Gas-phase Reaction of Free Isopropyl Ions with Phenol and Anisole

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Unsolvated isopropyl ions, obtained in the dilute gas state from the radiolysis of propane, react with PhOH yielding isomeric isopropylphenols and isopropyl phenyl ether, in the ratio of *ca.* 3 : 1 at 320 Torr. At lower pressures, the ratio is further shifted in favour of ring alkylation, reaching a value in excess of 10 : 1 at 22 Torr. The isomeric composition of isopropylphenols passes from 83% *ortho*, 3% *meta*, 14% *para* at 720 Torr to 61% *ortho*, 3% *meta*, 36% *para* at 22 Torr. A similar pressure dependence characterizes the isomeric composition of products from the alkylation of PhOMe, which passes from 85% *ortho*, 5% *meta*, 10% *para* in C_3H_8 at 720 Torr to 64% *ortho*, 21% *meta*, and 15% *para* at 20 Torr. The substrate selectivity of isopropyl ion, referred exclusively to the alkylation, is measured by the apparent ratios $k_{PhOH} : k_{PhH}$ = 1.0—1.6 and $k_{PhOMe} : k_{PhMe}$ = 0.6—0.9 at 720 Torr. The results are consistent with a model involving *kinetically* predominant attack to the oxygen atom, *i.e.* to the *n*-type nucleophilic centre of the ambident substrate, and competition between proton transfer and alkylation channels, reflecting respectively the Brønsted acid and the Lewis acid reactivity of the alkyl cation. The role of isomerization processes in determining the orientation has been independently evaluated by protonating isopropyl phenyl ether with gaseous Brønsted acids, such as H_3^+ and $C_nH_5^+$ (*n* = 1 or 2), thus obtaining *via* an independent route the same oxonium ion arising from the attack of isopropyl ion on PhOH. The results demonstrate dealkylation to PhOH and *intramolecular* isomerization to *o*- and *p*-isopropylphenols, whose ratio depends on the nature of the Brønsted acid, and the exothermicity of the proton transfer to the ether.

It has been previously shown that alkylation of phenol and anisole by free t-butyl cations in the dilute gas state occurs predominantly at the oxygen atom of the substrate, yielding substituted oxonium ions as the major primary condensation products.[1,2]

In order to ascertain whether the remarkably selective attack on the *n*-type nucleophilic centre of these typical ambident substrates represents indeed a general feature of the gas-phase reactivity of free carbonium ions, or is rather a peculiar behaviour of the t-butyl cation, the investigation has been extended to the isopropyl ion, a reagent characterized by a considerably more pronounced electrophilic character and by appreciably reduced steric requirements when compared with t-$C_4H_9^+$.

EXPERIMENTAL

Materials.—Phenol, anisole, benzene, toluene, and cumene were research grade chemicals, or gas chromatographic standards from Merck and C. Erba. Propane, oxygen, and ammonia were research grade gases from Matheson or SIO. The cymenes, used as g.l.c. standards, were prepared and purified as described elsewhere.[2] A mixture of isopropylanisoles was obtained from the reaction of C_6H_5OMe with Me_2CHCl in the presence of $AlCl_3$ at 50° for 4 h, the individual isomers being resolved by preparative g.l.c. over a 4 m Apiezon L grease column at 130°, and identified by i.r. and n.m.r. spectroscopy. The isopropylphenols were prepared from the corresponding pure isopropylanisoles on treatment with HI, according to established procedures.[3] Isopropyl phenyl ether was obtained by alkylation of phenol with isopropyl iodide in alkaline solution,[4] and purified by preparative g.l.c. over an 8-m Apiezon L grease column at 130°.

Irradiation.—The gaseous reaction mixtures were prepared introducing the bulk constituent of the system, C_3H_8 (or, respectively, CH_4 and H_2, in the protonation of i-$C_3H_7OC_6H_5$) and the required additives (O_2, NH_3) together with fragile, weighed glass ampoules containing the aromatic substrates, into evacuated and carefully outgassed Pyrex bulbs, as described elsewhere.[1,2]

After sealing off the bulbs, the fragile ampoules were broken and sufficient time was allowed for equilibration of the system. The irradiation was then carried out at room temperature, at a dose rate of 5.5 KGy h^{-1}, to a total dose of *ca.* 12 KGy in a 220 Gammacell from Nuclear Canada.

