$); 71 : 7 : 22 ($MeC_6H_4OPr^n$)].[5] It should be noted that formation of cresols in the radiolytic experiments is below the detection limit. The reaction between $CH_3FCH_3^+$ ion and propyl phenyl ethers has been investigated also in the cell of a Fourier Transform mass spectrometer. Attack of $CH_3FCH_3^+$ on the aromatic ether quantitatively and irreversibly yields a *m/z* 109 daughter ion, corresponding possibly to protonated anisole or isomeric cresols. A bimolecular rate constant of $(2.3 \pm 0.2) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} has been measured for the reaction of $CH_3FCH_3^+$ with either of the propyl phenyl ethers at an ion-source temperature of 27 °C. The *m/z* 109 ion finally transfers its proton to a neutral PhOPr molecule, eventually yielding a stable *m/z* 137 species.

Discussion

Phenylium Ion Attack on Dialkyl Ethers.—The nature and the properties of free phenylium ion produced by nuclear

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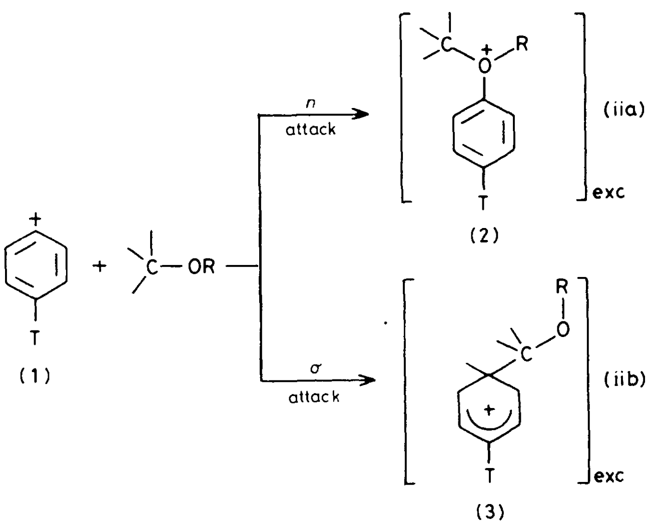
* Multiple fragmentation processes in the adducts between Ph^+ and the ether are favoured by the high exothermicity of their formation ($-\Delta H^\circ$ = 230—385 kJ mol^{-1}) and by the low efficiency of collisional deactivation operated in the low-pressure ion source of the spectrometer by the D_2 gas.



decay in tritiated benzene and used in the present study as phenylating reactant, have been previously described in detail.[2] Any reaction scheme for gas-phase attack of the phenylium ion on the chosen ethers should account for the relatively high extent of *O*-phenylation observed under all experimental conditions (Tables 1—3). It is, therefore, suggested that the phenylation mechanism occurring in the decay systems involves competitive attack of the phenylium ion on the *n*- and σ-type centres of the aliphatic ether, giving predominantly the corresponding dialkylphenyloxonium ion (2) and, to a lesser extent, the isomeric arenium ions (3), both excited by the exothermicity of their formation processes [equation (ii)].*

The remarkable affinity of phenylium ions toward the oxygen of the substrates is inferred from the relatively high yield of aromatic ethers. In the case of methyl propyl ethers, they amount to *ca.* 80%, *cf.* the 95% overall relative yield of phenol and anisole recovered from gas-phase attack of phenylium ion on MeOH.[2] The distinct site selectivity observed in both systems confirms the singlet-state nature of the decay-formed phenylium ion, which preferentially attacks the *n*-centre of the acceptor, although an increased fraction of products from phenylium-ion insertion into the alkyl groups of the substrate is observed in the MeOPr systems. This trend is even more evident if the product distribution from Pr^{i}OPr^n is taken into account (Table 3). This effect can be ascribed to several factors, including the enhanced hydrocarbon character of the selected ethers with respect to MeOH, which increases the probability of attack of the ionic reactant on the σ electrons of the acceptor. An additional factor may be the decreased magnitude of the dipole moments as the hydrocarbon chains of the acceptor are increased in length [μ 1.69 D (MeOH); 1.15 D (MeOPr); 1.00 D (Pr_2O)],[12] which may affect the degree of orientation of the negative end (the oxygen atom) of the acceptor dipole towards the cation.[13]

