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Gas-Phase Acid-Induced Nucleophilic Displacement Reactions. 8.[1] Structural Analysis of Intermediate Ions Formed by the Decomposition of β-Arylethyl Onium Ions

Simonetta Fornarini,*[2a] Cinzia Sparapani,[2b] and Maurizio Speranza*[2c]

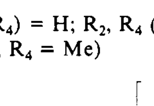
Contribution from the Istituto di Chimica Farmaceutica, Università di Roma "La Sapienza", 00185 Rome, Italy, Istituto di Chimica Nucleare del CNR, Monterotondo Stazione, 00016 Rome, Italy, and Dipartimento di Scienze Chimiche, Università di Camerino, 62032 Camerino, Macerata, Italy. *Received March 30, 1987*

Abstract: The existence of the stable unsubstituted ethylenebenzenium ion **3** as a stable gaseous species is inferred as occurring in the reaction pathway induced by the attack of radiolytically formed gaseous acids GA^+ ($GA^+ = D_3^+$, $C_nH_5^+$ (n = 1, 2), and $CH_3FCH_3^+$) on β-phenyl-Y-ethanes (Y = F, Cl, and OH). Neutral product analysis allows use to define the detailed reaction mechanism and to extend previous conclusions concerning adjacent phenyl group participation in the nucleophilic displacement process, which takes place in competition with 1,2-H migration. Occurrence of alternative cyclic structures, e.g., **7**, in the participation step is ruled out on the grounds of results of specifically designed radiolytic experiments. The mechanistic picture that characterizes neighboring phenyl-group participation in cationic nucleophilic substitutions occurring in the gas phase presents interesting analogies with related processes occurring under solvolytic conditions and in superacidic media. The results from the present gas-phase radiolytic approach are discussed and contrasted with pertinent mass spectrometric data and theoretical predictions.

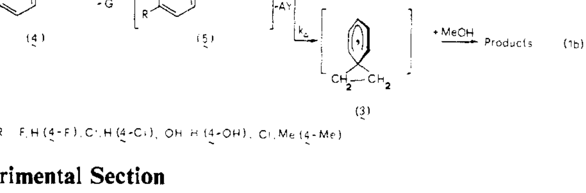
In the preceding papers of this series, the dependence of the structural and stereochemical features of gas-phase acid-induced nucleophilic displacement at saturated carbon upon the presence and the nature of nucleophilic groups adjacent to the reaction center has been thoroughly evaluated by a radiolytic method.[1] In particular, the almost complete stereospecificity characterizing these processes when occurring on *erythro*- ((ret/inv) $\geq$ 160) and *threo*-3-phenyl-2-chlorobutane (5 < (ret/inv) < 48) suggests very efficient anchimeric assistance of the vicinal phenyl moiety, in qualitative analogy with related substitutions in solution.[3] Extensive phenyl-group participation has been inferred as well in cationic nucleophilic substitutions occurring at primary carbon, based upon structural analysis of the neutral isomeric products formed in these processes from isomeric β-phenyl-Y-propanes (Y = Cl, OH). The intermediates involved in such anchimerically assisted nucleophilic displacements, namely the alkylenebenzenium ions **1** and **2**, are found to be relatively stable species in the gas phase (155–760 Torr), displaying a scarce tendency for isomerization to the corresponding most stable open-chain structures.[4]

The same methodology is now extended to the assessment of a long-standing structural problem in gas-phase ion chemistry,[5] concerning the occurrence of the ethylenearenium ions **3** as well as of other conceivable bridged isomers as stable species in the diluted gas state and the evaluation of structural effects, if any, on their stability. To this end, we selected a set of gaseous Brønsted ($GA^+ = D_3^+$, $C_nH_5^+$ (n = 1, 2)) and Lewis acids ($GA^+ = C_2H_5^+$, $CH_3FCH_3^+$), obtained in known yields by γ-radiolysis of their appropriate precursors (D_2, CH_4, and CH_3F).[6] In the presence of suitable nucleophilic substrates, such as the β-arylethyl halides **4-F**, **4-Cl**, and **4-Me** and alcohols **4-OH**, the GA^+ acids are expected to generate inter alia the corresponding "onium" derivatives **5**, wherein the loss of the potential leaving group YA may be assisted by the participation of the vicinal phenyl moiety (k_Δ) to give the corresponding ethylenearenium ions **3**, much like analogous processes carried out under solvolytic conditions.

The present work is aimed at determining the structural features of the intermediates involved in the decomposition of β-arylethyl onium ions **5** from eq 1, in the presence of an external nucleophile CH_3OH, in order to gather positive evidence on the existence and the stability of conceivable bridged intermediates (e.g., **3**) in the gas phase, where interference from solvation, ion pairing, etc. typical of the condensed phase is excluded.



