a solvent in the data space. Unfortunately, there are no experimental values available for comparison purposes. However, a paper has recently appeared by Bohme, *et al.*,[2a] where many experimental relative gas phase acidities are reported. The order of magnitude of our results for the relative gas phase acidity rates reported in Table VIII is quite reasonable in the light of their experimental data. Our data indicate that an ortho substituent has a greater effect on gas phase acidities than on the corresponding solution acidities. This effect decreases as the substituent is moved to the metal and para positions. However, a more detailed critique of our predicted values must wait until the appropriate experimental data are available.

Referring back to Table VII, it is interesting to further note that the solute coefficients of the uniqueness for ethylene glycol solvent have relatively high values only for *o*-OCH_3 and *p*-NO_2. This might indicate that either a true unique type of solute–solvent interaction is occurring for these two solutes in ethylene glycol, or possibly that there is some error in the reported values of these cases.

In conclusion, an attempt was made to show that the mathematical technique of factor analysis can be quite useful in studying the effects of solvent on reaction rates. In the present case, it was shown that for substituted benzoic acids in various solvents only two main solvent effects must be accounted for, namely electrostatic and van der Waals' interactions, and that the latter interaction can be calculated in terms of the continuum model of Linder.[12a] Further, the linear free energy model, as expressed by eq 4, can be used to isolate and predict relative gas phase acidities from solution data. Listings of the factor analysis computer program are available on request.

Acknowledgments. The author would like to thank Dr. Andrew P. Stefani, Dr. Robert B. Scott, Dr. Robert M. Metzger, Dr. Norman E. Heimer, and Dr. John I. Brauman for their helpful comments and discussions during the preparation of this manuscript.

Gas-Phase Reaction of *tert*-Butyl Ions with Arenes. Remarkable Selectivity of a Gaseous, Charged Electrophile

Fulvio Cacace* and Pierluigi Giacomello

Contribution from the Laboratorio di Chimica Nucleare del C.N.R.,
Istituto di Chimica Farmaceutica, University of Rome, 00100 Rome, Italy.
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Abstract: *tert*-Butyl ions from the γ radiolysis of neopentane were allowed to react in the gas phase with benzene, toluene, and their mixtures, contained at low concentrations in the gas. The reaction was studied at neopentane pressures ranging from 8.7 to 720 Torr, in the presence of a thermal radical scavenger (O_2). The effects of a gaseous base (EtOH) and of an inert gas (Ar) on the reaction were also investigated. The *tert*-butyl ions react with toluene in the gas phase, yielding *p*- and *m-tert*-butyltoluenes, whose ratio markedly increases with the pressure of neopentane and the concentration of the base. At the higher neopentane and base pressures, the isomeric composition of the products appears to be kinetically controlled and corresponds to a para : $^1/_2$ meta ratio in excess of 35. This value is fully comparable to the highest ratios measured in the study of the liquid-phase *tert*-butylation and reflects the remarkable *positional* selectivity of the gaseous, unsolvated *tert*-butyl cation. Furthermore, the gaseous reagent displays a significant *substrate* selectivity, as indicated by a k_T/k_B ratio in excess of 55 measured in the competition experiments. The mechanism of the gas-phase alkylation is discussed and compared with those of different gaseous electrophiles, characterized by a considerably lower selectivity. It is concluded that a low *positional* and *substrate* selectivity does not necessarily represent a typical mechanistic feature of the gas-phase aromatic substitutions by charged reagents and that the low selectivity observed in previous studies is likely to arise from the extreme electrophilic character of the reagents so far investigated.

New experimental techniques that allow the determination of the neutral reaction products and their isomeric composition have been recently applied to the study of gas-phase aromatic substitutions involving charged electrophiles, whose positional selectivity could be therefore measured for the first time.

The results indicate that the reagents employed, including He^3H^+ from the β decay of $^3H_2$,[1-3] $^{80}Br^+$ from the isomeric transition of $CH_3{}^{80m}Br$,[4] and radiolytically formed $^2H_2{}^3H^+$[5] and i-$C_3H_7^+$,[6,7] display indeed a significant *positional* selectivity.

On the other hand, the selectivity measured in the gas phase was always substantially lower than in most aromatic substitutions occurring in solution.