Analysis of Products.—The irradiated vessels were frozen at 77 K, then a known amount of diethyl ether was added, and the contents of the bulbs subjected to repeated freeze–thaw cycles. The walls of the vessel were carefully washed with the ether solution, and known portions of the latter were subjected to g.l.c. using either a Hewlett–Packard model 5700A, or a C. Erba model 2400T gas chromatograph, equipped with f.i.d. units. The products from the competitive isopropylation of phenol and benzene were separated with a 4-m Apiezon L grease column, initially at the constant temperature of 120° for 60 min, then raising the temperature at a rate of 32° min^{-1} to the final value of 150°. The products from the competitive alkylation of anisole and toluene were analysed with an 8-m column, packed with Apiezon L grease and operated isothermally at 140°. Identification of the products was accomplished by comparing their retention times with those of authentic samples under the same chromatographic conditions, or, when required, by g.l.c.–mass spectrometry, using a Hewlett–Packard model 5982A instrument.

The *relative* yields of products were determined from the area of the correspondent elution peak, corrected for the specific response of the f.i.d. unit to the various compounds of interest. The *absolute* yields could be roughly determined from the total amount of products formed, as deduced from the chromatographic analysis of precisely measured portions of the ether solution, taking into account the total volume of the latter, and the total dose received by the gaseous system. Suitable blank analyses were carried out to verify the absence of the relevant irradiation products in the reagents and the solvent used.

RESULTS

The *relative* yields of the products from the competitive reaction of phenol and benzene with the gaseous isopropyl ion are given in Table 1 as a function of the pressure and composition of the gaseous system.

It should be noted that in these experiments, benzene has been used instead of toluene, generally adopted as the reference substrate in competitive gas-phase alkylations,[5] to avoid the difficulties associated with a quantitative g.l.c. determination of the poorly resolved *p*-cymene–isopropyl phenyl ether pair.

Table 2 gives the *relative* yields of the products from the competitive reaction of anisole and toluene for gaseous i-$C_3H_7^+$. In order to provide a link between the relative reactivity data listed in Tables 1 and 2, a concise account of the benzene–toluene competition for the isopropyl cations is given in Table 3. As previously noted,[1,2] the *absolute* yields are of limited significance, owing to the alternative reaction channels, *i.e.* protonation *versus* alkylation, available to the electrophile, and to the presence of other nucleophiles, either deliberately added to the system (*e.g.* NH_3), or formed in variable amounts from its radiolysis, which compete with the aromatic substrate(s) for the alkyl cation.

TABLE 1

Gas-phase competition of phenol and benzene for i-$C_3H_7^+$

System composition (Torr)						Relative yield of products (%)		Isomeric composition of Isopropylphenols		
Propane	O_2	NH_3	Phenol	Benzene	$k_{phenol} : k_{benzene}$	ROC_6H_5	HOC_6H_4R	*o*	*m*	*p*
720	10		0.55	0.57	1.0	28.9	71.1	83.2	2.5	14.3
720	10		0.59	1.69	1.6	24.0	76.0	83.4	2.9	13.7
400	5		0.52	0.85	2.0	32.2	67.8	81.0	2.7	16.3
100	3		0.50	0.50	3.2	24.0	76.0	79.0	2.5	18.5
22	2		0.59	0.71	2.6	8.4	91.6	60.9	3.2	35.9
20	4	2	0.52	1.11	1.5	8.3	91.7	45.1	n.d.	54.9

TABLE 2

Gas-phase competition of anisole and toluene for i-$C_3H_7^+$

System composition (Torr)						Relative yields of products (%)					
						Isopropylanisoles			Cymenes		
Propane	O_2	NH_3	Anisole	Toluene	$k_{anisole} : k_{toluene}$	*o*	*m*	*p*	*o*	*m*	*p*
720	10		0.86	1.29	0.7	90.7	4.5	4.8	47.7	28.2	24.1
720	10		1.73	0.31	0.9	86.3	5.3	8.4	46.6	31.5	21.9
720	10		0.36	1.67	0.6	82.3	6.0	11.7	44.4	30.3	25.3
720	10	5	0.79	0.84	0.7	79.7	4.8	15.5	42.5	34.9	22.6
100	2		0.75	0.82	0.6	85.0	9.5	5.5	31.0	43.2	25.8
20	2		0.84	0.84	0.5	63.8	21.0	15.2	13.0	68.8	18.2
20	2	2	0.66	0.63	0.5	57.8	16.6	25.6	7.2	81.8	11.0

Competition by other nucleophiles accounts, *inter alia*, for the observed dependence of the absolute yield on the concentration of the aromatic substrate(s). In any event, alkylation represents a significant reaction channel for the i-$C_3H_7^+$ ions from the radiolysis of propane. Thus, in neat C_3H_8 at 720 Torr, [PhOH] = 10^{-4}M, and at a dose of 12 RGy, the combined $G(+M)$ values of alkylated aromatic compounds amount to *ca.* 0.5, which corresponds to an absolute yield of *ca.* 15%.