1 (R_1, R_3 (or R_4) = H; R_2, R_4 (or R_3) = Me)
2 (R_1–R_3 = H; R_4 = Me)



Y,R = F,H (4-F), Cl,H (4-Cl), OH,H (4-OH), Cl,Me (4-Me)

Experimental Section

Materials. Deuterium, methane, methyl fluoride, oxygen, and trimethylamine were high-purity gases from Matheson Co., used without further purification. Methanol, β-phenylethyl chloride (**4-Cl**), and alcohol **4-OH**, as well as styrene, benzyl methyl ether, and benzaldehyde, are commercially available from Fluka A.G. and Aldrich-Chemie GmbH. Those compounds, which are not available from commercial sources, such as β-phenylethyl fluoride (**4-F**), β-*p*-tolylethyl chloride (**4-Me**), isomeric methoxyethylbenzenes and -toluenes, and benzocyclobutene and its methylated derivatives, were synthesized by conventional procedures, their identity being checked by mass spectrometric and NMR analyses.[7] Before irradiation, the starting compounds **4** were repeatedly purified on a preparative gas chromatographic column (2-m 20% DC-200/6% Bentone 34 on 60–80 mesh Chromosorb W-AW) and their purity checked

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[1] Part 7: Fornarini, S.; Sparapani, C.; Speranza, M. *J. Am. Chem. Soc.*, preceding paper in this issue.

[2] (a) University of Rome. (b) Istituto di Chimica Nucleare del C.N.R., Monterotondo Stazione. (c) University of Camerino.

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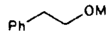
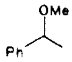
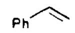
Table I. Product Yields from the Gas-Phase Attack of GA^+ Acids on β-Phenylethyl Halides and Alcohols

system composition[a]				relative distribution of products (%)							total absolute yield	
substrate (Torr)	bulk gas (Torr)	GA^+	CH_3OH (Torr)			(β/α) ratio	PhCHO	$PhCH_2OMe$		$10^2G_{(M)}$[b]	%[c]
4-F (1.0)	CH_4 (680)	$C_nH_5^+$	1.3	54	35	1.5	9	n.d.[d]	2	88.8	32
4-F (1.0)	CH_4 (700)	$C_nH_5^+$	4.8	50	27	1.8	11	3	9	69.2	25
4-Cl (0.2)	D_2 (750)	D_3^+	1.3	27	16	1.7	33	3	20	28.0	9
4-Cl (0.2)	D_2 (700)	D_3^+	4.0	20	15	1.4	39	n.d.	26	29.0	10
4-Cl (0.9)	D_2 (660)	D_3^+	4.8	20	15	1.3	27	3	35	80.5	27
4-Cl (0.3)	CH_4 (175)	$C_nH_5^+$	0.5	49	11	4.3	26	n.d.	13	139.0	50
4-Cl (0.9)	CH_4 (730)	$C_nH_5^+$	1.2	61	11	5.4	19	n.d.	8	96.0	34
4-Cl (0.9)	CH_4 (700)	$C_nH_5^+$	1.3[e]	5	1	4.8	20	n.d.	74	33.3	12
4-Cl (1.0)	CH_4 (740)	$C_nH_5^+$	4.1	55	7	7.4	24	1	12	63.0	23
4-Cl (0.9)	CH_4 (670)	$C_nH_5^+$	4.6	57	8	7.3	24	1	10	86.6	31
4-Cl (0.3)	CH_3F (160)	$CH_3FCH_3^+$	0.3	64	4	16.2	30	n.d.	2	41.6	
4-Cl (0.9)	CH_3F (700)	$CH_3FCH_3^+$	1.2	76	4	19.6	20	n.d.	n.d.	23.0	
4-Me (0.5)	CH_4 (700)	$C_nH_5^+$	1.5	57	14	4.1	17	n.d.	11	43.4	16
4-OH (0.3)	CH_4 (700)	$C_nH_5^+$	1.3	31	6	5.1	60	n.d.	3	30.1	11
4-OH (0.3)	CH_4 (730)	$C_nH_5^+$	4.2	18	3	6.0	79	n.d.	n.d.	6.7	2

[a] O_2: 4 Torr. Radiation dose: 3×10^4 Gy (dose rate: 1×10^4 Gy h^{-1}). [b] $G_{(M)}$ is the number of molecules M produced per 100 eV of absorbed energy. Standard deviation of data, ca. 10%. [c] Total absolute yields estimated by using the $G_{(GA^+)}$ values available from the literature (ref 6 and 8). No value for $G_{(CH_3FCH_3^+)}$ is available. [d] n.d. = not detectable ($G_{(M)} \leq 1 \times 10^{-4}$). [e] 4 Torr of NMe_3 added to the gaseous mixture.

by analytical GLC, using flame ionization detection (FID).