From the available data it could hardly be decided whether the low positional selectivity represented a general mechanistic feature of the gas-phase attack or should rather be traced to the specific reactivity of the

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(1) F. Cacace and S. Caronna, *J. Amer. Chem. Soc.*, **89**, 6848 (1967).
(2) F. Cacace and G. Perez, *J. Chem. Soc. B*, 2086 (1971).
(3) F. Cacace, R. Cipollini, and G. Ciranni, *J. Chem. Soc. B*, 2089 (1971).
(4) F. Cacace and G. Stöcklin, *J. Amer. Chem. Soc.*, **94**, 2518 (1972).
(5) F. Cacace, R. Cipollini, and G. Occhiucci, *J. Chem. Soc., Perkin Trans. 2*, 84 (1972).
(6) S. Takamuku, K. Iseda, and H. Sakurai, *J. Amer. Chem. Soc.*, **93**, 2420 (1971).
(7) F. Cacace and E. Possagno, *J. Amer. Chem. Soc.*, **95**, 3397 (1973).

few electrophiles so far investigated. In fact, He^3H^+, $^2H_2{}^3H^+$, $^{80}Br^+$, and i-$C_3H_7^+$ ions can all be regarded as extremely powerful electrophiles, and their highly exoergic attack on the substrate is likely to be intrinsically indiscriminate, irrespective of the environment.

The considerable mechanistic and theoretical significance attached to the aromatic substitutions occurring in the gas phase, under conditions where the attacking electrophile and the substituents effects are not affected by interactions with the solvent, stimulated an investigation concerning the selectivity of a considerably milder gaseous cation.

The reagent chosen for the experiments presented in this paper was the *tert*-butyl ion, which can be conveniently generated in the gas phase by radiolytic techniques. In fact, a series of careful investigations carried out by Ausloos and coworkers[8-11] conclusively demonstrated that the irradiation of gaseous neopentane leads to the predominant formation of the *tert*-butyl cation, which represents by far the major charged fragment from the radiolysis, with a ion pair yield approaching 0.75 at a pressure of 200 Torr.[10]

Furthermore, the t-$C_4H_9^+$ ion does not react with neopentane at any appreciable extent,[12] which allows the study of its reactivity toward aromatic substrates introduced at low concentrations into the gaseous system. According to the information currently available on the standard formation enthalpy of gaseous t-$C_4H_9^+$, its attack on benzene and toluene was expected to be considerably less exothermic than the other aromatic substitutions so far investigated in the gas phase.

Experimental Section

Materials. Benzene, toluene, and *tert*-butylbenzene were gas chromatographic standards from C. Erba Co., and their analysis, carried out by glc on the same columns used for the resolution of the reaction products, revealed an impurities content below 0.2% and the absence of *tert*-butyltoluenes.

A sample of *p-tert*-butyltoluene was obtained from Aldrich Chemical Co. and was purified by preparative glc. The *m-tert*-butyltoluene was prepared from the para isomer by equilibration over a water-promoted $AlCl_3$ catalyst[13] and was purified by preparative glc with an 8-m Apiezon "L" grease column. The same column was used for the purification of the *o-tert*-butyltoluene prepared from *o*-bromobenzene and *tert*-butyl bromide, according to the Wurtz reaction.[14]

The neopentane was a Research Grade product from Matheson Co., and its purity exceeded 99 mol %, as indicated by a glc analysis, the major impurities being butanes ($\leq 1\%$) and traces of butenes ($\leq 0.1\%$). Oxygen, ethanol, argon, and the other chemicals used were Research Grade products employed without further purification.

Procedure. The gaseous samples were prepared by conventional techniques, using a greaseless vacuum line. The reagents and the additives were introduced into carefully outgassed Pyrex bulbs having volumes of 500 or 1000 ml and equipped with a break-seal tip.

The bulbs were filled at the desired pressure with gaseous neopentane (dried with a 50-cm column containing activated 5A molecular sieves), cooled to the liquid nitrogen temperature, and sealed off.

The irradiation was carried out at a temperature of *ca.* 37.5° in a 220 GAMMACELL from Nuclear Canada Ltd., at dose rates ranging from 0.4 to 0.7 Mrad hr^{-1}, as determined by a Fricke dosimeter.

The analysis of the irradiation products was accomplished by injecting known aliquots of the homogeneous gaseous system into a Model 800, or a Model F-30, Perkin-Elmer gas chromatograph, equipped with a flame ionization detector.

Different columns, in particular a 4-m Apiezon "L" grease column and a 4-m tricresyl phosphate column, were used at temperatures ranging from 90 to 120° for the analysis of the alkylation products, whose identity was established by comparison of their retention volumes (on two columns) with those of authentic samples, and whose yield was determined by integration of their peak areas, using individual calibration curves.