TABLE 3

Gas-phase competition of benzene and toluene for i-$C_3H_7^+$

System composition (Torr)					
Propane	O_2	NH_3	Benzene	Toluene	$k_{toluene} : k_{benzene}$
720	10		1.18	1.14	0.8
720	10		1.18	1.25	0.8
400	5		1.24	1.04	0.8
100	3		1.06	0.78	0.6
22	2		0.68	0.70	0.6
22	2		0.81	0.56	0.5
20	4	2	0.70	0.53	1.1

The precision of the data given in the Tables, as measured by the standard deviation of duplicate runs, is of the order of slightly less than 10%, unless indicated otherwise.

DISCUSSION

The Reagent.—Extensive radiolytic[6-9] and mass spectrometric studies[10-13] show that the isopropyl ion, formed either directly or *via* fast hydride transfer from C_3H_8 to fragment cations, *e.g.* $C_2H_5^+$ and $C_3H_5^+$, is the major charged species formed from the radiolysis of propane, with a $G(+M)$ value of *ca.* 3 in the pressure range of interest in the present study.[14]

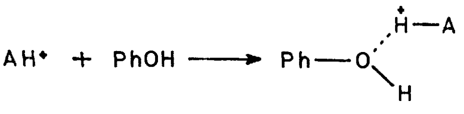
The n-propyl ions, that are also formed from the C_3H_8 radiolysis, are known to rearrange rapidly[15] to the secondary structure, consistent with our observation that only minute traces of n-propylated products are formed from phenol and anisole.

Owing to the known lack of reactivity of the i-$C_3H_7^+$ ion toward propane, and to the large excess of the latter over the aromatic substrate, it is reasonable to assume that the thermolysed i-$C_3H_7^+$ ion is the only charged reagent whose attack to phenol and anisole needs to be considered. In addition, the presence of an efficient scavenger, O_2, is expected to suppress any contribution of thermal radical reactions to the alkylation process, whose ionic character is independently confirmed by the strong depression of the absolute yields caused by the addition of small amounts of NH_3, an effective interceptor of the i-$C_3H_7^+$ cation, which is deprotonated to propene.

Energetics of Isopropyl Ion Attack.—Two major exothermic reaction channels, *i.e.* protonation and alkylation, are available to the isopropyl cation, characterized by a H_f^0 value of 795—803 kJ mol^{-1}, as deduced from mass spectrometric measurements[16] and from theoretical calculations.[17] Protonation, widely exploited in chemical ionization mass spectrometry, is exothermic for all substrates investigated, with ΔH^0 values ranging from *ca.*

-8 kJ mol^{-1} for benzene and *ca.* -42 kJ mol^{-1} for toluene to *ca.* -54 kJ mol^{-1} for phenol and *ca.* -75 kJ mol^{-1} for anisole.[18]

On the site of protonation, the available data suggest that proton transfer from i-$C_3H_7^+$ is energetically allowed both to the ring positions and to the oxygen atom, despite the recognized lower proton affinity (PA) of the latter.[19] In this connection, it should be noted that proton transfer from t-$C_4H_9^+$ to the ring positions of PhOH and PhOMe is also allowed, while the PA of i-C_4H_8 is *higher* than that of the oxygen atom, making its protonation by t-$C_4H_9^+$ an energetically unfavourable process.



$$\mathrm{AH^{+} + PhOH \longrightarrow Ph{-}O(H)\cdots \overset{+}{H}{-}A} \qquad (7)$$

(III)

Scheme

Calculation of the enthalpy changes for the alkylation processes (2a and b) is prevented by the lack of thermochemical data on the arenium and oxonium ions formed. Reasonable estimates * lead to ΔH^0 values of *ca.* -145 kJ mol^{-1} for *O*-isopropylation, and *ca.* -167 kJ mol^{-1} for ring isopropylation of phenol.