Procedure. The preparation and irradiation of the gaseous samples were carried out according to experimental techniques described in detail in the preceding paper.[1] Typical experimental conditions were as follows: bulk gas, 160–740 Torr; substrate **4**, 0.2–1.0 Torr; O_2, 4 Torr; CH_3OH, 0.3–4.8 Torr; NMe_3, 0–4 Torr; radiation dose, 3×10^4 Gy; dose rate, 1×10^4 Gy h^{-1}; irradiation temperature, 37.5 °C. Control experiments, carried out at doses ranging from 1×10^4 to 1×10^5 Gy, showed that the relative yields of products and their isomeric composition are largely independent of the dose.

The analysis of the irradiation products was performed with a Perkin-Elmer Model Sigma 1 gas chromatograph, equipped with a FID unit. The following columns were used: (i) a 2 m long, 2 mm i.d. glass column, packed with 10% SP 2100 + 6% Bentone 38 on 100–120 mesh Chromosorb W-AW, operated at 100 °C; (ii) a 2 m long, 3.2 mm i.d. stainless steel column, packed with 5% SP 1200 + 1.75% Bentone 34 on 100–120 mesh Supelcoport support, operated at 100 °C. The products were identified by comparison of their retention volumes with those of the authentic standard compounds. Their yields were determined from the areas of the corresponding eluted peaks, using individual calibration curves. The identity of the products was further confirmed by GLC–mass spectrometry, using a Hewlett-Packard HP 5982 A mass spectrometer.

Results

The absolute yields and the relative distribution of the products formed from the gas-phase attack of the GA^+ acids on the β-arylethyl-Y (Y = F, Cl, OH) substrates **4**, in the presence of CH_3OH as the external nucleophile, are given in Table I (eq 1). The table reports the $G_{(M)}$ values, expressed as the number of product molecules generated per 100 eV of energy absorbed by the gaseous mixture at a total dose of 3×10^4 Gy (dose rate = 1×10^4 Gy h^{-1}). The reported figures represent the mean $G_{(M)}$ values obtained from several separate irradiations, carried out under the same experimental conditions, whose reproducibility is expressed by the standard deviations quoted. Table I summarizes also the total absolute yields of the radiolytic products, given as the percent ratio of their $G_{(M)}$ values to the $G_{(GA^+)}$ values of their gaseous acid precursors.[6,8]

Table I shows that the major products from β-phenylethyl-Y substrates **4-F**, **4-Cl**, and **4-OH** are β-methoxyethylbenzene (β) and α-methoxyethylbenzene (α), accompanied by variable amounts of fragmentation (benzyl methyl ether), elimination (styrene), and oxidation (benzaldehyde) products. Their para-methylated analogues are formed in similar proportions from **4-Me** in the CH_4 runs. In these systems, there is no evidence for the formation of meta- and ortho-methylated isomers of the recovered products. Limited yields of ring-alkylation derivatives of **4** were recovered as well from the runs involving Lewis acids ($C_2H_5^+$ and $CH_3FCH_3^+$). Since their formation is not directly relevant to the present study, these ring-alkylated products do not appear in Table I and will not be discussed further. The total absolute yields of products listed in Table I are found to generally decrease with the total pressure of the system and the concentration of competing nucleophiles (i.e., NMe_3, CH_3OH). The latter effect demonstrates the ionic character of the reaction channels leading to the listed products.

As to the distribution of products, it should be noted that the substitution derivatives α and β of the selected substrates **4** are predominantly formed in all systems, except in the D_2 samples where they are accompanied by comparable amounts of benzaldehyde and styrene, the latter becoming predominant in the presence of the added NMe_3 base. In all experiments, no detectable amounts of benzocyclobutene or its ring-methylated analogues could be observed, in spite of a specific search.

Direct information on the structural features of the substitution processes is obtained from the isomeric distribution of the substituted products, expressed by the β/α ratios of Table I. Inspection of the table indicates that these ratios depend upon several factors, including the following: (i) the nature of the GA^+ acid (the β/α ratio from **4-Cl** amounts to over 16 in CH_3F, whereas it progressively decreases to 4.3–7.4 in CH_4 and 1.3–1.7 in D_2); (ii) the nature of the n-type center Y of the substrate (the β/α ratio increases by a factor of ca. 4 in the F < OH < Cl order, under similar experimental conditions); (iii) the concentration of CH_3OH (the β/α ratio increases with the CH_3OH concentration); (iv) the total pressure of the system (the β/α ratio increases with the sample pressure); (v) the presence of a substituent group on the aromatic ring (the β/α ratio decreases by a factor of 5–20% in the CH_4 systems, when the hydrogen at the para position of the phenyl group of **4-Cl** is replaced by a methyl substituent, as in **4-Me**).

