

abundance of EtS^- for the vanadium system may indicate a preference for S-S bond insertion. Interestingly, the metal cation experiments show that V^+ and Ti^+ form stronger sulfur bonds than either Fe^+ or Co^+ ,⁶⁴ although it is unclear if a valid correlation with anions can be made through arguments involving the relative electron deficiency of earlier transition metals. The relatively low product intensities coupled with the isotope overlap of $\text{MoSSC}_2\text{H}_3^-$ and MoSSEt^- prevented an accurate product branching ratio from being obtained for the molybdenum system.

Conclusion

It has been shown in this study that atomic metal anions react with organosulfur compounds in the gas phase. These reactions generally involve cleavage of the carbon-sulfur bond, and retention of the charge by the metal-bearing species. With the limited number of compounds studied, it appears that V^- , Cr^- , Mo^- , Fe^- , and Co^- all react similarly with regards to the product ions formed, but differ in the reactivity and extent of secondary reaction processes.

Reactions of metal anions with H_2S , thiols, and CS_2 yield useful limits on a variety of thermochemical parameters (refer to Tables III and IV). It was also noted in the thiol study that the direct cleavage pathway became more favorable over other reaction pathways as the stability of the alkyl radical increased. Reactions of Fe^- and Co^- with thiols are remarkable in their similarity to reactions involving the corresponding cations, Fe^+ and Co^+ .⁶⁴ The major difference arises apparently from the immediate alkene loss upon hydrogen transfer to the metal anion center without subsequent transfer to the thiol portion of the species to form an H_2S -ligated system.

Both Fe^- and Co^- react rapidly with dimethyl disulfide and diethyl disulfide showing a distinct preference of cleaving the C-S bond over the S-S bond. Reactions involving diethyl disulfide also show a greater extent of dehydrogenation for the iron system relative to the cobalt. An estimate for the electron affinity of MSCH_3^- and a limit for MSC_2H_5^- ($\text{M} = \text{Fe}^-$ and Co^-) were also presented and are based on the assumption that a representative charge distribution occurs before cleavage.

In contrast to thiol and disulfides, the sulfides reacted sluggishly or displayed a complete lack of reactivity. Only the small, ring-strained cyclic sulfides reacted readily. At present, we have no valid explanation for this lack of reactivity.

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Registry No. Co^- , 16727-18-7; Fe^+ , 22325-61-7; H_2S , 7783-06-4; MeSH , 74-93-1; EtSH , 75-08-1; *n*-PrSH, 107-03-9; *i*-PrSH, 75-33-2; *n*-BuSH, 109-79-5; *s*-BuSH, 513-53-1; *t*-BuSH, 75-66-1; PhSH, 108-98-5; PhCH_2SH , 100-53-8; FeS^- , 116784-36-2; FeSH^- , 116784-38-4; FeSH_2^- , 116784-37-3; CS_2 , 75-15-0; CoS^- , 116784-39-5; CoSH^- , 116784-40-8; CoSH_2^- , 116784-41-9; FeS , 1317-37-9; CH_3SSCH_3 , 624-92-0; $\text{C}_2\text{H}_5\text{SSC}_2\text{H}_5$, 110-81-6; MeSMe , 75-18-3; MeSEt , 624-89-5; EtSEt , 352-93-2; *i*-PrS(*i*)Pr, 625-80-9; *n*-BuS-*n*-Bu, 544-40-1; *s*-BuS-*s*-Bu, 626-26-6; *t*-BuS-*t*-Bu, 107-47-1; (*n*- C_5H_{11}) $_2\text{S}$, 872-10-6; *c*- $\text{C}_2\text{H}_4\text{S}$, 420-12-2; *c*- $\text{CH}(\text{CH}_3)\text{CH}_2\text{S}$, 1072-43-1; *c*- $\text{C}_3\text{H}_6\text{S}$, 287-27-4; V^- , 16727-17-6; Cr^- , 19498-56-7; Mo^- , 54604-28-3; CrS^- , 116784-42-0; MoS^- , 116784-43-1.

Direct Evidence for the Existence and the Relative Stability of Gaseous Ethylenebenzenium Ions from a ^{13}C -Labeling Study

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Abstract: Direct evidence is reported for the existence of unsubstituted ethylenebenzenium ions in the gas phase, based on ^{13}C -labeling of a methylene position in the precursor β -phenylethyl alcohol or chloride. The ^{13}C location in the products of the substitution reaction induced by gaseous cations in the presence of methanol is consistent with the occurrence of ethylenebenzenium ions **3** which do not display a facile isomerization to benzylic ions **6**. The fate of the ^{13}C label in the reaction has been established by the mass spectrometric analysis of the products. It has been verified further by NMR spectrometry, applied for the first time to the analysis of an ion-molecule product from a gas-phase radiolytic study.

