rather satisfactory framework for the interpretation of the gas-phase protonation of phosphoramides and phosphine oxide derivatives.

Conclusion

The determination of experimental gas-phase basicities indicates that the protonation of phosphines, phosphine oxides, and phosphoramides all lead to formation of phosphonium ions. Stabilization of the latter via π back-donation to the d orbitals of the phosphorus is evidenced by the spectacular effects of substituents in P^{III} and P^V compounds. In the case of phosphoramides, these effects permit us to conclude that O-protonation is the thermodynamically favored process.

These conclusions are substantiated by ab initio calculations on the protonation of model compounds. They point out the importance of including the d orbitals on phosphorus in order to describe the properties (geometry, energy) of these compounds. They also show that O-protonation of phosphoramides is the lowest energy process of protonation. These conclusions are in accordance with general concepts used to describe chemical reactivity. On the one hand, the principle of "hard and soft acids and bases" developed by Pearson can be applied.[36] Gas-phase protonation

is concerned with bare reactants and thus deals with hard acid reagents. The oxygen atom is known to be a harder base than a nitrogen center, in agreement with our experimental and calculational conclusions. On the other hand, the versatile behavior of phosphoramides in solution (change in site of protonation) can be understood on the basis of the experimentally determined solvation energies for onium ions.[37] The larger solvation energies have been determined for the stronger Brønsted acids BH$^+$; thus this effect tends to weaken the difference in basicity between O and N as solvation increases.

(36) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 643. (c) Ho, T. L. "Hard and Soft Acids and Bases Principle in Organic Chemistry"; Academic Press: New York, 1977.

(37) (a) Davidson, W. R.; Sunner, J.; Kebarle, P. *J. Am. Chem. Soc.* **1979**, *101*, 1675. (b) Meot-Ner (Mautner), M. *Ibid.* **1984**, *106*, 1265.

Gas-Phase Reactions of Free Vinyl Cation with Benzene and Free Phenylium Ion with Ethylene. A Comparative FT–ICR and Nuclear Decay Study

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Abstract: The results of a comparative FT–ICR (ca. 10^{-6} torr) and nuclear-decay study (6–65 torr) of the gas-phase reaction of vinyl cation with benzene and of phenylium ion with ethylene are reported. The isomeric population of the $C_8H_9^+$ intermediates obtained from both reactions and their interconversion pattern have been sampled by direct analysis of the reaction products. Stable (lifetime $>10^{-7}$ s) ring-protonated styrenes are primarily formed by vinyl cation attack on benzene, while ethylenebenzenium ion arises from phenylium ion addition to ethylene. At low pressures (ca. 10^{-6} torr), both species undergo appreciable hydrogen scrambling prior to fragmentation. At higher pressures (6–65 torr), fragmentation of $C_8H_9^+$ is efficiently prevented in favor of rapid isomerization to the thermodynamically more stable α-methylbenzyl cation. The present investigation provides no evidence for further isomerization to other conceivable structures. The benzene vinylation and the ethylene phenylation reaction mechanisms, as well as the isomerization pathways of the ensuing primary adducts, are discussed and compared to relevant mass spectrometric and kinetic data.

Spontaneous β decay of a tritium atom in multitritiated compounds affords a convenient means to generate free carbocations of defined structure into any system of interest and to study their reactions by tracer techniques.[1] The method was recently applied to gather otherwise inaccessible information on the reactivity of a free vinyl cation toward liquid benzene and methanol.[2] The results point to the high reactivity of the vinyl cation which efficiently adds to the nucleophilic site of the substrate to give as the major products, respectively styrene and methyl vinyl ether. In the liquid phase, no evidence of further isomerization of the vinylated adducts was observed.

In the gas phase, the $C_2H_3^+$ ions can easily be produced by mass spectrometric methods and their heat of formation evaluated.[3]

However, very little is known about the reactivity of vinyl cation toward organic substrates and the nature of the ionic intermediates involved. In fact, the gas-phase reaction of a $C_2H_3^+$ cation with benzene has been examined thus far only in a triple quadrupole mass spectrometer.[4] The unexpected hydrogen abstraction 1 was

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(2) Fornarini, S.; Speranza, M. *Tetrahedron Lett.* **1984**, *25*, 869.