The fate of the oxonium ions (2) derived from addition of Ph^+ to the oxygen atom of dialkyl ethers appears to be highly sensitive to the nature of the alkyl groups and of the reaction environment. In the MeOPr^n systems (Table 1), formation of anisole is invariably accompanied by appreciable yields of PhOPr^n and minor amounts of PhOPr^i. It should be noted that, while the relative yield of PhOPr^i as well as that of anisole increases at low pressure (20 Torr), formation of PhOPr^n is favoured at high ether pressure (400 Torr) and in the presence of ammonia (4 Torr). If we consider that unimolecular loss of methyl cation is endothermic by at least 46 kJ mol^{-1}, it follows that formation of PhOPr^n most likely involves a bimolecular nucleophilic displacement at the saturated carbon of the methyl group by the nucleophilic species present in the system, *i.e.* the ether MeOPr^n and NH_3.†

It cannot be excluded *a priori* that a similar bimolecular mechanism could operate in the formation of anisole. This hypothesis, however, contrasts with the large anisole yield observed at low pressure (*i.e.* at low concentration of MeOPr^n) and in the absence of the powerful nucleophile NH_3. It is therefore suggested that any conceivable bimolecular pathway to anisole is largely overwhelmed by a unimolecular dealkylation mechanism, favoured under high-energy conditions (*i.e.* at low pressure) and leading to the same product *via* formal loss of the propyl moiety from the excited oxonium intermediate (2). Scheme 1 shows the simplest reaction network compatible with the results of Table 1.

According to Scheme 1, the relative yields of anisole and PhOPr^n are determined by $k_1/(k_2[\mathrm{MeOPr^n}] + k_3[\mathrm{NH_3}])$, which favours formation of anisole with decreasing [MeOPr^n] and [NH_3], *i.e.* at the lowest ether pressure and in the absence of ammonia. Furthermore, the trends of Table 1 reveal that a minor addition (1 mole %) of NH_3 to MeOPr^n (400 Torr) is effective in shifting the product distribution in favour of PhOPr^n (from 24 to 33%). This implies that NH_3 is much more reactive than MeOPr^n in the nucleophilic displacement at the methyl group of (2) (k_3/k_2 = *ca.* 50).

A sterically congested transition state in the nucleophilic displacement by MeOPr^n may account for such a difference.[15] Structural effects on the rates of bimolecular nucleophilic displacements in the gas phase, however, are not easily predictable since, according to Brauman's double-well potential surface involved in these processes, large nucleophiles are expected to display lower rates than those exhibited by smaller ones.[16] Closely spaced internal energy levels in large molecules favour reversion of the collision complex to reactants rather than progress towards a transition state, where normally some rotational degrees of freedom are inhibited.

Scheme 1 may account for the results from the MeOPr^i systems as well (Table 2). Here, however, the high yield of anisole appears rather insensitive to the system composition and is accompanied by only very minor amounts (0—2%) of PhOPr^i. These results fit Scheme 1 if a unimolecular Pr^i group departure from the corresponding oxonium (2) [equation (iiia)] takes place at rates much higher than any conceivable bimolecular displacement at the methyl group centre [equation (iiib)], under all conditions.