Discussion

Nucleophilic Displacement on β-Phenylethyl Onium Ions. The gaseous acids GA^+ (D_3^+, $C_nH_5^+$ (n = 1, 2), and $CH_3FCH_3^+$)[1], produced by γ-radiolysis of their precursor gases (D_2, CH_4, and CH_3F, respectively) are used as sources of the onium ions **5** from **4**. The experimental features of the radiolytic processes, such as the marked effects of the nature of the GA^+ acids and of the concentration of added bases (i.e., CH_3OH and NMe_3) on the end product yields, are consistent with the ionic substitution pattern outlined in eq 1. Accordingly, the first step of sequence 1 involves the formation of the onium intermediates **5** from the exothermic

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Table II. Thermochemical Data (kcal mol^{-1})

neutral molecule (M)	PA[a]	MCA[b]	ΔH°_f (MH^+)	ΔH°_f (MMe^+)	ΔH°_f (MEt^+)
H_2	101		264		
CH_4	132		216		
C_2H_4	163		216		
CH_3F		59[c]		146[c]	
CH_3OH	182	83[d]	136	130[d]	113[d]
C_2H_5OH	188	86[d]	121	119[d]	107[d]
C_2H_5Cl	169	71[e]	170	164[e]	ca. 152[f]
C_2H_5F	165	ca. 72[f]	138	ca. 127[f]	ca. 115[f]

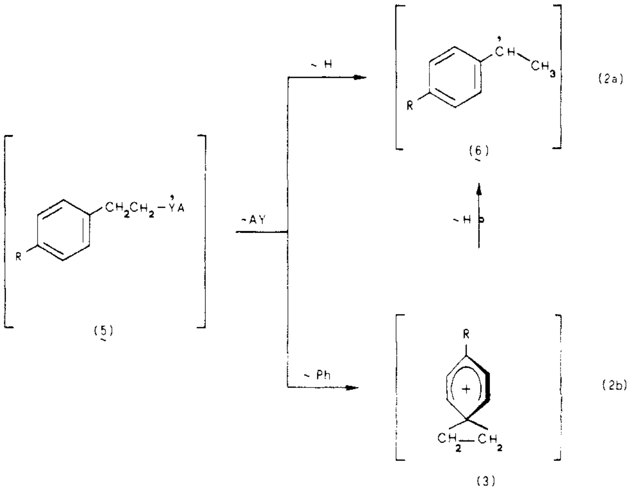
[a] PA = proton affinity; ref 9 and 10. [b] MCA = methyl cation affinity, as defined by: Holtz, D.; Beauchamp, J. L.; Woodgate, S. D. *J. Am. Chem. Soc.* **1970**, *92*, 7484. [c] Reference 11. [d] Values calculated from the PA's of the corresponding ethers (ref 9). The heats of formation of the neutrals were taken from: Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969. [e] Reference 12. [f] Approximate values calculated by using the group additivity rules (Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976).

attack of GA^+ on the Y substituent of substrates **4**. Approximate estimates of the reaction enthalpies involved in this step can be obtained by using the thermochemical data of Table II concerning model compounds (ethanol and ethyl halides), under the assumption that the β-aryl substituent exerts the same effect on the neutral substrates **4** and on their onium derivatives **5**. In this context, it can be concluded that formation of the relevant onium derivatives **5** from the same neutral substrate is increasingly exothermic in the following order: $CH_3FCH_3^+ < C_2H_5^+$ (addition) and $C_2H_5^+ < CH_5^+ < D_3^+$ (proton transfer). For each individual GA^+ acid, the exothermicity increases in the following order: **4-F** $\simeq$ **4-Cl** $\leq$ **4-Me** $<$ **4-OH**.