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(4) Morrison, J. D.; Stanney, K.; Tedder, J. M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 838.

[†] University of Rome.
[§] Istituto di Chimica Nucleare del CNR, Monterotondo Stazione.

Table I. Yields of Tritiated Products from the Gas-Phase Attack of Vinyl Cation on Benzene

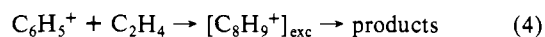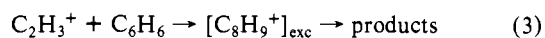| | system composition[a] | | | rel yields of products (%)[b] | | |
run no.	C_6H_6 (torr)	CH_3OH (torr)	$N(CH_3)_3$ (torr)	A	B	B/A
i	7.7		0.8	100		0
ii	5.2	0.7	0.4	80	20	0.25
iii	7.9	1.4	0.4	59	41	0.69
iv	7.9	3.0	0.4	29	71	2.45
v	8.0[c]	3.0	0.4	30	70	2.33
vi	7.8[d]	3.0	0.4	28	72	2.57
vii	32.0	6.5	0.4	22	78	3.54
viii	57.0	7.3	0.4	17	83	4.88

[a] All gaseous systems contain O_2 (4 torr) and tritiated ethylene (ca. 2 mCi). [b] Expressed as percentage of the total activity of the recovered aromatic products; standard deviation of data, ca. 10%. [c] 720 torr of helium is added to the gaseous mixture. [d] 720 torr of argon is added to the gaseous mixture.

the only process observed in addition to the charge exchange reaction 2, whereas no $C_8H_9^+$ adduct ion was detected. From

$$C_2H_3^+ + C_6H_6 \rightarrow C_2H_5^· + C_6H_4^{+·} \qquad (1)$$

$$C_2H_3^+ + C_6H_6 \rightarrow C_2H_3^· + C_6H_6^{+·} \qquad (2)$$
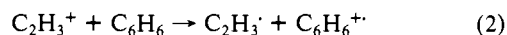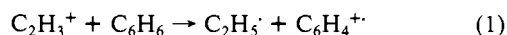
these and other results, obtained under peculiar experimental conditions, the general conclusion was advanced that simple ions, such as the vinyl cation, do not combine in the gas phase with aromatic nuclei to give σ-bonded adducts corresponding to the "Wheland intermediates" involved in related substitutions in solution, but rather they give rise to transient high-energy complexes losing their excess energy by fragmentation.[4]

The present paper reports a comparative study of the reactivity of gaseous vinyl cations toward benzene under largely different experimental conditions, namely at the very low pressures (ca. 10^{-6} torr) typical of FT–ICR mass spectrometry and at the much higher pressures (6–65 torr) accessible to the decay technique (eq 3). Apart from the possibility to extend directly to the gas phase the reactivity data that characterize vinyl cation in solution,[2] it was hoped to gather information upon the actual occurrence and the nature of the charged reaction intermediate, i.e., the $C_8H_9^+$ ion, whose formation from electron impact on different precursors together with its predominant isomerization pathways has been investigated in the gas phase.[5] In this context, an additional route to the gaseous $C_8H_9^+$ adduct has been followed, namely the ionic phenylation of ethylene (eq 4), whose behavior under comparable FT–ICR and nuclear decay conditions has been contrasted with that of the benzene vinylation reaction 3.

$$C_2H_3^+ + C_6H_6 \rightarrow [C_8H_9^+]_{exc} \rightarrow products \qquad (3)$$

$$C_6H_5^+ + C_2H_4 \rightarrow [C_8H_9^+]_{exc} \rightarrow products \qquad (4)$$

Experimental Section

Materials. The key substrates for the nuclear-decay experiments, namely multitritiated ethylene and benzene, were synthesized and purified with previously described procedures.[2,6] He, Ar, O_2, $N(CH_3)_3$, and C_2H_4 were obtained from Matheson Gas Products Inc.; their stated purity exceeded 99.3 mol %. Aldrich Chemical Co. and Fluka AG provided all the other products used as components in the FT–ICR and nuclear-decay experiments. Isomeric methoxyphenylethylenes and -ethanes were prepared according to established procedures.[7] Their identity was checked by conventional IR and NMR spectroscopy.