Results

The relative yields of the alkylation products from the reaction of *tert*-$C_4H_9^+$ on toluene and benzene/toluene mixture in gaseous neopentane at different pressures and in the presence of different additives are given in Table I.

From the data, it appears that only *m*- and *p-tert*-butyltoluene are formed from the attack of t-$C_4H_9^+$ on C_7H_8, while the formation of the ortho isomer could never be detected.

An interesting feature of the results is that the relative yields of *m*- and *p-tert*-butyltoluene, while insensitive to a tenfold change of the radiation dose received by the system, markedly depend on the neopentane pressure, as illustrated in Figure 1.

Furthermore, at the lowest neopentane pressures the isomeric composition of the products appears to be sensitive to the presence of a gaseous base (EtOH) or of a noble gas (Ar), whose addition significantly enhances the yield of the para isomer.

Finally, the reactivity of t-$C_4H_9^+$ toward benzene is remarkably lower than toward toluene, as indicated by the competition experiments that were generally carried out with mixtures of aromatic substrates containing a larger molar fraction of C_6H_6, in order to obtain a sufficiently accurate measurement of the minute amounts of *tert*-butylbenzene formed.

Discussion

A. The Reagent and Its Substrate Selectivity. The results of the extensive investigations carried out by Ausloos and coworkers with kinetic and mass spectrometric techniques[8-12] show conclusively that under the conditions prevailing in the present study, *i.e.*, relatively high pressures of neopentane, the presence of a radicals scavanger, and a large excess of neopentane over the aromatic substrate(s), the formation of the *tert*-butylated arenes must be traced to the reactions of the gaseous t-$C_4H_9^+$ ion, produced in high yields[10] from the radiolysis of neopentane

$$neo\text{-}C_5H_{12} \longrightarrow t\text{-}C_4H_9^+ + CH_3 + e \qquad (1)$$

and conveniently thermalized by a large number of unreactive collisions with the neopentane molecules.

The t-$C_4H_9^+$ electrophile is known as a relatively stable alkyl cation, characterized by a planar carbon skeleton, with a preferred conformation corresponding to a C_{3h} structure in the gas phase.[15]

A recent mass spectrometric determination of its

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[8] S. G. Lias and P. Ausloos, *J. Chem. Phys.*, **43**, 2748 (1965).

[9] P. Ausloos, *Progr. React. Kinet.*, **5**, 113 (1969).

[10] P. Ausloos and S. G. Lias, *J. Amer. Chem. Soc.*, **92**, 5037 (1970).

[11] R. E. Rebbert and P. Ausloos, *J. Res. Nat. Bur. Stand., Sect. A*, **76(4)**, 329 (1972).

[12] S. G. Lias, R. E. Rebbert, and P. Ausloos, *J. Chem. Phys.*, **57**, 2080 (1972).

[13] G. A. Olah, M. W. Meyer, and N. A. Overchuck, *J. Org. Chem.*, **29**, 2310 (1964).

[14] K. T. Serijan, N. F. Hipser, and L. C. Gibbons, *J. Amer. Chem. Soc.*, **71**, 873 (1949).

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

Table I. Alkylated Products from the Gas-Phase Attack of *tert*-$C_4H_9^+$ Ions on Benzene and Toluene

					Relative yields[a] of				
Neopentane pressure, Torr	Substrate pressure, Torr	O_2 pressure, Torr	Added base pressure, Torr	Dose, Mrad	*tert*-Butyltoluenes/ *tert*-Butylbenzene	*tert*-Butyltoluenes % para	% meta	Para : $^1/_2$ meta ratio	C_7H_8/ C_6H_6 rel rate
720	Toluene, 3.5	8.0		3		94.3	5.7	33.2	
710	Toluene, 4.4	10.0		11		93.8	6.2	30.4	
710	Toluene, 4.2	8.0	EtOH, 8.1	16		94.6	5.4	35.0	
700	Toluene, 5.9	5.0		31		93.9	6.1	30.8	
500	Toluene, 3.9	4.0		12		94.4	5.6	33.2	
206	Toluene, 0.45	2.0		14		86.5	13.5	12.8	
80	Toluene, 0.54	1.1		14		66.5	33.5	4.0	
43	Toluene, 0.80	1.0		17		66.6	33.4	4.0	
22	Toluene, 0.5	1.1		18		42.6	57.4	1.5	
20, + Ar (720 Torr)	Toluene, 5.6	2.0		11		84.6	15.4	11.0	
20	Toluene, 0.17	2.0	EtOH, 0.57	9		68.9	31.3	4.4	
10	Toluene, 0.64	1.0		19		48.3	51.7	1.8	
8.7	Toluene, 0.25	1.0		10		37.0	63.0	1.2	
710	Toluene, 0.29 Benzene, 2.3	2.0		10	7.2	94.0	6.0	31.3	57
710	Toluene, 0.56 Benzene, 2.1	5.0		8.5	14.7	95.0	5.0	38.0	54