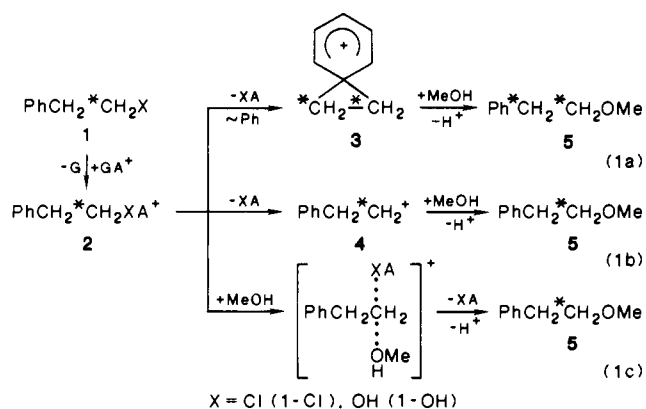
It is known, since Cram's pioneering work, that the presence of a β -aryl substituent markedly influences the reactivity of arylalkyl derivatives both in solvolytic and Friedel-Crafts alkylation reactions.¹ The extent of the intramolecular nucleophilic assistance by the β -aryl group depends on structural features of the substrate, such as the presence of substituents either in the side chain or on the aromatic nucleus, and on the medium, increasing in more ionizing, less nucleophilic solvents. With regard to the substrate structure, protonation of unsubstituted β -phe-

nylethyl chloride in superacidic media leads irreversibly to symmetrical ethylenebenzenium ions, at variance with β -phenylethyl chlorides bearing methyl substituents in their side chain.² As to the medium effect, it is the purpose of this work to extend the investigation to the gas phase, where phenyl participation should be enhanced, due to the low concentration of external nucleophiles, provided of course that formation of ethylenebenzenium ion is energetically allowed. Indeed, formation of gaseous alkylbenzenium ions was recently unambiguously inferred from the isomeric composition and the stereochemical features of the products obtained from the protonation or alkylation of 2-phenyl-3-X-butane, 2-phenyl-1-X-propane, and 1-phenyl-2-X-propane ($\text{X} = \text{Cl}, \text{OH}$), followed by trapping of the intermediate

(1) (a) Lancelot, C. J.; Cram, D. J.; Schleyer, P. v. R. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol III, Chapter 27. (b) Vogel, P. In *Carbocation Chemistry*; Elsevier: Amsterdam, 1985; Chapter 7. (c) Roberts, R. M.; Khalaf, A. A. In *Friedel Crafts Alkylation Chemistry*; Marcel Dekker: New York, 1984. (d) Lee, C. C.; Zohdi, H. F.; Sallam, M. M. *J. Org. Chem.* **1985**, *50*, 705. (e) Diaz, A.; Ladzins, I.; Winstein, S. *J. Am. Chem. Soc.* **1968**, *90*, 6546.

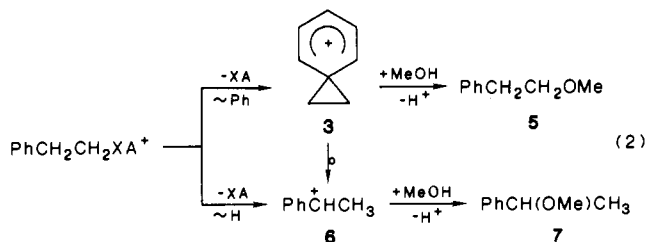
(2) (a) Olah, G. A.; Spear, R. J.; Forsyth, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 6284. (b) Olah, G. A.; Spear, R. J.; Forsyth, D. A. *Ibid.* **1977**, *99*, 2615.

Scheme 1



ions by methanol.^{3a} As suggested by the results obtained in superacidic media, formation of unsubstituted ethylenebenzenium ion **3** should be even more favored. The occurrence of this ion in the reaction with MeOH of 2-phenyl-1-X-ethane (**1**, X = F, Cl, OH), promoted by attack at X by gaseous acids (GA⁺), is supported by a body of evidence which excludes, at the same time, protonated benzocyclobutene as a possible alternative intermediate.^{3b} Still, a confirmation based on the chemical identity of the reaction product is lacking in this case, since the same β -phenylethyl methyl ether (**5**) may be formed either by the reaction of a primary β -phenylethyl cation with MeOH (reaction 1b) or by a concerted S_N2 displacement on the PhCH₂CH₂XA⁺ intermediate (reaction 1c) (Scheme 1).