Alkylation versus *Protonation following Isopropyl Ion Attack*.—Any reaction scheme concerning the gas-phase attack of i-$C_3H_7^+$ to phenol and anisole should account for the apparent lack of substrate selectivity, *e.g.* $k_{PhOH} : k_{PhH}$ *ca.* 1, and for the low extent of *O*-alkylation, *e.g.* the much lower yield of isopropyl phenyl ether when compared with those of isopropylphenols, especially in the experiments carried out at the highest C_3H_8 pressures, under conditions favouring kinetic control of products. Both these features can be contrasted with those observed in the strictly related gas-phase t-butylation, characterized by a much higher substrate selectivity and by the predominance (up to 8 : 1) of *O*-alkylation over ring alkylation.[1,2]

The significant variation of the relative *k* ratios measured in the competition experiments with the [PhOH] : [PhH], or the [PhOMe] : [PhMe] ratios, suggesting the occurrence of intermolecular alkyl transfer processes, must also be taken into account.

A schematic outline of the suggested reactivity pattern of i-$C_3H_7^+$ toward phenol is illustrated in the Scheme, which applies to anisole as well, with the obvious exception of process (3a). Discussing i-$C_3H_7^+$ attack, it should be considered, in the first place, that protonation products cannot be detected under the experimental conditions prevailing in the present study, and consequently the apparent *k* ratios given in the Tables *refer exclusively to the alkylation channel* [equations (2a and b)], rather than to the overall nucleophilic reactivity of the aromatic substrates toward the charged electrophile.

Therefore, the reactivity data deduced from competition experiments are necessarily affected by the relative rate of the alkylation and the protonation processes promoted by the i-$C_3H_7^+$ attack to each substrate involved. The typical features of isopropylation, and the substantial differences with t-butylation can be rationalized assuming, in agreement with previous conclusions,[1,2] that the gas-phase attack of the unsolvated alkyl cation to typical ambident substrates such as PhOH and PhOMe is kinetically biased in favour of the oxygen atom (*n*-type nucleophilic centre).

In addition, the rate of proton transfer from i-$C_3H_7^+$ to the oxygen atoms, whenever energetically allowed, predominates over the rate of *O*-alkylation.

This view is strongly supported by recent mass spectrometric evidence,[20] showing that *exothermic* proton transfer from a gaseous Brønsted acid to the oxygen atom of phenol is *kinetically* predominant over ring protonation.

Accordingly, we suggest that the i-$C_3H_7^+$ reagent, which is capable of exothermically protonating the oxygen atom of PhOH and PhOMe, reacts predominantly with the *n*-type centre of these substrates, acting as a Brønsted acid, which accounts for the relatively low yields of *O*-isopropylated product. On the other hand, as proton transfer from t-$C_4H_9^+$ to the oxygen atom of PhOH and PhOMe is endothermic, the electrophile can only react with the *n*-type centre of these substrates as a Lewis acid, which accounts for the high extent of *O*-alkylation, and for the higher overall (*i.e.* including both *O*- and ring-alkylation) substrate selectivity measured in the gas-phase t-butylation under conditions of kinetic control of products.

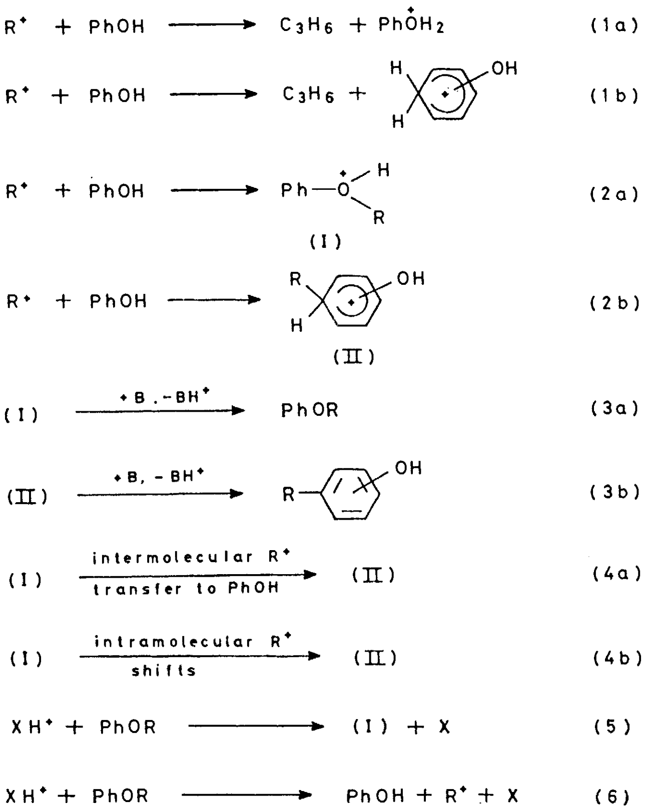
It should be noted in this connection that if one refers exclusively to *ring* alkylation, where competition between protonation and alkylation channels is energetically allowed for both electrophiles, the substrate selectivity of i-$C_3H_7^+$ and t-$C_4H_9^+$ becomes comparable, as also observed in their reactions with anisole, whence, of course, no stable *O*-alkylated products can be isolated.