(5) (a) Nibbering, N. M. M.; Nishishita, T.; Van de Sande, C. C.; Mc Lafferty, F. W. *J. Am. Chem. Soc.* **1974,** *96,* 5668. (b) Koppel, C.; Van de Sande, C. C.; Nibbering, N. M. M.; Nishishita, T.; Mc Lafferty, F. W. *Ibid.* **1977,** *99,* 2883. (c) Koppel, C.; Mc Lafferty, F. W. *J. Chem. Soc., Chem. Commun.* **1976,** 810. (d) Koppel, C.; Mc Lafferty, F. W. *J. Am. Chem. Soc.* **1976,** *98,* 8293. (e) Barbalas, M. P.; Mc Lafferty, F. W. *Org. Mass Spectrom.* **1982,** *17,* 640.

(6) Speranza, M.; Cacace, F.; Wolf, A. P. Erhenkaufer, R. *J. Labelled Compd. Radiopharm.* **1982,** *19,* 905.

(7) Loudon, G. M.; Smith, C. K.; Zimmerman, S. E. *J. Am. Chem. Soc.* **1974,** *96,* 465.

Decay Experiments. Multitritiated ethylene or benzene (ca. 1–2 mCi), diluted with the corresponding unlabeled hydrocarbons to a specific activity of 363 and 84 Ci mol^{-1}, respectively, was introduced into carefully outgassed and evacuated Pyrex vessels containing measured amounts of the organic substrate, i.e., benzene and ethylene, respectively, together with appropriate additives (He, Ar, CH_3OH, O_2, and $N(CH_3)_3$). The vessels were then sealed off and stored for 10–14 months in the dark at room temperature. The composition of the decay systems is shown in Table I.

The ampules were then opened under airtight conditions and their contents analyzed on a C. Erba Fractovap 4200 gas chromatograph equipped with a high-sensitivity hot-wire detector (Model 450) coupled in series with a Berthold proportional counter tube, kept at 180 °C. Two different sampling techniques were adopted: (i) Small portions of the homogeneous gaseous content of the decay vessels, heated at ca. 100 °C, were withdrawn with a gas syringe and injected directly in order to analyze the gaseous tritiated products. (ii) The vessels were cooled and thoroughly washed with ethyl acetate. Measured aliquots of the acetate solution were injected into the radio gas chromatograph.

The tritiated products were identified by comparing their retention volumes with those of authentic samples on the following columns: (a) a 2 m long glass column containing 1% SP 1000 on Carbopack B at temperatures ranging from 30 to 190 °C; (b) a 2 m long stainless steel column containing 5% SP 1200:5% Bentone 34 on 100–120 mesh Supelcoport at 100 °C; (c) a 6 m long stainless steel column containing 20% E 301 on 60–80 mesh Chromosorb W at 100 °C.

Fourier Transform (FT–ICR) Mass Spectrometric Experiments. All mass spectrometric experiments were performed on a Nicolet FT-MS 1000 ICR spectrometer equipped with a 2.54 cm cubic trapping cell situated between the poles of a superconducting magnet operated at 2.0 T. Sample pressures (uncorrected) were measured with a Granville-Phyllips 280 Bayard-Alpert Ion Gauge with resolution typically 1000 fwhh (full width half height) at mass 100. Inlet system and trapping cell were kept at room temperature. Ions were trapped in the cell by a differential trapping voltage of about 1.0 V. Typical operating conditions were as follows: nominal electron beam energy: 20 eV, electron beam pulse: 3 ms, emission current: 400 nA, total pressure: 1.5×10^{-6} torr. The vinyl cation/benzene and phenylium ion/ethylene reaction sequences were investigated by double and triple resonance experiments on the appropriate ionic species with variable reaction times up to 1 s.