While the intermediacy of ion **4** is unlikely on account of the lower stability of the primary cation and its predicted easy collapse to the ethylenebenzenium isomer,⁴ both possible pathways 1b and 1c can be verified by labeling one of the methylene groups. In fact, retention of their position in a S_N2 reaction is expected, while a label randomization between the side-chain methylenes in the product **5** is to be found if the reaction proceeds via the symmetrical ion **3**. A substrate labeled with ¹³C in the β position has been used in the present study with the aim of answering this question, and to ascertain the possible rearrangement of **3** into the more stable α -phenylethyl isomer **6**, a process observed in solution, under stable ion conditions, on increasing the temperature.^{2a}



On the other hand, it is reported⁵ that **3**, once formed in the gas phase, is stable and does not isomerize to **6** during its lifetime prior to assay by structurally diagnostic mass spectrometric techniques, whose results however are, in this case, a matter of debate.^{3b} A different behavior is observed under high-pressure conditions, where **3** is primarily obtained from the highly exothermic addition of phenylum ion to ethylene but is rapidly converted to **6** within a time lapse of ca. 10⁻⁹ s.⁶ Against such varied background it is of interest to ascertain whether **3** and **6**

are formed by parallel, independent routes, or whether an isomerization process takes place from the cyclic to the benzylic ion. We have addressed these two problems, within the framework of our previous studies,³ by exploiting the technique based on the γ -radiolysis of gaseous systems at nearly atmospheric pressure to generate gaseous ions GA⁺ of varying acidic strength.⁷ The intermediate ions from the attack of GA⁺ on the labeled substrate PhCH₂¹³CH₂X are captured by MeOH, and the desired mechanistic information is based on the analysis of the neutral end products.

Experimental Section

Materials. The gases (O₂, CH₄, H₂) were research-grade products (Matheson Gas Products) of purity 99.9 mol %. When necessary, they were freed from traces of water by passage over molecular sieves. MeF (99 mol %) was purchased from Columbia Organic Chemical Co. The ¹³C-labeled substrates were synthesized from phenylacetic [1-¹³C]acid of 99% ¹³C isotope content (Cambridge Isotope Laboratories), reduced to 2-phenyl[1-¹³C]ethyl alcohol with the BH₃-tetrahydrofuran complex.⁸ The alcohol was converted into the corresponding chloride with retention of the ¹³C position by reaction with SOCl₂ in pyridine.⁹ The alcohol and the chloride were purified by preparative GLC, respectively, on the following columns: (i) 4 m long, 4-mm i.d. column, packed with Silicone DC-550, 10% w/w on 30/60 mesh Chromosorb W-AW; (ii) 2.5 m long, 4-mm i.d. column, packed with Versamid 900, 20% w/w on 30/60 mesh Chromosorb P.

The identity of the labeled reactants and the ¹³C location in their molecule were checked by NMR and mass spectrometry. In particular, the electron-impact mass spectrum of the end product, 2-phenylethyl chloride, is characterized by the fission of the PhCH₂-CH₂Cl bond, yielding a C₇H₇⁺ ion at the same *m/z* ratio (91) both from ¹³C-labeled 2-phenylethyl chloride and from an unlabeled reference sample, thus confirming the retention of ¹³C in the position β to the phenyl group in the two-step synthesis. A sample of PhCH₂¹³CH₂OMe was prepared by the Williamson reaction from MeI and the corresponding alcohol in diethyl ether.

Radiolytic Experiments. The gaseous samples were prepared according to an established procedure by introducing the gaseous components into Pyrex vessels of 250–350-mL volume. The irradiations were carried out in a 220 Gammacell (Nuclear Canada Ltd.) at 37 °C and dose rate 0.6 × 10⁴ Gy h⁻¹, usually to a total dose of 1.8 × 10⁴ Gy. The radiolytic products were analyzed by GLC-MS on a 12 m long, 0.2-mm i.d. fused-silica column, coated with a 0.33- μ m-thick film of cross-linked methylsilicone polymer, using a Hewlett-Packard HP 5890 gas chromatograph coupled with a HP 5970 B mass detector. Precise ion abundance ratios were obtained in the selected-ion monitoring acquisition mode.

NMR Analysis. The ¹H and ¹³C NMR spectra were recorded on a Varian XL 300 spectrometer, with the deuterium or the ¹³C signal of the solvent CDCl₃ as the lock and reference frequency for assignment of chemical shifts. The ¹H probe operated at 299.94 MHz. The ¹³C probe operated at 75.43 MHz, with proton broad-band noise decoupling when required. The preparation of the sample of 2-phenylethyl methyl ether formed in the radiolytic experiment was critical because of the comparably small amount of product formed. The limiting factor in radiolytic reactions is the amount of energy absorbed by the system; that was increased using a relatively high dose (6 × 10⁴ Gy) and the largest sample (1 L) allowed by the inner volume of the Gammacell, while the concentration ratio of the gaseous reactants was kept constant. The irradiated product mixture was recovered by freezing the vessel in liquid nitrogen and repeatedly washing its walls with ethyl acetate. The solution was then concentrated, and the product was isolated and purified by preparative GLC, removing the large excess of unreacted ¹³C-labeled 2-phenylethyl chloride. The estimated amount of 2-phenylethyl methyl ether recovered was 0.2 mg, on which ¹H and proton-decoupled ¹³C spectra could be recorded.