Incidentally, the occurrence of exothermic reaction channels for both alkylation and protonation of benzene and toluene by i-$C_3H_7^+$ helps explain the lack of substrate selectivity of the reagent toward these arenes, in sharp contrast with the remarkable selectivity of t-$C_4H_9^+$, whose only exothermic reaction channel is alkylation of toluene.[21]

The kinetically predominant attack on the oxygen atom can be rationalized by postulating the preliminary solvation (or ' clustering ') of the gaseous cation, that is more likely to involve the *n*-type substituent of the ambident substrate, *e.g.* reaction (7), followed by the collapse of the adduct either by a fast [22] proton transfer, if energetically favourable, or by a condensation process like (2a). Ion–molecule pairs similar to (III) are well known and quite stable in the gas phase, as shown by the

* Value arrived at by estimating the ΔH_f^0 value of i-C_3H_7Ph (A) and *p*-isopropylphenol (B) from data taken from D. R. Stull, E. T. Westrum, jun., and G. C. Sinke, ' The Chemical Thermodynamics of Organic Compounds,' Wiley, New York, 1968, and with the further assumptions (i) that the PA of the ring position of (B) bearing the isopropyl group is approximately equivalent to that of phenol, and (ii) that the PA of the oxygen atom of (A) corresponds to *ca.* 795 kJ mol^{-1} (*cf.* refs. 18 and 19).

extensive mass spectrometric work of Kebarle.[23] Their role in enhancing specific reaction pathways has been frequently postulated,[24] showing in particular the ability of oxygen atoms, or other *n*-type nucleophilic centres, to establish strong ' solvation ' or ' clustering ' bonds with a variety of gaseous cations.



Clearly, preliminary formation of the adduct (III) would favour the attack of the alkyl cations to the oxygen atom of phenol and anisole, thus enhancing the relative rate of processes (1a) or (2a), depending on the energies of the proton transfer reaction, over that of the competing channels (1b) and (2b).

Predominant ortho-*Orientation: Role of Intramolecular Isomerization of* (I).—Initial electrophilic attack to a substituent with unshared electron pairs, implying the intermediacy, and the subsequent intramolecular isomerization of a primary *n*-adduct, has been frequently postulated to account for disproportionately high yields of the *ortho*-isomers.[25]

This time-honoured mechanistic hypothesis deserves special consideration in the present case, owing to (i) the unusual degree of *ortho*-orientation, the highest so far measured in gas-phase aromatic substitution by unsolvated cations, and (ii) the evidence from low-pressure alkylations, suggesting the possible isomerization of the oxonium ion (I) to the arenium ion (II).

Per se, the alkylation experiments do not show conclusively the occurrence of isomerization, and do not establish the intermolecular [equation (4a)] or intramolecular [equation (4b)] nature of the process, even though some indication of intermolecular R^+ transfer between aromatic substrates is provided by the dependence of the apparent *k* ratios on the relative concentration of the competing aromatic compounds (Tables 1 and 2).

In order to gather independent evidence on the isomerization of (I), isopropyl phenyl ether has been protonated in the gas phase with Brønsted acids of different strength, namely H_3^+ from the irradiation of H_2, and $C_nH_5^+$ ($n = 1$ or 2) from the irradiation of methane, as illustrated in Table 4. The exothermicity of the proton transfer (5) to the oxygen atom of the substrate can be estimated [18, 26, *] to range from *ca.* −376 for $X = H_2$ to *ca.* −250 for $X = CH_4$, to *ca.* −125 kJ mol^{-1} for $X = C_2H_4$. Direct dealkylation (6) is also exothermic for all acids concerned. It should be noted that, under the present experimental conditions, formation of isopropylphenols cannot involve *intermolecular* isomerization, since R^+ transfer from (I) to another aromatic molecule should give instead ROC_6H_4R, owing to the enormous excess of PhOR over any PhOH present in the gas.