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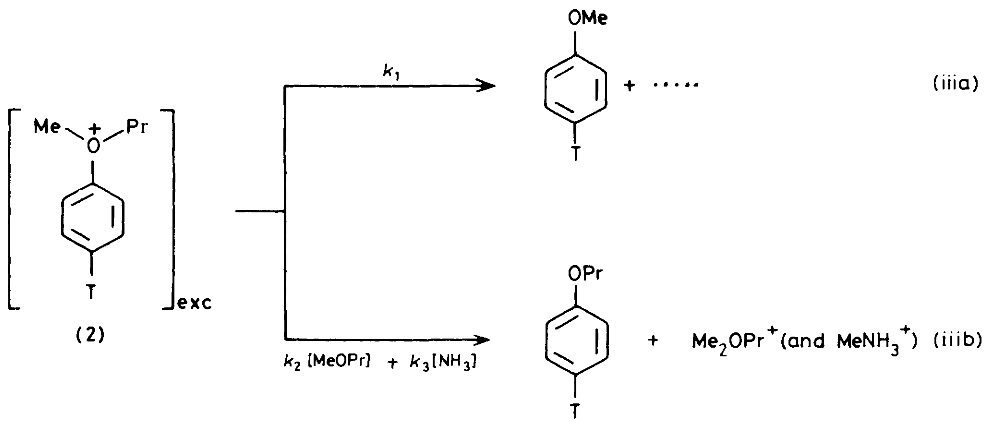
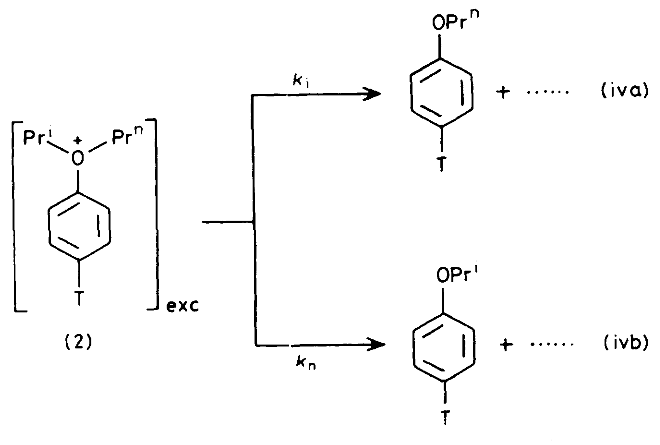
* An exothermicity of $-\Delta H$ = 230—385 kJ mol^{-1} is estimated for the formation of the oxonium ion (2) [equation (iia)], using a value of ΔH° = 1 025—1 129 kJ mol^{-1} for the formation enthalpy of phenylium ion (which depends on its vibrational energy, ref. 2), and approximate values of *ca.* 544 kJ mol^{-1} (R^1, R^2 = Me, Pr) and *ca.* 514 kJ mol^{-1} ($R^1 = R^2$ = Pr) for the ΔH° values of the isomeric intermediates (2). Even a rough estimate of the reaction enthalpy of equation (iib) is impossible owing to the lack of reliable data on the ΔH°_f values of the arenium intermediates (3). However, since the addition of phenylium ion to CH_4 is calculated to be exothermic to the extent of 188—293 kJ mol^{-1}, it is likely that the analogous insertion of (1) into the C–H or C–C bonds of the selected ethers to give ions (3) is an exothermic process.

† Nucleophilic displacement by MeOPr and NH_3 at the methyl group of methylpropylphenyloxonium ions (2) is roughly calculated to be exothermic by *ca.* 33 kJ mol^{-1}. This sort of nucleophilic substitution is found to occur readily in solution as well, as demonstrated by the irreversible formation of PhOMe and Me_3O^+ from $PhOMe_2^+$ and Me_2O in SO_2ClF solution (ref. 14).



Scheme 1.



This behaviour can be ascribed to the greater tendency of Pr^i, with respect to Pr^n, to assume the character of a carbocation and, hence, to dissociate unimolecularly. An alternative explanation can be found in the much lower rate for the bimolecular displacement (iiib), when Pr = Pr^i. That the former factor is the most important is suggested by the results of the phenylium ion attack on Pr^{i}OPr^n (Table 3). A considerable yield of PhOPr^n, which places it among the major products (32—34%), is counterbalanced by the total absence of PhOPr^i. This is only compatible with the unimolecular pattern (iv), with k_i much larger than k_n. In fact, if there is any significant bimolecular contribution by Pr^{i}OPr^n to the dealkylation process, it should be equally efficient at the C$_\alpha$ centre of the two propyl groups or, at most, favour formation of the PhOPr^i isomer, on account of the more hindered and less activated C$_\alpha$ centre of the Pr^i group with respect to Pr^n. However, this is contrary to the experimental results.

Unimolecular Dealkylation Mechanism.—From the previous section, it is concluded that oxonium intermediates (2) undergo extensive unimolecular dealkylation in the gas phase, and that, when involving formal Pr^i group loss, this process is much faster than cleavage of the Pr^n moiety. Given the relatively high excitation energy of the oxonium ions (2), two different mechanisms can be involved in the unimolecular dealkylation pattern, *i.e.* equations (va and b). Both fragmentations are, in fact, thermochemically allowed, being *ca.* 46—167 and 134—238 kJ mol^{-1} exothermic, respectively, when R = Me. Discrimination between these mechanisms is, therefore, allowed only by resort to a mass spectrometric technique, since the neutral anisole would be expected to arise from both mechanisms in the decay experiments. The fragmentation pattern of dialkylphenyloxonium ions, formed from attack of Ph$^+$ on R^{1}OR^2 or from methylation of PhOPr by CH$_3$-FCH$_3^+$ in the source of a mass spectrometer under quite different conditions [total pressure 2×10^{-6} (FT-ICR) and 1.0 (CIMS) Torr], indicates that the unimolecular fragmentation of the oxonium ion (2) invariably follows the most exothermic pathway (vb), involving formation of the protonated ether (4) and propene.[*] The elementary steps which may be involved in the unimolecular dealkylation process (vb) are shown in detail in Scheme 2.