Results

Table I shows the total and the relative yields of the products obtained in the γ -radiolysis of selected gaseous mixtures from

(3) (a) Fornarini, S.; Sparapani, C.; Speranza, M. *J. Am. Chem. Soc.* **1988**, *110*, 34. (b) Fornarini, S.; Sparapani, C.; Speranza, M. *Ibid.* **1988**, *110*, 42.

(4) Hehre, W. J. *J. Am. Chem. Soc.* **1972**, *94*, 5919. Thermochemical estimates show that ion **4** is attainable only by protonation of **1** with GA⁺ = H₃⁺ or CH₃⁺.^{3b}

(5) (a) Köppel, C.; Van de Sande, C. C.; Nibbering, N. M. M.; Nishishita, T.; McLafferty, F. W. *J. Am. Chem. Soc.* **1977**, *99*, 2883. (b) McEwen, C. N.; Rudat, M. A. *Ibid.* **1981**, *103*, 4355.

(6) Fornarini, S.; Speranza, M. *J. Am. Chem. Soc.* **1985**, *107*, 5358.

(7) For a survey of recent applications of this technique, see: (a) Speranza, M. *Gazz. Chim. Ital.* **1983**, *113*, 37. (b) Cacace, F. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G. Eds.; Reidel: Dordrecht, 1987.

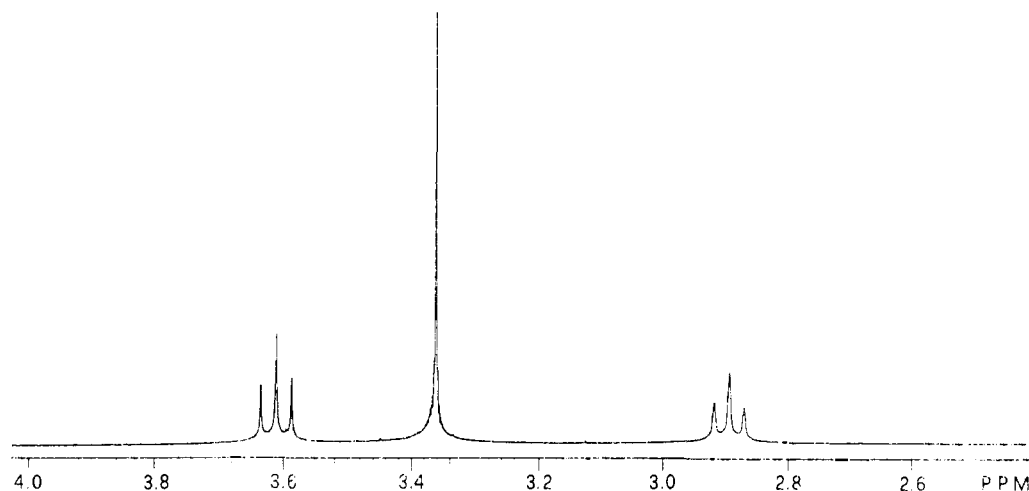
(8) Yoon, N. M.; Pak, C. S.; Brown, H. C.; Krishnamurthy, S.; Stocky, T. P. *J. Org. Chem.* **1973**, *38*, 2786.

(9) Murray, A., III; Williams, D. L. *Organic Synthesis with Isotopes*; Interscience: New York, 1958.

Table I. Product Yields from the Gas-Phase Attack of GA⁺ Acids on 2-Phenyl[1-¹³C]ethyl Chloride (1-Cl) and 2-Phenyl[1-¹³C]ethyl Alcohol (1-OH)

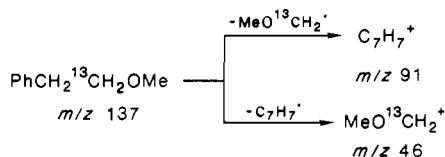
entry	system composition ^a (Torr)			relative distribution of products (%)				absolute yield ^b (<i>G_M</i>)
	substrate	bulk gas	MeOH	PhCH ₂ CH ₂ OMe (5)	PhCH(OMe)CH ₃ (7)	PhCH=CH ₂	PhCHO	
1	1-Cl (0.8)	MeF (700)	1.0	78	4	n.d. ^c	18	0.27
2	1-Cl (0.9)	CH ₄ (670)	1.3	64	8	7	20	1.15
3	1-Cl (0.4)	CH ₄ (160)	0.7	55	8	12	25	1.69
4	1-OH (0.4)	CH ₄ (700)	1.6	43	6	3	49	0.35
5	1-Cl (0.2)	H ₂ (700)	1.0	30	9	20	41	0.32

^aO₂, 10 Torr, was present in each system as radical scavenger. ^bThe radiochemical yield, *G_M*, indicates the number of product molecules M, formed per 100 eV of absorbed energy. Standard deviation of data ca. 15%. ^cn.d. = not detected.