Results

Gas-Phase Vinylation of Benzene. When tritiated ethylene is allowed to decay in gaseous benzene, in the presence of variable concentrations of CH_3OH and $N(CH_3)_3$, two tritiated aromatic products are exclusively formed, namely styrene and α-methoxyphenylethane, whose relative distribution as a function of the decay system composition is reported in Table I. Reaction conditions were chosen to span a factor of 11 in the partial pressure of benzene (from 5.2 to 57 torr),[8] whereas the concentration ratio of the minor additives, i.e., [CH_3OH]:[$N(CH_3)_3$], ranges from 0 to approximately 20. The overall absolute yield of the tritiated aromatic products in Table I is around 60%,[9] the remainder being

(8) In a few instances, the total pressure of the decay system was raised to ca. 730 torr by adding inert gases, such as helium or argon (see footnotes c and d of Table I).
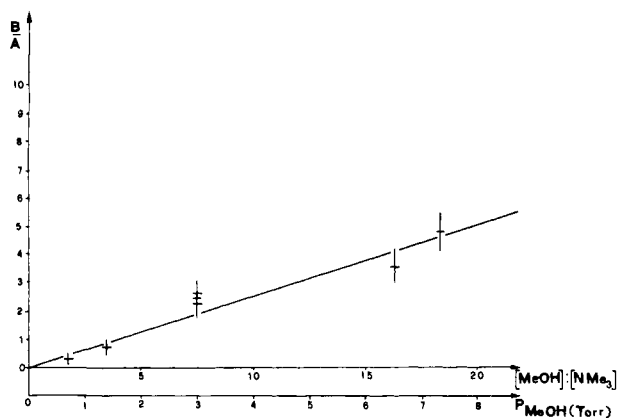
Figure 1. Relative distribution of radioactive products from the $C_2H_3^+$–C_6H_6 decay samples as a function of the system composition.

accounted for by low boiling products, arising either directly from fragmentation processes or deriving from the direct attack of vinyl cation to CH_3OH and $N(CH_3)_3$.

Analysis of Table I reveals that while styrene (A) is exclusively formed in the systems containing only benzene and $N(CH_3)_3$, it is invariably accompanied by α-methoxyphenylethane (B) when CH_3OH is present. Their yield ratio (the B/A ratio of Table I) is markedly dependent upon the system composition, whereas it appears rather insensitive to the total pressure.

An illustration of the results of Table I is given in Figure 1, which displays the linear dependence of the B/A ratio on the $[CH_3OH]:[N(CH_3)_3]$ ratio. No evidence for significant deviation from linearity emerges from the plot of Figure 1, at least within the $[CH_3OH]:[N(CH_3)_3]$ ratio investigated.

In order to obtain independent information on the mechanism of formation of the vinylation products, the $C_2H_3^+$ ion has been produced in the cell of a Fourier transform–ICR mass spectrometer by 20 eV electron impact on vinyl bromide. Its reaction pattern toward benzene and benzene-d_6 has been investigated by double and triple resonance experiments. Apart from the charge transfer process 2 (Table II), attack of $C_2H_3^+$ on benzene leads to the formation of both $C_6H_7^+$ and $C_8H_7^+$ (eq 5 and 6), whereas no evidence for the formation of the adduct $C_8H_9^+$ could be obtained. Use of benzene-d_6 shows that the proton transfer 5' from vinyl cation to benzene involves appreciable hydrogen atom scrambling. A similar process is observed in the formation of the $C_8X_7^+$ (X = H, D) addition intermediate, which however seems to occur via preferential HD loss (eq 6').