Intervention of the ion–molecule complexes (5) was recently proposed by Morton [17] in a re-examination of the dealkylation mechanism in the gas-phase protonation of PhOPr^n by gaseous Brønsted acids of various strengths.[18] Mechanistic information was obtained by using PhOPr^n selectively deuteriated at the α-, β-, or γ-position of the Pr^n group.

It was noted that high-energy protonation of PhOPr^n induces unimolecular loss of propene *via* non-specific hydrogen transfer from all carbon atoms of Pr^n to the oxygen of the oxonium intermediate (path *a*). The oxonium fragmentation pattern following protonation of PhOPr^n by the least energetic acid is instead consistent with a preliminary intramolecular alkyl isomerization *via* the sequence $(2)^n \longrightarrow (5)^n \longrightarrow (5)^i \longrightarrow (4)$ (path *b*). Intermediacy of species (6) is also consistent with the formation of a doubly deuteriated oxonium (4), observed in these studies.

Several considerations point to the mechanism of Scheme 2 as operative in the decay systems as well. In our high-pressure samples (20—400 Torr), unimolecular cleavage of (2)^n *via* the (5)^n adduct involves a relatively high energy barrier due to the limited tendency of the Pr^n group to assume partial carbocation character. Therefore, this process competes with the accompanying bimolecular displacement (iiib). However, at low pressure (20 Torr), *i.e.* under conditions where high-energy processes are allowed by the lack of efficient collisional deactivation of intermediate (2)^n, sequence $(2)^n \longrightarrow (5)^n \longrightarrow (5)^i \longrightarrow (4)$ can take place efficiently, leading to anisole as the predominant product ([anisole]/[PhOPr^n] = 75). The

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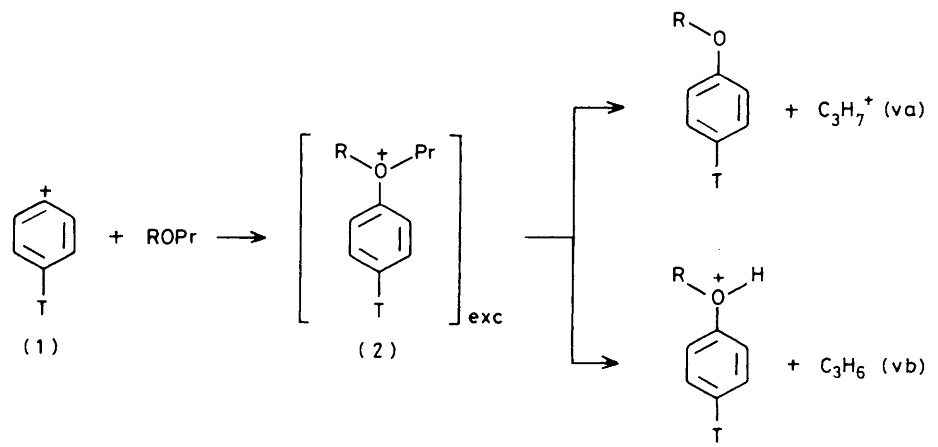
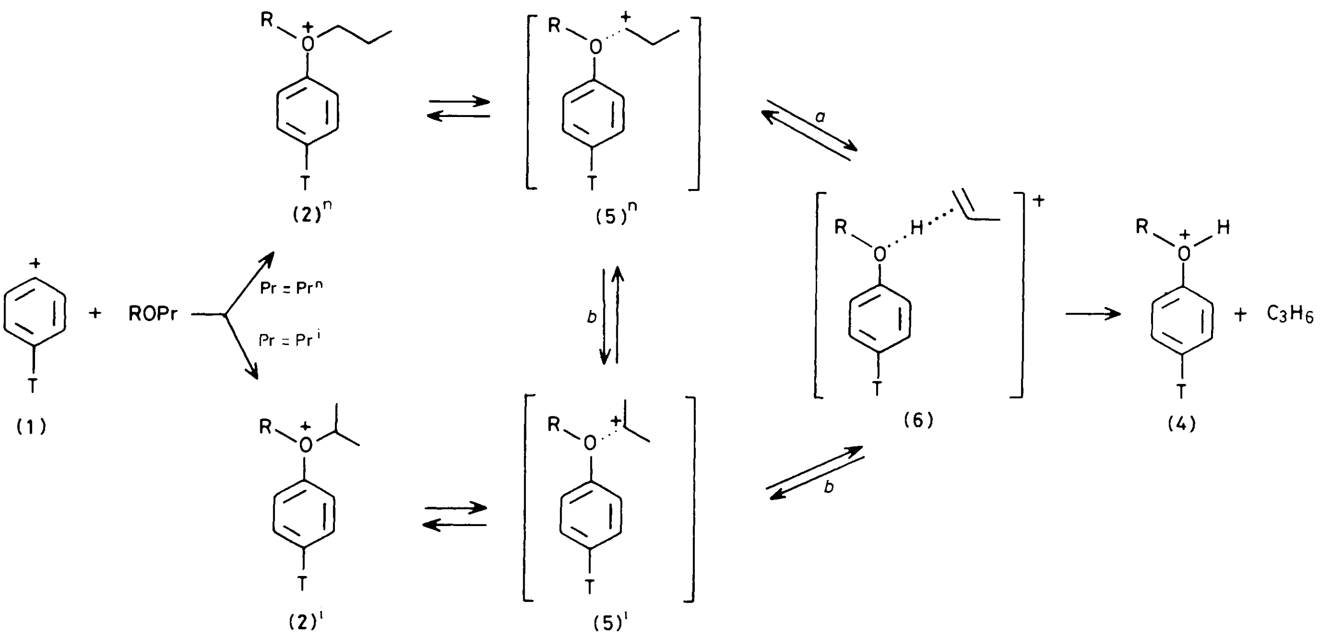
[*] Predominant occurrence of fragmentation (vb) appears rather insensitive to the energy content of oxonium intermediates (2) as well. In fact, it should be noted that, whereas the excitation energy of (2) from Ph$^+$ attack on R^{1}OR^2 amounts to 230—385 kJ mol^{-1}, it is calculated to be 170—190 kJ mol^{-1} when the oxonium ion is generated by the attack of CH$_3$FCH$_3^+$ on the oxygen atom of PhOPr.