[a] The *absolute* yield of *tert*-butyltoluenes, *i.e.*, the ratio of the *tert*-butyltoluenes formed to the total amount of *t*-$C_4H_9^+$ ions produced, is of the order of 10% in the experiments carried out with no added base and decreases in the presence of ethanol which competes with C_7H_8 for the gaseous electrophile. The *absolute* yield is sensibly independent of the dose in the range 3 to 31 Mrad. Standard deviation of the data 5%.

standard formation enthalpy[16] gave a value of 167 kcal mol^{-1}, which is consistent with the value of 163 kcal mol^{-1} derived from *ab initio* molecular orbital calculations.[15]

A comparison of these values with the standard formation enthalpies of the charged electrophiles whose substrate and positional selectivity has been determined in the gas phase is illustrated in Table II and underlines the relative stability of the gaseous *t*-$C_4H_9^+$ reagent, whose attack on the aromatic substrate is therefore considerably less exothermic, as discussed in section D.

Table II. Aromatic Substitutions by Different Gaseous Cations

			Relative yields of isomers from toluene[a]			Para :
Reagent	$\Delta H_f°$, kcal mol^{-1}	k_T/k_B ratio	Ortho %	Meta %	Para %	$^1/_2$ meta ratio
He^3H^+	323[b]	2.1 ± 0.2[1]	57.0[1]	18.6	23.4	2.6
$^{80}Br^+$	300[c]	*ca.* 2[4]	43.2[4]	28.6	28.3	2
$^2H_2{}^3H^+$	256[d,e]	1.3 ± 0.1[5]	52.2[5]	15.9	31.9	4.1
i-$C_3H_7^+$	192[16]	0.6/0.9[6]	35.5[7]	27.2	37.2	2.7
t-$C_4H_9^+$	163,[15] 167[16]	55.5	0	5.4	94.6	35

[a] Only nuclear substitution taken into account. [b] W. A. Chupka and M. E. Russel, *J. Chem. Phys.*, **49**, 5426 (1968). [c] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957. [d] R. E. Christoffersen, *J. Chem. Phys.*, **41**, 960 (1964). [e] H. Conroy, *ibid.*, **41**, 1341 (1964).

In analogy with the conclusions reached in the study of related gas-phase substitutions, we are led to suggest that the *tert*-butylation proceeds *via* a mechanism whose primary step involves the attack of the gaseous *tert*-butyl cation on the substrate, yielding a substituted arenium ion, whose subsequent reactions, including intramolecular rearrangements and the loss of a proton to a base, lead to the formation of the final products.

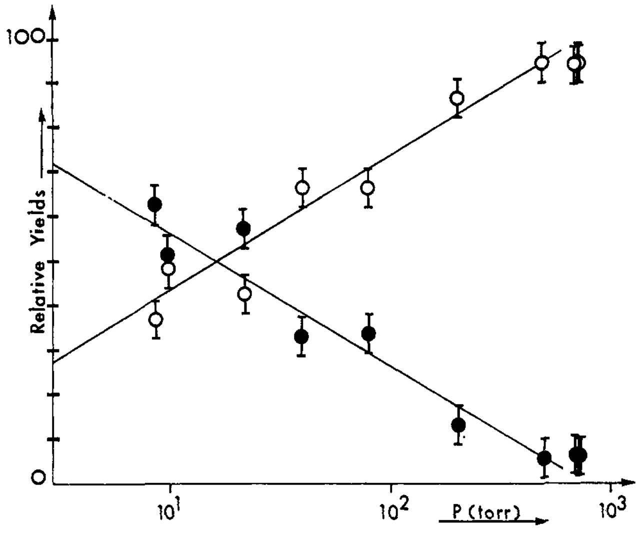
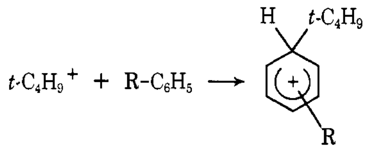


Figure 1. Relative yields of *m*- and *p*-*tert*-butyltoluenes as a function of the pressure, in the absence of any added base. Full circles refer to the meta-isomer yield.