Gas-Phase Phenylation of Ethylene. An independent route to a $C_8H_9^+$ adduct in the gas phase is provided in principle by the ionic phenylation of ethylene. When tritiated benzene is allowed to decay in ethylene (55 torr), in the presence of a nucleophile $(CH_3OH, 4.4$ torr) and of a radical scavenger $(O_2, 4$ torr), formation of α-methoxyphenylethane predominates (relative yield 82%), minor amounts of styrene (4%) and anisole (14%) being formed as well. The overall absolute yield of these aromatic products amounts to ca. 45%, the remainder being accounted for by fragmentation and polymerization products.

It is worth mentioning that no other aromatic compounds, such as phenylacetylene, β-methoxyphenylethane, isomeric methoxyphenylethylenes, diphenylethylenes, etc., could be detected among the tritiated products from the phenylation of ethylene, nor from the vinylation of benzene.

Ionic phenylation of ethylene also has been investigated by the FT–ICR technique, under conditions comparable to those employed in the analogous study of the ionic vinylation of benzene. Both $C_6H_5^+$ and $C_6D_5^+$ ions were efficiently produced by 20 eV electron impact on the corresponding chlorobenzene and nitro-

Table II. Observed Product Ions from Vinyl Cation Attack on Benzene[a]

[a] [Benzene] : [C_2H_3Br] = 2:1; total pressure = 1.5×10^{-6} torr. Reaction time = 50 ms. [b] The relative abundance of ionic species with the same nominal mass (e.g., $C_6D_6^+$· and $C_6D_5H_2^+$) was deduced by taking into account the ion distribution observed in the ICR spectra from C_6H_6. [c] A small fraction of the m/e 107, 109 ion abundances may be due to the formation of protonated vinyl bromide ($C_2H_4^{79}Br^+$ m/e 107 and $C_2H_4^{81}Br^+$ m/e 109).

benzene precursors ($1-2 \times 10^{-7}$ torr). These ionic species were isolated by triple resonance experiments and allowed to react with ethylene (1.5×10^{-6} torr). As expected,[10] attack of $C_6H_5^+$ ion on C_2H_4 leads to the formation of both $C_6H_7^+$ (60%) and $C_8H_7^+$ (40%).[11] The adduct $C_8H_9^+$ was completely absent even at the highest pressures (up to 5×10^{-6} torr) and at the longest reaction times (up to 1s) employed. Formation of m/e 79 ($C_6D_2H_3^+$), m/e 80 ($C_6D_3H_2^+$), and m/e 81 ($C_6D_4H^+$) in almost equal proportions from the $C_6D_5^+$ attack on ethylene suggests that partial hydrogen scrambling takes place in the collision complex prior to formation of the addition–elimination products.

Discussion

Nature of the Ionic Reactants. A common feature of the spontaneous β decay of a tritium atom in a tritiated hydrocarbon molecule RT is the formation of the corresponding carbocation R^+ in high yields (ca. 80%), together with minor amounts of many smaller fragments (eq 7). This statement is based on a series

$$RT \xrightarrow[\text{decay}]{\beta^-} [R^3He^+] \xrightarrow[-^3He]{\text{fast}} R^+ \qquad (7)$$

$$R = \text{alkyl, aryl}$$
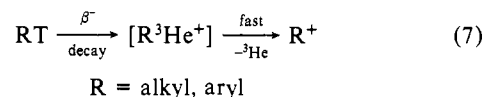
of mass spectrometric studies[12] showing that ca. 80% of the decay events in RT lead invariably to formation of stable R^+ ions, which survive undissociated for more than 10^{-5} s. A minor fraction (ca. 20%) of the decay ions receives instead a large excess of internal energy, mostly due to the β-electron and antineutrino recoil, and to the "shaking" of the electron cloud as the β particle leaves the tritium atom, causing further extensive fragmentation. The mass spectrometric data are consistent with the theoretical treatment of the molecular consequences of β^- decay, which predicts that a large fraction of the primary daughter ions are formed in the ground electronic state, with little or no excitation energy.[13]

In this way, ground-state vinyl and phenyl cations were efficiently formed from the β decay of respectively multitritiated ethylene and benzene. The nature and the properties of the

(9) The absolute yields, expressed as the ratio of total activity of the end products to the activity originally contained in the nuclear-decay-produced vinyl cation, can be estimated from the initial activity and the isotopic content of the tritiated ethylene sample, the decay rate of the tritium, and the absolute counting efficiency of the detector employed.