The onium intermediates **5**, excited by the exothermicity of their formation process, can undergo unimolecular C–YA$^+$ bond fission, which may be assisted by vicinal nucleophilic groups (e.g., the aryl moiety), nucleophilic displacement by the external nucleophile CH_3OH, as well as elimination and fragmentation processes. The excitation level of the onium ion **5** is a major factor in determining the relative rate of the above competing channels, as demonstrated by the extensive formation of secondary fragmentation and elimination products from the highly exothermic D_3^+ attack on **4-Cl** ($-\Delta H^\circ = 68$ kcal mol^{-1}) and the $C_nH_5^+$ attack on **4-OH** ($-\Delta H^\circ = 25 \div 56$ kcal mol^{-1}). In the less exothermic protonation and/or alkylation of **4-F**, **4-Cl**, and **4-Me**, by $C_nH_5^+$ and $CH_3FCH_3^+$ acids, the efficient collisional quenching of the ensuing onium derivatives **5** significantly reduces the extent of the secondary fragmentation and elimination processes. In these systems, major components of the radiolytic product mixture are isomeric β-methoxyethylbenzene (β = 49–76%) and the α-methoxyethylbenzene (α = 4–35%), whose genesis is particularly relevant to ascertain the occurrence of ethylene arenium ions **3** or of other cyclic isomer in the gas phase.

The conclusions reached in the previous paper on the nature and the formation mechanism of the substituted products apply to the present systems as well. Even when thermochemically allowed,[13] unimolecular C–YA$^+$ bond scission of **5** to yield a primary β-phenylethyl cation is hardly an efficient process leading to β and, after isomerization, to α. In fact, the same process does not occur to any significant extent in the corresponding 3-phenylbutyl-2 and β-phenylpropyl-2 onium intermediates, as discussed in the preceding paper, wherein secondary C–YA$^+$ bond scission should be even more favored. On the other hand, direct bimolecular CH_3OH-to-AY nucleophilic substitution on **5** (S_N2) cannot be a significant route to the β-substituted products, in view of the relatively high "effective concentration" (k_Δ/k_S) of a phenyl group adjacent to the reaction center.[1] Further evidence against an S_N2 process is provided by the peculiar effects of both the leaving group YA and the CH_3OH concentration on the absolute yield of the β-substituted products that in most cases is just opposite than expected (Table I).[14] Finally, a pure CH_3OH-to-AY S_N2 displacement on **5** cannot account for the formation of the α-substituted isomer.[15] It is, therefore, concluded that formation of the α- and β-substituted products of Table I is best accounted for by neighboring group assistance to the C–YA$^+$ bond dissociation in **5** before being attacked by the external nucleophile CH_3OH, as in the butyl and propyl systems discussed in the preceding paper.[1]

Concerning the nature of this assistance, it should be noted that the reaction route to the substituted isomer requires at least an α,β-hydrogen shift. Since intermediacy of a persistent β-phenylethyl cation has been excluded, two alternative isomerization steps can be envisioned to account for the formation of α, namely, (i) the vicinal H-atom participation to the C–YA$^+$ cleavage in **5** to give the α-methylbenzyl cation **6** (eq 2a) and (ii) the neighboring Ph-group assistance to the leaving AY group (eq 1b), followed by unimolecular isomerization of the ensuing ethylene arenium ion **3** to **6** (eq 2b). It should be noted, in this connection, the distinct tendency of the ethylenarenium ion **3** to isomerize to **6** when generated in the gas phase at relatively high excitation levels from the addition of phenylium ion to ethylene ($-\Delta H^\circ \geq$ 64 kcal mol^{-1}).[16] Discrimination between paths 2a and 2b is allowed from the analysis of the β/α ratios of Table I. Within the hypothesis of path 2b as the sole process leading to α and β, the β/α ratios are expected to depend primarily upon the excitation level of the cyclic arenium ion **3**, which in turn is proportional to the exothermicity of its formation process. In this view, the ethylenebenzenium ions **3** are formed from $C_nH_5^+$ attack on **4-F**, **4-Cl**, and **4-OH** with a rather limited excess energy, which is significantly lower than that of the same cyclic ion when formed from D_3^+ attack on **4-Cl**. In spite of this, the β/α ratios from D_3^+ attack on **4-Cl** (β/α = 1.3–1.7) are fully comparable to those from $C_nH_5^+$ attack on **4-F** (β/α = 1.5–1.8), whereas these latter are much lower than those from $C_nH_5^+$ attack on **4-Cl** (β/α = 5.4–7.4) and **4-OH** (β/α = 5.1–6.0). On these grounds, it is



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[13] According to the thermochemical data of Table II, formation of β-phenylethyl cation from GA^+ attack on **4** is energetically allowed only for CH_5^+ protonation on **4-F** and **4-OH** ($-\Delta H^\circ = 2/3$ kcal mol^{-1}) and for D_3^+ protonation of **4-Cl** ($-\Delta H^\circ = 43$ kcal mol^{-1}).