(2)

We further suggest that the formation of the benzenium ion represents the rate-determining step and that the substrate selectivity of the *t*-$C_4H_9^+$ reagent can be accordingly deduced from the relative yields of *tert*-butylbenzene and respectively of the *tert*-butyltoluenes formed in the competition experiments.

Under these assumptions, the k_T/k_B ratio characteristic of the gas-phase alkylation by the *t*-$C_4H_9^+$ ion can be calculated from the data of Table I to range from 54 to 57, the rather large uncertainty arising from the

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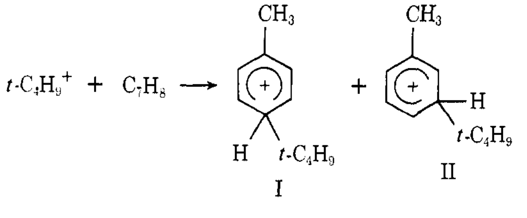
(16) F. P. Lossing and G. P. Semeluck, *Can. J. Chem.*, **48**, 955 (1970).

analytical difficulties associated with the determination of the small amounts of *tert*-butylbenzene formed in the competition experiments. As illustrated in Table II, the substrate selectivity of $t\text{-}C_4H_9^+$ considerably exceeds the selectivity of the other charged electrophiles studied in the gas phase and represents a distinctive feature of the reagent.

B. Positional Selectivity and Isomerization of the Primary Arenium Ions. In order to account for the isomeric composition of the products, and its dependence on the reaction environment, we suggest that the attack of *tert*-$C_4H_9^+$ on toluene leads, in the kinetically controlled step of the reaction, to the predominant formation of the *p*-*tert*-butyltoluenium ion (I), together with a substantially lower amount of the meta isomer (II), in a ratio of at least 20 to 1.

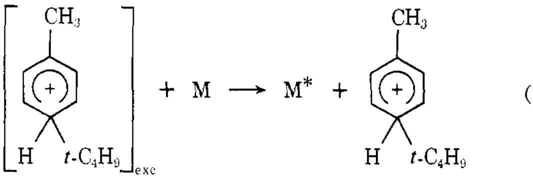


(2a)

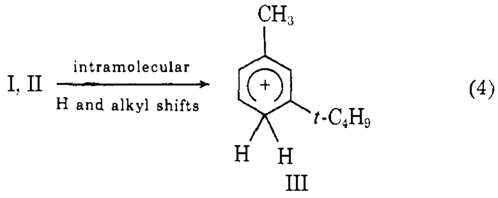
Owing to the well-established[17] higher basicity of the position 4 of toluene with respect to positions 3 (positions 2, which display an intermediate basicity, are ruled out by the very large[18] steric requirements of the electrophile), I is undoubtedly the most stable species among the possible arenium ions from reaction 2a, which are necessarily protonated at the ring position bearing the *tert*-butyl group. However, if *all* the isomeric *tert*-butyltoluenium ions are taken into account, the most stable one corresponds to the species III, where the ring position para to the methyl group, and ortho to the *tert*-butyl group, is protonated.

The higher stability of III justifies the isomerization of the primary arenium ion I observed in the present study when the reaction was carried out under conditions favorable to intramolecular rearrangement.

In this connection, we suggest that owing to the exothermicity of the electrophilic attack (eq 2a), the primary arenium ions are formed in an excited state and, unless stabilized by collision with gaseous molecules (neopentane, Ar, etc.), tend to isomerize to the thermodynamically stable isomer III.

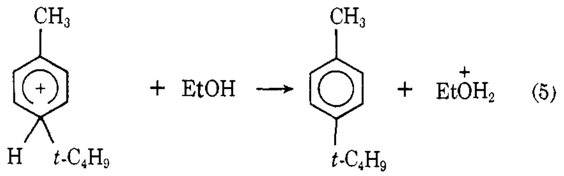


(3)



(4)

It should be noted that isomerization of II to III, requiring only a fast 1 → 2 intramolecular proton shift, is likely to proceed to completion in the gaseous systems investigated, while isomerization of I to III requires, in addition, a slower 1 → 2 intramolecular *tert*-butyl shift, and its extent is determined by the specific reaction environment, as indicated by the dependence of the isomeric composition of the final products on the reaction conditions. All the arenium ions, in fact, lose eventually a proton to a base,[19,20] *e.g.* yielding a mixture of *tert*-butyltoluenes. The isomeric composition of the products, *i.e.*, the relative yields of *m*- and *p*-*tert*-butyltoluene, depends on the competition of the isomerization processes 4, more specifically of the 1 → 2 intramolecular alkyl shift leading to the ion III and therefore to *m*-*tert*-butyltoluene, with the deactivation process 3, whose efficiency depends on the nature and the pressure of the bulk constituent of the gaseous system, and with the proton-transfer process 5, whose rate is controlled by the concentration of the base(s) in the gas.