**Figure 1.** ¹H NMR spectrum of PhCH₂CH₂OMe (5).

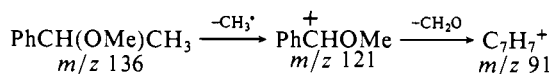
2-phenyl-1-X-[1-¹³C]ethane (1-Cl, 1-OH). Routine control experiments show that these products are not formed during the workup, but their formation necessitates γ -irradiation of the gaseous mixtures. The dependence of the products distribution from these and other substrates on the environmental conditions has already been discussed elsewhere.^{3b} Here attention is focused on the position of the ¹³C label in the major and most significant ether products, 5 and 7.

Mass Spectrometric Analysis. The mass spectrum of a PhCH₂¹³CH₂OMe reference sample is characterized by the neat cleavage of the side-chain C-C bond, with no carbon atom scrambling in the molecular ion prior to fragmentation.



It follows that the *A₉₁:A₉₂* and *A₄₆:A₄₅* abundance ratios measure the relative distribution of ¹³C in the positions β and α to the phenyl group, respectively. Such ratios are listed in Table II for the ether 5 formed under the selected reaction conditions. In all cases, no significant deviation from unity is observed, which indicates an equal ¹³C abundance in the α and β side-chain positions.

A ¹³C-labeled specimen of ether 7 was not easily available, but the analysis of the products from the radiolytic experiments is self-explanatory. The major fragmentation involves side-chain methyl loss while formation of the C₇H₇⁺ ion is also significant:



The presence of a ¹³C atom adjacent to the phenyl group would shift the above *m/z* ratios from 121 to 122 and, respectively, from 91 to 92. The mass spectrum of 7 formed from experiments 1-5 demonstrates the presence of only the ions at *m/e* 121 and 91, indicating that the label is exclusively retained in the original

Table II. Relative Ion Abundances in the Substitution Products 5 and 7 from the Gas-Phase Attack of GA⁺ Acids on 2-Phenyl[1-¹³C]ethyl Alcohol and Chloride

entry ^a	ion abundance ratios			
	PhCH ₂ CH ₂ OMe (5)		PhCH(OMe)CH ₃ (7)	
	<i>A₄₆:A₄₅</i>	<i>A₉₁:A₉₂</i>	<i>A₁₂₁:A₁₂₂</i>	<i>A₉₁:A₉₂</i>
1	50:50	49:51	94:6	100:ca. 0 ^b
2	50:50	47:53	93:7	100:ca. 0 ^b
3	49:51	48:52	93:7	96:4
4	48:52	50:50	92:8	100:ca. 0 ^b
5	47:53	51:49	95:5	100:ca. 0 ^b

^aExperimental conditions are as those reported in Table I for the same entry number. ^bThe *m/z* 92 peak does not exceed the natural abundance ¹³C contribution to *m/z* 91.

position, β to the phenyl group.

NMR Spectra. Direct NMR observation of the ¹³C nucleus and indirect observation using ¹³C-satellite analysis of the ¹H spectra are powerful tools in quantitative and mechanistic investigations for systems which are enriched in ¹³C.¹⁰ NMR analysis of a product of the ion-molecule reaction from gas-phase γ -radiolysis experiments was, however, never attempted before, because of the lower sensitivity of NMR with respect to capillary GLC or mass spectrometry. This first application was directed to determine the position of the ¹³C label in the major product of interest, PhCH₂CH₂OMe, under conditions where its yield is comparatively high, i.e., expt 2, Table I, maximizing the available amount as described in the Experimental Section.

A standard sample of unlabeled PhCH₂CH₂OMe gives the following NMR data.

¹H spectrum (Figure 1): C₆H₅- δ 7.2-7.4 (m); PhCH₂- δ 2.89 (t) ³J_{H-C-C-H} 7.2 Hz; MeOCH₂- δ 3.60 (t), ³J_{H-C-C-H} 7.2 Hz; CH₃O- δ 3.36 (s). ¹³C spectrum: C₆H₅- δ 126.3 (para), 128.4, 128.9 (meta, ortho), 139.0 (ipso); PhCH₂- δ 36.3, ¹J_{13C-H} 126 Hz; MeOCH₂- δ 73.7, ¹J_{13C-H} 141 Hz; CH₃O- δ 58.7, ¹J_{13C-H} 140 Hz.

(10) Hinton, J.; Oka, M.; Fry, A. In *Carbon-13 in Organic Chemistry*; Buncl, E., Lee, C. C., Eds.; Elsevier: Amsterdam, 1977.