(10) Speranza, M.; Sefcik, M. D.; Henis, J. M. S.; Gaspar, P. P. *J. Am. Chem. Soc.* **1977**, *99*, 5583.
(11) This relative distribution was measured after 50 ms reaction time.
(12) Wexler, S. In "Actions Chimiques et biologiques des radiations"; Haissinsky, M., Ed.; Masson et cie: Paris, 1965.
(13) (a) Ikuta, S.; Okuno, K.; Yoshihara, T.; Shiokawa, T. *Radiochem. Radioanal. Lett.* **1975**, *23*, 213. (b) Okuno, K.; Yoshihara, K.; Shiokawa, T. *Radiochim. Acta* **1978**, *25*, 21.
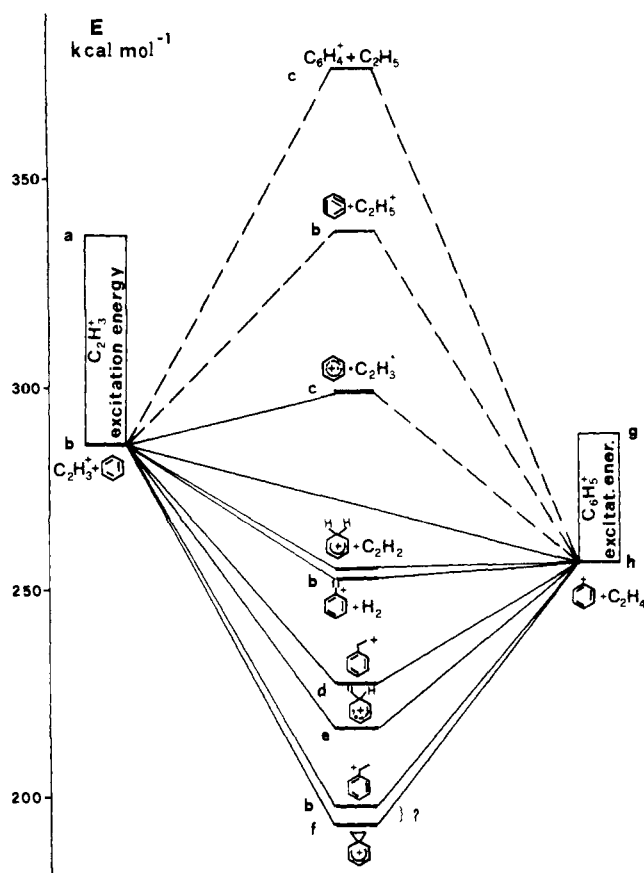
Figure 2. Energetics of several relevant ion–molecule reactions. (a) See ref 16; (b) Aue, D. H., Bowers, M. T. In "Gas-Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press, New York, 1979; (c) Field, F. H.; Franklin, J. L. In "Electron Impact Phenomena"; Academic Press: New York, 1970; (d) Hehre, W. J. *J. Am. Chem. Soc.* **1972**, *94*, 5919; (e) a tentative estimate of this reaction enthalpy can be arrived at by assuming that the proton affinity of styrene at the ring position bearing the vinyl group is the same as that of benzene (PA = 185.8 kcal mol⁻¹; see part b); (f) Schoeller, W. W. *J. Chem. Soc., Chem. Commun.* **1974**, 872; (g) see ref 18; (h) see ref 17.

so-produced free phenylium ions have been previously described in detail.[14] As to the vinyl cations, it should be mentioned that the nuclear transition is a vertical process converting the tritiated ethylene molecule into a $[C_2X_3{}^3He^+]$ transient (with X = H, T), which promptly releases ^3He. The vinyl cation, formed in its electronic ground state, is characterized by a certain excess of internal energy due, inter alia, to the relaxation from its original geometry, reminiscent of the neutral precursor, to the linear structure of the vinyl cation, which is generally accepted as the most stable structural arrangement for the $C_2H_3{}^+$ ion.[15] In the extreme hypothesis of an overall adiabatic process for the nucleogenic vinyl cation, semiempirical calculations set an upper limit of ca. 50 kcal mol⁻¹ to its vibrational excitation.[16] Therefore, the actual enthalpy of formation of the vinyl cation in the decay systems may span from ca. 266 kcal mol⁻¹, which is the heat of formation of a vibrationally ground-state vinyl cation,[3a,b] to ca.