(5)

From the pressure dependence of the products composition, it appears that at high pressures of neopentane the deactivation process 3 predominates, and the intramolecular alkyl shift, characterized by a comparatively high activation energy, is largely suppressed, as indicated by the essentially constant value of the para : $^1/_2$ meta ratio in the pressure range 500–720 Torr, irrespective of the base(s) concentration.

On these grounds, the inherent positional selectivity of the $t\text{-}C_4H_9^+$ ion, or at least its lower limit, can be calculated from the isomeric composition of the products obtained at the highest pressures of neopentane. We conclude that the positional selectivity of the reagent is characterized by a para : $^1/_2$ meta ratio in excess of 35, that greatly exceeds the selectivity displayed by the other gaseous ions so far studied, as illustrated in Table II.

At a fixed value of the *total* pressure, replacement of neopentane with argon reduces the efficiency of collisional deactivation, as indicated by the significant increase of the yield of *m*-*tert*-butyltoluene at the expense of the para isomer. As the greater deactivating ability of the neopentane molecules, in comparison with the noble gas atoms, is well established,[12] the effect observed supports the view that skeletal isomerization requires indeed the intervention of *excited* intermediates.

As the pressure is lowered, the efficiency of collisional deactivation 3 gradually decreases and the extent of isomerization correspondingly increases, as demon-

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(17) *Cf.* F. M. Brouwer, E. L. Mackor, and C. Maclean, "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer Ed., Wiley-Interscience, New York, N. Y., 1970, p 851.

(18) *Cf.* E. Baciocchi and G. Illuminati, *Progr. Phys. Org. Chem.*, 5, 2 (1967).

(19) *Cf.* ref 17, p 884.

(20) Even in those experiments where no gaseous base was deliberately introduced into the system, bases such as H_2O, $i\text{-}C_4H_8$, alcohols, etc., were undoubtedly formed during the radiolysis of neopentane, carried out in the presence of O_2. In order to ensure a known and constant concentration of base, EtOH was used in several irradiations. The choice of ethanol was suggested by the sufficiently high value of its proton affinity, 187 ± 2 kcal mol^{-1}, and by the lack of reactivity toward gaseous *tert*-butyl ions: *cf.* L. Hellner and L. W. Sieck, *J. Res. Nat. Bur. Stand., Sect. A*, 75 (5), 487 (1971).

strated by the dependence of the *m-tert*-butyltoluene yield upon the neopentane pressure illustrated in Figure 1. The highest extent of isomerization was observed at the lowest pressure of neopentane, in the absence of any added base, and corresponded to a relative yield of *m-tert*-butyltoluene exceeding 63%.

Although increasing analytical difficulties, reflected by the spread of the data in the low-pressure region of Figure 1, prevented the extension of the study to still lower pressures, the slope of the yield curve suggests that isomerization to the most stable arenium ion (III) is likely to proceed further and the *m-tert*-butyltoluene will become the only significant reaction product, when the alkylation is carried out in a gaseous system at sufficiently low pressure, in the presence of a sufficiently low concentration of base.

The latter factor cannot be ignored, as the data reveal that the dependence of the isomeric composition of products on the concentration of the base becomes increasingly significant as the pressure is lowered.

This observation can be rationalized taking into account the reduced efficiency of the collisional deactivation processes 3 in the low-pressure range, where the proton-transfer reactions (reaction 5), whose rate is controlled by the base concentration, emerge as a significant factor in limiting the lifetime of the arenium ions, and therefore the time allowed for their isomerization to III.

C. Comparison with Friedel–Crafts Alkylation. A comparison of the gas-phase *tert*-butylation with related reactions occurring in solution is of interest.

Concerning the *positional* selectivity of the attack on toluene, the gas-phase reaction appears fully comparable with Friedel–Crafts alkylation in solution, when both are studied under conditions preventing secondary isomerization, transalkylation, etc.

Thus, the reaction carried out by Olah, Flood, and Moffat,[21] using $t\text{-}C_4H_9Br$ or $i\text{-}C_4H_8$ as the reagent, $SnCl_4$ or $AlCl_3$ as the catalyst, and excess toluene or nitromethane as the solvent, gave 6.4 to 7.8% *m*- and 92.2 to 93.6% *p-tert*-butyltoluene, with a maximum value of the para:$^1/_2$ meta ratio of the order of 30, which is strikingly close to the value observed in the gas phase.