Inspection of Table 4 shows that both dealkylation and isomerization of the ether occur, in a ratio depending on the nature and the strength of the acid, that also considerably affects the *ortho* : *para* ratio of the isopropylphenols from the isomerization channel.

In contrast with the predominant dealkylation promoted by H_3^+, the milder $C_nH_5^+$ reagents give comparable yields of PhOH and isopropylphenols, whose isomeric composition is shifted in favour of the *ortho*-isomer.

TABLE 4

Reaction of gaseous Brønsted acids with isopropyl phenyl ether

System composition (Torr)					PA of X	Relative yields (%)		RC_6H_4OH isomeric composition (%)	
H_2	CH_4	O_2	Substrate	Acid HX^+	(kJ mol^{-1})	PhOH	RC_6H_4OH	*o*	*p*
720		10	1.2	H_3^+	422.6 [a]	90 [b]	10 [b]	*ca.* 38 [c]	*ca.* 62 [c]
	720	10	0.6	CH_5^+ $C_2H_5^+$	535.6 [a] 636.0 [d]	44 [b]	56 [b]	59 [b]	41 [b]

[a] Ref. 18. [b] Standard deviation of data *ca.* 10%. [c] Standard deviation of data *ca.* 20%. [d] Ref. 26.

The evidence from the protonation of i-C_3H_7OPh does not unambiguously answer the central mechanistic question concerning the role of (I) in determining the predominant *ortho*-alkylation.

In fact, on one hand, i-C_3H_7OPh appears to undergo *intramolecular* isomerization to (II), following gas-phase protonation, contrary to the behaviour of t-C_4H_9OPh, which undergoes, in a comparable experiment, exclusively dealkylation and/or intermolecular R^+ transfer, as expected from the higher stability of free t-$C_4H_9^+$ with respect to i-$C_3H_7^+$.

On the other hand, intramolecular isomerization of (I) leads to the *p*-, in addition to the expected *o*-isopropylphenol, whose yields, at least with the gaseous acids investigated, fall short of accounting for the high degree of *o*-alkylation of PhOH and PhOMe by i-$C_3H_7^+$.

While intramolecular R^+ transfer to the *para*-position of the ring in the gas-phase isomerization of (I) is *per se* an interesting, if not entirely unexpected result,† which deserves further investigation, a possible clue to the discrepancy between alkylation and protonation can perhaps be found in the strong dependence of the *ortho* : *para* ratio on the exothermicity of the process leading to the formation of (I), which in turn determines the excitation level of oxonium ion.

It appears that a higher exothermicity of the proton transfer to PhOR enhances the yield of the *para*-alkylated phenol from its isomerization. In this connection, proton transfer from H_3^+ and CH_5^+ to PhOR are considerably more exothermic than reaction (2a), which could explain the lower extent of *ortho*-substitution from (5) when compared with alkylation of phenol and anisole.

Finally, it has been observed that $C_2H_5^+$, a major ion from the radiolysis of CH_4, behaves toward isopropyl phenyl ether as a Lewis acid as well, yielding ethylphenylisopropyl ethers, whose isomeric composition is roughly 60% *ortho*, 10% *meta*, 30% *para*, *without appreciable formation of ethyl phenyl ether*. This observation supports the view that interaction of alkyl ions at the oxygen atom of phenols (or their ethers) occurs predominantly by proton transfer, if energetically allowed.

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† The *intramolecular* isomerization of alkyl ethers to *o*- and *p*-alkylphenols has been frequently suggested in solution chemistry studies. See ref. 25 and 'The Chemistry of the Ether Linkage,' ed. S. Patai, Interscience, New York, 1967, p. 628, and references therein.

REFERENCES

[1] M. Attinà, F. Cacace, G. Ciranni, and P. Giacomello, *J. Amer. Chem. Soc.*, 1977, **99**, 4101.

[2] M. Attinà, F. Cacace, G. Ciranni, and P. Giacomello, *J. Amer. Chem. Soc.*, 1977, **99**, 5022.

[3] W. J. Close, B. D. Tiffany, and M. A. Spielman, *J. Amer. Chem. Soc.*, 1949, **71**, 1265.