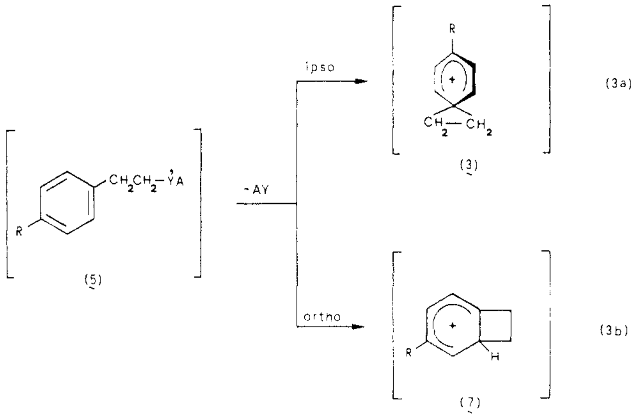
[14] (a) Speranza, M.; Angelini, G. *J. Am. Chem. Soc.* **1980**, *102*, 3115. (b) Attinà, M.; Angelini, G.; Speranza, M. *Tetrahedron* **1981**, *37*, 1221. (c) Kim, J. K.; Findlay, M. C.; Henderson, W. G.; Caserio, M. C. *J. Am. Chem. Soc.* **1973**, *95*, 2184. (d) Harrison, A. G.; Onuska, F. I. *Org. Mass Spectrom.* **1978**, *13*, 35. (e) Jardine, I.; Fenselau, C. *J. Am. Chem. Soc.* **1976**, *98*, 5086.

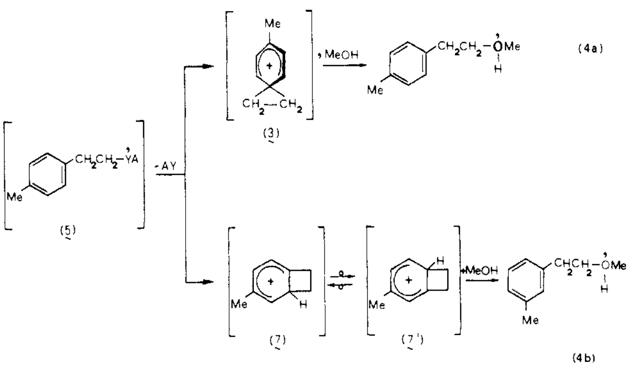
[15] The hypothesis of a β → α isomerization within the ionic adduct from CH_3OH-to-AY nucleophilic displacement on **5** can be disregarded in view of the fact that this conceivable process should be effectively inhibited by rapid neutralization by NMe_3 of the ionic oxonium ion involved. On the contrary, the β/α ratio from the CH_4 systems with **4-Cl** slightly decreases from 5.4 to 4.8 (Table I) instead of increasing in the presence of NMe_3. Further independent evidence against gas-phase β → α isomerization within the $PhCH_2CH_2O(CH_3)H^+$ oxonium intermediate has been obtained from the lack of any significant yield of α-methoxyethylbenzene by gas-phase $CH_3FCH_3^+$ methylation of **4-OH** under experimental conditions similar to those of Table I.

[16] Fornarini, S.; Speranza, M. *J. Am. Chem. Soc.* **1985**, *107*, 5358.

concluded that the β/α ratios of Table I cannot be determined solely by the excess energy of the intermediates involved but that other factors, such as the leaving ability of the group AY, may play a role as well. It is, in fact, evident from Table I that the β/α ratio decreases dramatically in the following order: HOA $\simeq$ ClA < FA and, within the **4-Cl** systems, $ClCH_3$ < ClH, i.e., by increasing the leaving group AY ability. It follows that channel 2a, whose extent is expected to be dependent upon the leaving group AY ability, is mostly responsible for the direct formation of the α-substituted products, although partial contribution from the indirect route 2b cannot be a priori excluded. Finally, the comparatively much higher abundance of the β-substituted isomer with respect to the α one, and its dependence upon both the leaving group AY ability and the experimental conditions (Table I), indicates that the phenyl-group participation within **5** (eq 2b) involves a limited activation barrier with respect to that of the competing H-atom transfer (eq 2a and **3** $\xrightarrow{\Omega}$ **6**), in complete agreement with the conclusions reached in the butyl and propyl experiments reported in the preceding paper.[1]