The *substrate* selectivity of the Friedel–Crafts alkylation in nitromethane at 25° is characterized by a k_T/k_B ratio ranging from 15.2 to 16.6, a value that seems comparable, if somewhat *lower*, with the substrate selectivity of the gas-phase *tert*-butylation.

As a whole, the selectivity of the gaseous $t\text{-}C_4H_9^+$ reagent displays a striking similarity with the selectivity measured in solution, in sharp contrast with the results concerning other gaseous cations and despite the enormous differences in the reaction environment.

In addition, the solution chemistry of alkylbenzenes offers a number of significant analogies with the mechanistic details of the gas-phase *tert*-butylation, as described by eq 2–5.

In the first place, arenium ions protonated at the ring site bearing the alkyl group, similar to intermediates I and II, have been directly observed by nmr spectroscopy[22] in cold solutions of strong acids, and their lower stability in comparison with the isomeric ions protonated at unsubstituted ring positions has been demonstrated by nmr spectroscopy and measurements concerning the basicity constants of the correspondent arenes.[17]

Furthermore, it has long been recognized that the alkylation of arenes in solution undoubtedly proceeds *via* a rate-determining σ-complex formation, analogous to reaction 2, at least in those cases when the alkylating agent is able to generate a relatively stable carbonium ion. Thus, the relative stability of $t\text{-}C_4H_9^+$ sets the reagent apart from more energic alkyl cations, *e.g.*, CH_3^+, $C_2H_5^+$, $i\text{-}C_3H_7^+$, both in solution[23] and in the gas phase.

Secondary isomerization *via* processes similar to reaction 4 is of course a well known general feature of Friedel–Crafts alkylation, and a more or less complete equilibration of the *tert*-butyltoluene isomers over a variety of catalysts has been specifically reported.[13,24–27]

The dealkylation (protolysis) of *tert*-butyl substituted arenes, a facile process in $HF\text{–}SbF_5$[28] and $HF\text{–}SbF_5\text{–}SO_2ClF\text{–}SO_2F_2$[29] solutions, proceeds *via* intermediate arenium ions, similar to I and II, protonated at the ring site bearing the side chain. As the direct protonation of this nuclear position is a sterically and electronically unfavorable process, the mechanism suggested for the dealkylation (or intramolecular alkyl migration) in superacid media involves[30] the attack of a proton to an adjacent nuclear position, followed by an intramolecular shift of the proton to the ring carbon bearing the side chain and by the loss (or the intramolecular migration) of the $t\text{-}C_4H_9^+$ group.

We conclude that the application of the principle of microscopic reversibility to the mechanisms postulated for the protolysis, the isomerization, and the H/D exchange[30] of *tert*-butyl substituted arenes in superacid media leads to an exactly correspondent sequence of individual reaction steps entirely consistent with those outlined in eq 2 to 4.

D. Energetics and Selectivity of Gas-Phase Substitutions. Examination of Table II reveals the striking difference in both substrate and positional selectivity existing between the $tert\text{-}C_4H_9^+$ ion and the other cations whose attack on arenes has been investigated in the gas phase. Since the gaseous $t\text{-}C_4H_9^+$ ion is also characterized by the lowest $\Delta H_f°$ value, it is natural to correlate the higher selectivity of the reagent with the considerably lower exothermicity of its attack on the substrate.

While of course a correlation between the rate and the overall enthalpy change associated to a chemical reaction is hard to justify in general, it seems nevertheless permissible to hold it, in the specific case concerned, as a tentative explanation of the unique selectivity of the $t\text{-}C_4H_9^+$ reagent.

In fact, taking into account the proton affinity of

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(21) G. A. Olah, S. H. Flood, and M. E. Moffat, *J. Amer. Chem. Soc.*, **86**, 1060 (1964).

(22) *Cf.* ref 17, p 866.

(23) *Cf.* ref 18, p 24.

(24) H. C. Brown and C. R. Smoot, *J. Amer. Chem. Soc.*, **78**, 6255 (1956).

(25) K. L. Nelson, *J. Org. Chem.*, **21**, 145 (1956).

(26) R. H. Allen and L. D. Yats, *J. Amer. Chem. Soc.*, **83**, 2799 (1961).

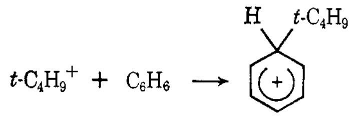
(27) R. H. Allen, *J. Amer. Chem. Soc.*, **82**, 4856 (1960).