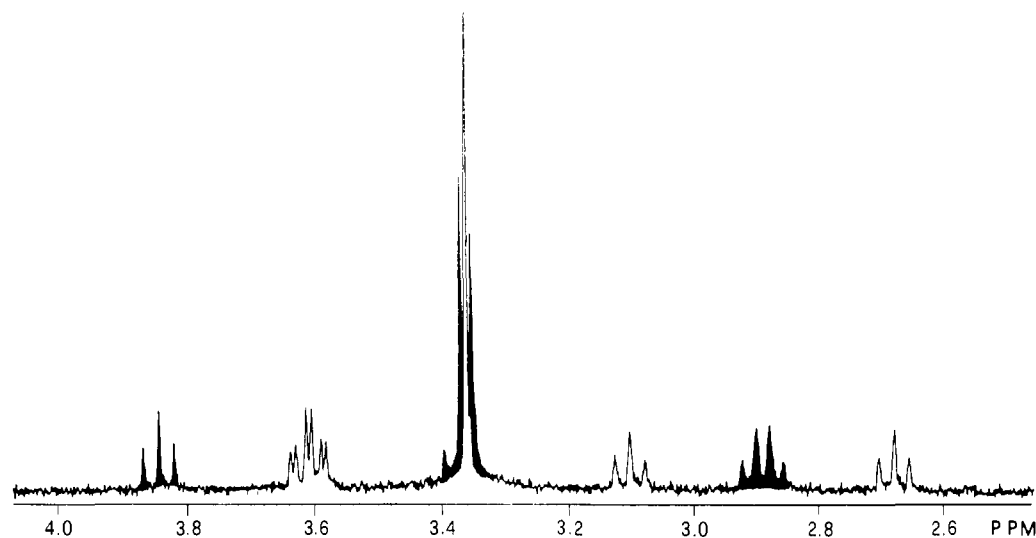


Figure 2. ^1H NMR spectrum of ^{13}C -labeled ether **5**, product of reaction entry no. 2, Table I.

The absorption patterns of aliphatic ^{13}C 's in the proton-coupled spectra are composite multiplets due to further, longer range coupling.

The ^{13}C labeled product **5** from expt 2 shows two signals at δ 36.3 and 73.7 of approximately equal intensity in its ^{13}C proton-decoupled spectrum. This is indicative that the ^{13}C label is spread over the two methylene side-chain positions in about equal proportions. However, in the lack of a straightforward correlation between the ^{13}C peak intensities and the number of carbon nuclei producing the peaks, a quantitative evaluation was based on the integrated intensities of the ^{13}C satellites in the ^1H spectrum. This spectrum, shown in Figure 2 in the relevant δ 2.5–4.0 interval, is the superposition of the spectra of two compounds, i.e., $\text{Ph}^{13}\text{CH}_2\text{CH}_2\text{OMe}$ and $\text{PhCH}_2^{13}\text{CH}_2\text{OMe}$ (darkened peaks).

$\text{Ph}^{13}\text{CH}_2\text{CH}_2\text{OMe}$ is characterized by the following signals: $\text{Ph}^{13}\text{CH}_2$ —, two triplets centered at δ 2.89, $^1J_{^{13}\text{C}-\text{H}}$ 127 Hz, $^3J_{\text{H}-\text{C}-\text{C}-\text{H}}$ 7.1 Hz; MeOCH_2 — δ 3.61 (doublet of triplets), $^3J_{\text{H}-\text{C}-\text{C}-\text{H}}$ 7.2 Hz, $^2J_{^{13}\text{C}-\text{C}-\text{H}}$ 2.5 Hz; CH_3O — δ 3.36 (s). The following signals belong to $\text{PhCH}_2^{13}\text{CH}_2\text{OMe}$: PhCH_2 — δ 2.89, quartet (J 6.6 Hz) due to degenerate coupling, $^3J_{\text{H}-\text{C}-\text{C}-\text{H}} \approx ^2J_{^{13}\text{C}-\text{C}-\text{H}}$; $\text{MeO}^{13}\text{CH}_2$ —, two triplets centered at δ 3.61, $^1J_{^{13}\text{C}-\text{H}}$ 141 Hz, $^3J_{\text{H}-\text{C}-\text{C}-\text{H}}$ 7.0 Hz (only one peak of the upfield triplet is detectable; the other two are hidden below the methoxyl group absorption); CH_3O — δ 3.36 (d) $^3J_{\text{H}-\text{C}-\text{O}-^{13}\text{C}}$ 5.1 Hz.

The integrated intensities of the pertinent methylene signals reveal that the two isotopomers are formed in exactly the 1:1 ratio.