Neighboring Phenyl-Group Participation in the Gas Phase. The findings of the present experiments consolidate the previous evidence[1] in favor of the occurrence of an effective phenyl-group assistance to the acid-induced CH_3OH-to-AY nucleophilic substitution in β-phenylalkyl onium intermediates, e.g., **5**. Unsaturated vicinal groups, such as the phenyl moiety, have the unique possibility to facilitate the leaving group loss by interaction of their π-system with the reaction center, via ionic intermediates which can be described as classical bridged alkylenearenium ions. The question arises as to whether such interaction occurs in **5** in such a way as to lead to an ethylenearenium ion structure **3**, or to some other bridged isomer, e.g., the protonated benzocyclobutene structure **7**, as suggested from independent gas-phase investigations (eq 3). In other words, is the phenyl-group participation essentially driven in the gas phase by structural factors allowing interaction only between the reaction site and the poorly activated, but close, ipso carbon of the phenyl moiety to yield **3** or do alternative factors play a role, favoring primary interaction between the more nucleophilic *o*-phenylcarbons and the reaction center?[17] Some insight into this structural problem can be obtained from the analysis of the radiolytic products of Table I. Under no circumstances could neutral benzocyclobutene, i.e., the neutral derivative from deprotonation of the conceivable intermediate **7**, be recovered in measurable yields from the irradiated samples. This negative evidence counts against the intermediacy of a persistent protonated benzocyclobutene species **7**, although its occurrence as a transient rapidly isomerizing to a more stable structure (e.g., **6**) before being quenched by an external nucleophile (CH_3OH or NMe_3) cannot be excluded. In order to verify the latter hypothesis it was necessary to resort to the ring-substituted substrate **4-Me**. Acid-induced nucleophilic displacement on this compound leads to the α- and β-substituted products containing exclusively the *p*-tolyl moiety. No evidence was obtained for appreciable formation of their meta (and ortho) isomers, in spite of the fact that fast 1,2-H shift within the protonated benzocyclobutene precursor **7** could give inter alia the thermodynamically more stable isomer **7′** (eq 4b). Such negative evidence suggests that neighboring phenyl-group participation to a cationic nucleophilic displacement takes place in the gas phase by a mechanism similar to that involved in analogous solvolytic processes,[3] i.e., via the intermediacy of a bridged ethylenearenium ion **3**. Other conceivable bridged structures, i.e., **7** or **7′**, do not appear to be plausible intermediates in these processes neither in the gaseous nor in the condensed phase.





Comparison with Related Experimental and Theoretical Data. The present gas-phase results are fully consistent with related solvolytic studies on β-arylethyl systems,[3] in that both point to the intermediacy of a persistent ethylenearenium ion **3**. Ionization of the same systems in superacidic media provided confirmatory NMR evidence for the occurrence of relatively stable ethylenebenzenium **3** and α-phenylethyl ions **6**, through the possible intermediacy of a β-phenylethyl cation structure.[18]

No such straightforward correlation could be obtained from purely mass spectrometric investigations, aimed at determining the structural properties of long-lived (lifetime $\geq 10^{-5}$ s) intermediates in the potential surface of the $C_8H_9^+$ ions from the unimolecular decomposition of suitable ionized β-phenylethyl precursors.[5] These gas-phase studies were all based upon collisional activation (CA) mass spectra of the $C_8H_9^+$ ions produced by electron impact on 2-phenyl-1-Y-ethanes (Y = I, Br, Cl, and CH_3). The spectral data for each precursor could be rationalized as arising from binary mixtures of isomeric $C_8H_9^+$ ions whose composition, according to the relevant CA spectra, changes dramatically with electron energy. Furthermore, at any given electron energy, the relative proportions and even the structure of the isomeric $C_8H_9^+$ ions appeared determined by the nature of the 2-phenyl-1-Y-ethane precursor employed. Thus, at 10–20 eV electron energies, 2-phenyl-1-bromoethane and 2-phenyl-1-iodoethane give $C_8H_9^+$ ions whose CA spectra are consistent with a mixture of ethylenebenzenium ion **3** and an unknown isomer X, whereas 2-phenyl-1-chloroethane and 2-phenylpropane yield a mixture of X and protonated benzocyclobutene **7**. At 70 eV electron energy, the relative proportion of the unknown X increases considerably (up to 80%). In no cases was β-phenylethyl cation identified as a persistent (lifetime $\geq 10^{-5}$ s) intermediate, in agreement with the present results and with theoretical prediction.[19]

The above picture, hardly consistent with the conclusions from the present work and with the results of pertinent solvolytic studies, arises from the comparison of the CA spectra of the stable fraction (lifetime $\geq 10^{-5}$ s) of the $C_8H_9^+$ species from the β-phenylethyl substrates with those of "structural specimens", i.e. of "model" $C_8H_9^+$ ions whose structure was inferred from that of their neutral precursors, e.g., the ion(s) obtained from the protonation of