(28) D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, **87**, 210 (1968).

(29) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and G. D. Mateescu, *J. Amer. Chem. Soc.*, **94**, 2034 (1972).

(30) G. Dallinga and G. Ter Maten, *Recl. Trav. Chim. Pays-Bas*, **79**, 737 (1960).

gaseous benzene[31] and the significant decrease of the basicity of a ring carbon caused by the presence of an alkyl substituent,[32] the available thermochemical data show that the attack of t-$C_4H_9^+$ on benzene is probably a slightly endothermic, or at most a thermoneutral, process. On the other hand, owing to the stabilizing effect of the methyl group, the t-$C_4H_9^+$ attack on the para position of toluene is more exothermic by *ca.* 10 kcal mol^{-1}, and its overall enthalpy change is certainly negative.[33] Incidentally, a limited exothermicity of reaction 2a is also consistent with the pressure dependence of the products composition, which involves the isomerization of the *excited* arenium ions I, as discussed in the previous section.


IV

(2b)

$$t\text{-}C_4H_9^+ + C_7H_8 \longrightarrow \text{I} \qquad (2a)$$

These considerations, and the generally accepted view that *exothermic* ion–molecule reactions are characterized by the lack of appreciable activation energy, while of course the activation energy of the *endothermic* ion–molecule reactions must at least match their enthalpy change, suggest that the difference in the activation energy of processes 2a and 2b, which determines the substrate selectivity of the *tert*-butyl ion, can be reasonably traced to the specific energetic details of its electrophilic attack on the substrate.

This interpretation does not conflict with the fact that the substrate selectivity of all other gaseous ions listed in Table II is remarkably uniform and largely independent of the exothermicity of their attack on the arenes.

In fact, while the standard formation enthalpies of these reagents are widely different, their attack on both benzene and toluene is invariably highly exothermic, and therefore the (low) substrate selectivity measured cannot be ascribed to the different activation energy for the attack on the two substrates and is probably associated with a completely unrelated mechanistic step, possibly the different cross sections of benzene and toluene for the capture of the gaseous cation by long-range electrostatic interactions.[5]

Finally, in connection with the postulated endothermicity of reaction 2b, it is interesting to point out that the inverse process, namely the protolytic dealkylation of *tert*-butylbenzene following its protonation by Brønsted acids, is apparently an energetically favored process, which occurs with ease both in the gas phase and in superacid solutions, as indicated by mass spectrometric[34] and kinetic[3,35] evidence.

Conclusions

The following pertinent conclusions may be drawn from the present study. In the first place, the t-$C_4H_9^+$ reagent is the first gaseous cation whose attack on aromatic substrates was found to occur with a remarkable degree of selectivity, fully comparable and in some respects even higher than the analogous Friedel–Crafts alkylation occurring in solution. In the second place, the present results indicate that the gas-phase electrophilic attack of ionic reagents on aromatic substrates is not necessarily characterized by a low substrate and positional selectivity.

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(31) S.-L. Chong and J. L. Franklin, *J. Amer. Chem. Soc.*, **94**, 6630 (1972).

(32) D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, **87**, 611 (1968).

(33) The $\Delta H_f°$ value of IV can be approximately estimated from the known values of gaseous H^+ and *tert*-butylbenzene and from the standard enthalpy change of the process *tert*-butylbenzene + $H^+ \rightarrow$ IV, which corresponds, apart from the sign, to the proton affinity (PA) of the position of the benzene ring bearing the *tert*-butyl substituent. If the PA of this specific position is taken equal to the PA of an unsubstituted but otherwise equivalent ring position of gaseous C_6H_6, the $\Delta H_f°$ value of IV would correspond to *ca.* 182 kcal mol^{-1}, and reaction 2b would be almost exactly thermoneutral. However, since replacement of H by a substituent alkyl group at a given ring position while increasing the overall PA of the molecule is known to decrease considerably the basicity, and therefore the PA, of the specific ring position bearing the substituent, the $\Delta H_f°$ value of IV is probably significantly higher than 182 kcal mol^{-1}, and reaction 2b is correspondingly endothermic. On the other hand, the stabilizing effect of a methyl group in the para position to the protonated site, demonstrated for instance by the different PA values of gaseous toluene and benzene, stabilizes the arenium ion I in comparison to IV, and causes reaction 2a to be more exothermic than 2b by some 10 kcal mol^{-1}.

(34) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **89**, 1047 (1967).

(35) *Cf.* ref 17, p 882.