[4] W. T. Olson, H. F. Hipsher, C. M. Buess, I. A. Goodman, I. Hart, J. H. Lamneck, jun., and L. C. Gibson, *J. Amer. Chem. Soc.*, 1947, **69**, 2451.

[5] See for instance (*a*) F. Cacace and P. Giacomello, *J. Amer. Chem. Soc.*, 1973, **95**, 5851; (*b*) P. Giacomello and F. Cacace, *ibid.*, 1976, **98**, 1823, and references therein. The choice of toluene, instead of benzene, as a reference substrate was suggested by the insufficient reactivity of the latter arene toward mild gaseous electrophiles, such as t-$C_4H_9^+$.

[6] P. Ausloos and S. G. Lias, *J. Chem. Phys.*, 1962, **36**, 3163.

[7] S. G. Lias and P. Ausloos, *J. Chem. Phys.*, 1962, **37**, 877.

[8] P. Ausloos, in 'Ion-molecular Reactions,' ed. J. L. Franklin, Plenum Press, New York, 1970.

[9] G. R. Freeman, *Radiation Res. Rev.*, 1968, **1**, 1, and references cited therein.

[10] M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Phys. Chem.*, 1964, **68**, 3039.

[11] K. R. Ryan and J. H. Futrell, *J. Chem. Phys.*, 1965, **42**, 819.

[12] L. I. Bone and J. H. Futrell, *J. Chem. Phys.*, 1967, **46**, 4084.

[13] G. A. W. Derwish, A. Galli, A. Giardini, and G. G. Volpi, *J. Chem. Phys.*, 1964, **41**, 2998.

[14] S. G. Lias, R. E. Rebbert, and P. Ausloos, *J. Amer. Chem. Soc.*, 1970, **92**, 6430.

[15] D. J. McAdoo, F. W. McLafferty, and P. F. Bent III, *J. Amer. Chem. Soc.*, 1973, **94**, 2027.

[16] For a review, see S. L. Fanklin, 'Carbonium Ions,' eds. G. A. Olah and P. v. R. Schleyer, Wiley, New York, 1968, vol. I, p. 77.

[17] L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1972, **94**, 5935.

[18] A recent review of gas-phase PA values is given by (*a*) P. Kebarle, *Ann. Rev. Phys. Chem.*, 1977, **28**, 445. See also (*b*) Yamdagni and P. Kebarle, *J. Amer. Chem. Soc.*, 1976, **98**, 1320; (*c*) Y. K. Lau and P. Kebarle, *ibid.*, 1976, **98**, 7452; (*d*) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, jun., J. L. Beauchamp, and R. W. Taft, *ibid.*, 1977, **99**, 5417.

[19] See ref. 18*c*, confirmed by mass spectrometric measurements of (*a*) F. M. Benoit and A. G. Harrison, *J. Amer. Chem. Soc.*, 1977, **99**, 3980; and by theoretical calculations of (*b*) D. J. De Frees, R. T. McIver, jun., and W. J. Hehre, *ibid.*, 1977, **99**, 3853.

[20] D. P. Martinsen and S. E. Buttrill, jun., *Org. Mass Spectrometry*, 1976, **11**, 762, and discussion of their data in ref. 19*a*.

[21] See, for instance, ref. 5*a*.

[22] D. Holtz, J. L. Beauchamp, and S. D. Woodgate, *J. Amer. Chem. Soc.*, 1970, **92**, 7485.

[23] P. Kebarle in 'Ion-molecule Reactions,' ed. J. L. Franklin, Butterworths, London, 1972, vol. I, p. 315.

[24] See D. P. Ridge and J. L. Beauchamp, *J. Amer. Chem. Soc.*, 1974, **96**, 637, and references cited therein.

[25] See for instance (*a*) H. J. S. Dewar, 'Molecular Rearrangements,' ed. P. de Mayo, Wiley, New York, 1963; (*b*) R. O. C. Norman and R. Taylor, 'Electrophilic Substitution of Benzenoid Compounds,' Elsevier, New York, 1965; (*c*) H. I. Shine, 'Aromatic Rearrangements,' Elsevier, New York, 1967; (*d*) E. C. Taylor and A. McKillop, *Accounts Chem. Res.*, 1970, **3**, 345 and references cited therein.

[26] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Heron, K. Draxl, and F. H. Field, 'Ionization Potentials and Heats of Formation of Gaseous Ions,' NSRDS–NBS 26, U.S. Government Printing Office, Washington, 1969.