Scheme 2.

same sequence also explains the increasing formation of PhOPr^{i} from MeOPr^{n} as the system pressure is lowered. It can be concluded therefore that, when energetically accessible, a fast $(5)^{n} \longrightarrow (5)^{i}$ isomerization process takes place prior to any fragmentation and in competition with the bimolecular demethylation (iiib). A species akin to (5)^{i} may also be regarded as the likely intermediate precursor to the formation of ring-isopropylated anisole *via* migration of the Pr^{i} moiety from the oxygen to the ring of (5)^{i}. The same intramolecular Pr^{i} group transfer is, in fact, observed within intermediate (2)^{i}, directly generated by phenylation of MeOPr^{i} (Table 2).* Finally, as demonstrated by the trends observed in the MeOPr^{i} and Pr^{i}OPr^{n} decay systems, the propensity of the Pr^{i} group of the corresponding oxonium intermediate (2) to assume a partial positive charge, as in (5)^{i}, makes its fragmentation to (4) much faster; this therefore becomes the predominant reaction pathway, irrespective of the experimental conditions.

In conclusion, the present investigation of the gas-phase reaction of phenylium ion with dialkyl ethers has not only extended our knowledge of the nature and the reactivity of the ionic reactant, but has also opened up a way to investigating the intimate nature and the kinetic behaviour of tertiary dialkylphenyloxonium ions in the gas phase. The detailed kinetic study of the reaction pattern accessible to dialkylphenyloxonium ions under different experimental conditions allows us to point out some inconsistencies between the present study and a related investigation of the same processes.[6] Nefedov *et al.*[6] attribute the formation of anisole and alkyl phenyl ethers from the gas-phase attack of phenylium ion on a set of methyl alkyl ethers to intervention of a purely unimolecular fragmentation of the oxonium intermediate to give a carbocation (*e.g.* Me^+ or Pr^{i+} from PhO^+MePr^i) and the ether counterpart, in proportions depending on the thermodynamic stability of the carbocation. This proposed mechanism contrasts with the endothermicity (ΔH = 46—150

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* Intermolecular routes to ring-propylated anisole, *e.g. via* propyl group transfer from (2) to the anisole formed from reaction (iiia), can be safely excluded on the grounds of the exceedingly low concentrations of the tritiated anisole in comparison with the other substrates present in the medium (*i.e.* MeOPr, NH_3, *etc.*).

kJ mol^{-1}) of the unimolecular methyl cation loss from methylalkylphenyloxonium ions and with their recognized tendency to lose alkyl groups as neutral alkene moieties, leaving the positive charge on the aromatic fragment.

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