Discussion

The ionization effected by the γ -radiolysis involves primarily the bulk reactant gases H_2 , CH_4 , MeF , from which gaseous Bronsted (H_3^+ , CH_5^+ , C_2H_5^+) or Lewis acids (C_2H_5^+ , Me_2F^+), are formed by a known sequence of reactions.¹¹ These ions are generally formed with excess internal energy, and reach thermal equilibrium by unreactive collisions with the bulk gas, before encountering a substrate molecule, whose relative concentration is typically 0.1 mol %. The ions may attack the substrate **1** either at its π center, in which case for $\text{GA}^+ = \text{C}_2\text{H}_5^+$, Me_2F^+ they give detectable substitution products at the phenyl ring, not further discussed, or else at the X group, yielding the onium ion **2**, precursor to the substitution products **5** and **7**.¹² Of the three

pathways to product **5** outlined in Scheme I, the direct $\text{S}_{\text{N}}2$ (reaction 1c) and a long-lived primary β -phenylethyl cation **4** may be discarded on the basis of the observed ^{13}C label scrambling over the two side-chain positions. At the same time, such result provides a definite proof for an ionic species, wherein phenyl migration has rendered the two positions equivalent, and therefore strong confirmatory evidence for the ethylenebenzenium ion **3**.^{3b} This behavior is uniformly observed, independently of the leaving group ability of the XA moiety, which decreases in the order $\text{HCl} > \text{MeCl} > \text{H}_2\text{O}$. The possibility that a radical rather than ionic pathway is responsible for the formation of **5** is in conflict with the very nature of this product. In fact, the β -phenylethyl radical is expected to abstract a hydrogen atom from MeOH rather than attack its oxygen atom. Furthermore, the β -phenylethyl radical is known to have no tendency to bridge, the reverse process being observed instead.¹³

The formation of ion **3** (reaction 1a) thus predominates over the $\text{S}_{\text{N}}2$ reaction 1c, meaning that a Ph to XA displacement at the electrophilic carbon is favored over the MeOH to XA displacement. In other cases, an opposite selectivity is apparently followed. Examples are found in the gas-phase attack of mild carbenium ions to arenes bearing OMe or OH substituents, mostly directed at the oxygen atom.¹⁴ However, in the present system a specific kinetic factor comes into play, i.e., the high "effective" concentration of the Ph group adjacent to the reaction center,³ which combines with a thermodynamic one. In fact, the arenium ion **3** benefits from the special stabilization due to the presence of the spiro cyclopropyl ring, which confers it with the character of a cyclopropylcarbinyl cation.^{2a}

As the leaving group departure is a unimolecular process in all the cases seen, it occurs much faster than the $\text{S}_{\text{N}}2$ substitution by a methanol molecule. If this reaction is controlled by the rate of collision between **2** and MeOH ,¹⁵ it follows that cleavage of XA is fast, occurring within 10^{-11} s. It is interesting to compare the gas-phase reactivity of substrates **1** with the solvolytic behavior of $\text{PhCH}_2^{14}\text{CH}_2\text{OTs}$ in ethanol, a solvent of closely similar nucleophilicity to MeOH . Under these conditions, almost complete retention of the ^{14}C position in the ether product is observed, complete scrambling occurring only in the poorly nucleophilic, highly ionizing trifluoroacetic acid.^{1a,e}

A second important piece of information concerns the conversion of the ethylenebenzenium ion **3** into the benzylic ion **6**, reaction

(11) (a) Herod, A. A.; Harrison, A. G.; McAskill, N. A. *Can. J. Chem.* **1971**, *49*, 2217. (b) Speranza, M.; Pepe, N.; Cipollini, R. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1179. (c) Ausloos, P.; Lias, S. G.; Gorden, R., Jr. *J. Chem. Phys.* **1963**, *39*, 3341.

(12) Taking into account the relative attack to the two nucleophilic sites of the substrates and to external nucleophiles as well, the absolute yields of products reported in Table I quantitatively account for the overall yield of the primary reactant ions formed in the radiolytic systems. The ionic nature of the products is confirmed by the effect of increasing base (MeOH , Me_3N) concentration, which markedly lowers their yield, by intercepting the precursor ions (ref 3).

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2. We observe that cleavage of XA may be accompanied by phenyl participation to form **3**, or by hydrogen migration to give **6**. The ether products **5** and **7** are obtained after nucleophilic trapping by MeOH of the two ions formed by *parallel, independent* routes. This is shown by the retention of ^{13}C label in position β to the phenyl group in ether **7**, which excludes a symmetrical ethylenebenzenium intermediate, and therefore a significant isomerization of **3** into **6**. This is so even under conditions where **3** might be formed with an excess energy content from the highly exothermic protonation of 1-Cl with H_3^+ , or in the CH_4 experiment at low pressure (entry no. 3) where collisional quenching of excited intermediates is less efficient. However, the reaction thermochemistry plays a role in the competition between the Ph and the H assistance to the leaving group departure, as the 7/5 product ratio increases (i) at low pressure, (ii) with the higher exothermicity of onium ion (**2**) formation from different bulk gases, which increases in the order $\text{MeF} < \text{CH}_4 < \text{H}_2$. This is indicative of a higher energy barrier for H, rather than Ph migration, which is conceivably related to the degree of positive charge developed at the reaction center. The attainment of a primary carbenium ion character, a structure close to **4**, may also determine the barrier to the **3** \rightarrow **6** isomerization. The **3** \rightarrow **6** isomerization was observed by Olah in superacids as a slow process.^{2a} A comparison may fairly be drawn between ion