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benzocyclobutene. In the less fortunate cases, as for instance for the ethylenebenzenium ion structure **3**, a "structural specimen" is not available and structural assignment rests only on the fragmentation pattern of specifically labeled precursors. While such conclusions from the structural analysis of gaseous $C_8H_9^+$ ions by CA techniques are undoubtedly consistent with the spectra reported, their more general significance, and especially their use in structural comparison between gaseous ion and their condensed-phase counterparts, is hardly consistent with the present results and appear questionable in the light of the following considerations. It is generally recognized[20] that even the most sophisticated mass spectrometric tools for structural discrimination, such as CA techniques, suffer from serious limitations, in particular from the relatively long delay ($\geq 10^{-5}$ s) between the generation of the ion in the source of the spectrometer and its structural assay. During such a long lapse of time, structural rearrangements may occur, whose course and extent depend on the initial structure of the ion and its energy content. These parameters can be dramatically different in the "unknown" ion under investigation and in the ion used as its "structural model", since necessarily they arise from different ionization processes and/or from different neutrals. It follows that the observed similarity of their CA spectra, no matter how close, is not sufficient for concluding that both species are structurally identical. An indirect support to this statement is provided by the reported coincidence of the CA spectrum of the unknown structure X of the $C_8H_9^+$ family with that of the *exo*-cyclopropanonorbornyl ion, which can hardly be recognized as the thermodynamically most stable structure where any initially formed excited $C_8H_9^+$ ions isomerize under long-lived ($\geq 10^{-5}$ s) conditions.[5e,f]

On the other hand, the radiolytic technique adopted in this study allows effective collisional quenching of all the ionic species involved and their rapid sampling (lifetime $\leq 10^{-8}$ s) by reactive collisions with suitable acceptors. Under these conditions, ion rearrangement before sampling is substantially reduced, and positive structural discrimination of the ionic species is allowed by the direct determination of the isomeric composition of their neutral derivatives. The approach reveals interesting analogies between gas-phase adjacent phenyl-group assistance to cationic nucleophilic substitutions and related processes occurring under solvolytic conditions as well as in non-nucleophilic solvent media. The same reaction model seems to be operative in both the liquid and the gaseous phase, dominated in the latter by the polarization of phenyl group by the incipient positive charge at the reaction site, which in passing to condensed phases is progressively replaced by specific solvent assistance to the substitution process.

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Registry No. 4-F, 458-87-7; **4-Cl**, 622-24-2; **4-Me**, 32327-68-7; **4-OH**, 60-12-8; D_3^+, 12595-96-9; CH_5^+, 15135-49-6; $C_2H_5^+$, 14936-94-8; $CH_3FCH_3^+$, 64710-12-9.

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Effects of Chemical Environment on Direct Recoil Ion Fractions

J. N. Chen and J. W. Rabalais*

Contribution from the Department of Chemistry, University of Houston, Houston, Texas 77004.

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Abstract: A qualitative model for describing a specific type of secondary particle emission, i.e., atoms which are directly recoiled (DR) from a surface as a result of a single primary ion collision, is developed. The model is used to interpret ion fractions of DR atoms from surfaces with differing chemical environments. Time-of-flight spectra of recoiled atoms resulting from 5-keV Ar^+ ions impingent on surfaces of Mg, MgO, $Mg(OH)_2$, Si, SiO_2, LiF, C_6F_6, and graphite have been obtained. Measurements of DR neutrals plus ions and neutrals only are used to calculate positive and negative ion fractions $Y_{+,-}$. These ion yields are sensitive to the chemical environment of the DR atom in the surface as follows. Y_+(Mg) from MgO is 10 times higher than from Mg metal and the SiO_2 surface yields higher $Y_{+,-}$(Si) than the Si surface. $Y_{+,-}$(F) from ionic LiF are larger than those from covalent C_6F_6 and Y_+(O) yields from oxides are particularly sensitive to the presence of hydrogen, decreasing as hydrogen concentration increases. Classical trajectory calculations are used to describe DR trajectories. The model for electronic charge exchange partitions the trajectory into two segments: (1) the close atomic encounter of the collision complex where electron promotions occur in the quasidiatomic molecule; (2) the outgoing trajectory where Auger and resonant electronic transitions occur. Analytical expressions for $Y_{+,-}$ are developed in terms of the probabilities involved and applied to interpretation of the experimental data.

I. Introduction

The mechanism by which specific charge states (positive, neutral, or negative) of secondary particles are produced during ion bombardment of surfaces remains an unsolved problem that is basic to a complete understanding of secondary ion mass spectrometry (SIMS),[1-4] ion scattering spectrometry (ISS),[5-9] and the sputtering behavior of materials.[10,11] Most investigations of charge states of secondary particles are concerned with particles emanating from a cascade sputtering mechanism,[12-14] and, although this is the ejection mechanism of most general interest,

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