reactivity in superacids and in the gas phase as specific ion solvation is limited in superacid media. There appears to be agreement between the two systems as the kinetic parameters derived by NMR in superacids for the **3** \rightarrow **6** process would make it undetectable in the 10^{-10} s time frame of the present gas-phase experiments.

In conclusion, the structural analysis by mass spectrometry and, for the first time, by NMR spectrometry, of the labeled end products of gas-phase ion-molecule reactions has revealed two major features of the C_8H_9^+ ion reactivity. In the first place, C_8H_9^+ , most likely of a static ethylenebenzenium structure, is unimolecularly formed from the acid-induced AX elimination from β -phenylethyl substrates, with no contribution of a $\text{S}_{\text{N}}2$ pathway or a long-lived primary cationic intermediate. Secondly, thermal gaseous ethylenebenzenium ions isomerize quite slowly, if at all, into benzylic ions, the two species being formed instead by independent Ph or H participation to the leaving group departure.

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Potential-Dependent Surface Chemistry of 3-Pyridinecarboxylic Acid (Niacin) and Related Compounds at Pt(111) Electrodes

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Abstract: Reported here are surface electrochemical studies of nicotinic acid (NA) and 11 related compounds adsorbed at well-defined Pt(111) electrode surfaces from aqueous solutions. Packing densities (moles adsorbed per unit area) adsorbed from solution at controlled pH and electrode potential are measured by means of Auger spectroscopy. Vibrational spectra of the adsorbed layer formed from each compound are obtained by means of high-resolution electron energy-loss spectroscopy (EELS). EELS spectra are compared with the IR spectra of the parent compounds. Electrochemical reactivity is studied by use of cyclic voltammetry. Surface structure is monitored by means of low-energy electron diffraction (LEED). Substances studied are as follows: 3-pyridinecarboxylic acid (nicotinic acid, NA, "niacin"); pyridine (PYR); benzoic acid (BA); (3-pyridyl)hydroquinone (3PHQ), synthesized here for the first time; 4-pyridinecarboxylic acid (isonicotinic acid, INA); 2-pyridinecarboxylic acid (picolinic acid, PA); 3,4-pyridinedicarboxylic acid (3,4PDA), and the analogous other pyridinedicarboxylic acids 3,5PDA, 2,3PDA, 2,4PDA, 2,5PDA, and 2,6PDA. Each of the pyridine derivatives is adsorbed at Pt(111) in a tilted vertical orientation, with an angle between the ring and the Pt surface of 70–75° being most common. Platinum–nitrogen bonding is evidently the predominant mode of surface attachment of these compounds, although coordination of carboxylate is significant at positive electrode potentials. Lacking an aromatic nitrogen, BA is oriented with its phenyl ring parallel to the Pt surface. EELS spectra display strong O–H stretching vibrations near 3550 cm^{-1} due to carboxylic acids in the meta and para positions, and weak/moderate signals near 3350 cm^{-1} due to carboxylic acids in the ortho positions. Nicotinic acid and related meta carboxylic acids display the remarkable characteristic that coordination of the pendant carboxylic acid moieties to the Pt surface is controlled by electrode potential. Oxidative coordination of the pendant carboxylate occurs at positive electrode potentials, resulting in disappearance of the O–H vibration and loss of surface acidity as judged by absence of reactivity toward KOH. Carboxylic acid moieties in the 4-position of pyridine are virtually independent of electrode potential, while those in the ortho positions are extensively coordinated to the Pt surface at all potentials. Adsorbed pyridinecarboxylic acids are relatively inert toward desorption and electrochemical oxidation/reduction and accordingly have a noticeable passivating effect on the Pt(111) electrode surface. Pyridinecarboxylic acids adsorbed from solution at Pt(111) are stable in vacuum. Adsorbed material is not removed in vacuum; when returned to solution, the adsorbed material displays the same chemical and electrochemical properties as prior to evacuation.

Adsorption of aromatic compounds from solution onto annealed Pt surfaces produces an oriented adsorbed layer.^{1–3} Adsorbate

molecular orientation is of fundamental as well as practical interest because of its influence upon the course of electrocatalytic oxidation/reduction processes and surface chemical reactions.^{4–7}

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