316 kcal mol⁻¹, which is estimated to be the maximum enthalpy of formation of a nucleogenic vibrationally exited vinyl cation.[16]

In the same way, the $\Delta H_f°$ of a nucleogenic phenylium ion may range from ca. 245[17] to over 270 kcal mol⁻¹.[18]

Several reaction channels are open to the tritiated vinyl cation in its attack on benzene, as illustrated in Figure 2. The figure gives the approximate reaction enthalpies for the relevant gas-phase processes together with those concerning the attack of phenylium ion on ethylene. Formation of $C_6H_4{}^+·$ and $C_2H_5{}^+$ ions from both ionic precursors is strongly endothermic and, therefore, a very inefficient reaction, as confirmed by their absence among the ionic processes occurring in a FT–ICR ion source (Table II). Vibrationally excited vinyl cations may undergo the slightly endothermic $(\Delta H° = +12$ kcal mol⁻¹) charge exchange reaction 2, when colliding with benzene, as shown by the small amount (ca. 13% relative abundance) of the benzene radical–cation observed in the ICR experiments. That this is a minor process in the decay experiments as well is suggested by the relatively high absolute yields of the tritiated aromatic products (ca. 60%).

A significant exothermicity characterizes all the remaining processes of Figure 2, including the hydride ion transfer from benzene to vinyl cation $(\Delta H° = -29$ kcal mol⁻¹). Of course, the reverse process, namely the hydride ion transfer from ethylene to phenylium ion, is endothermic $(\Delta H° = +29$ kcal mol⁻¹), being energetically allowed only if the phenylium ion is vibrationally excited. All the exothermic processes of Figure 2 therefore may be considered as potential sources of the radioactive products recovered in the decay experiments. Those leading to $C_6H_7{}^+$ and $C_8H_7{}^+$ intermediates have been directly observed by ICR mass spectrometric methods as well.

Vinyl Cation Attack on Benzene. Figure 1 shows a linear correlation between the α-methoxyphenylethane (B):styrene (A) yield ratio and the [CH₃OH]:[N(CH₃)₃] ratio (or the CH₃OH partial pressure, the P_{NMe_3} being kept constant at 0.4 torr) observed in the decay experiments. No significant deviation from the linearity is observed up to [CH₃OH]:[N(CH₃)₃] ≥ 18 (or up to $P_{CH_3OH} > 7$ torr). No similar linear dependence of the B/A ratio has been observed as a function of any other parameter or any combination of the parameters of Table I.

The linear trend of Figure 1 is suggestive of a vinylation mechanism leading to a α-methoxyphenylethane and styrene via two parallel and independent pathways (eq 3a,b), whose relative efficiency can be estimated to range around 0.3.
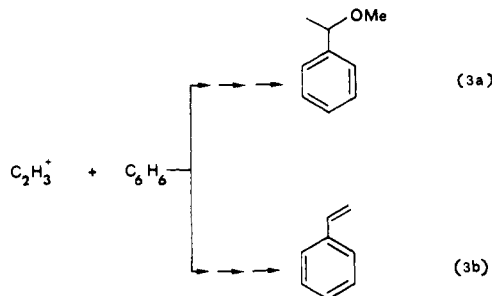
Accordingly, the first step of the vinylation of benzene is thought to be the formation of the corresponding arenium intermediate **1**, excited by the exothermicity of its formation process $(\Delta H° = -120 \pm 70$ kcal mol⁻¹) (eq 8). In the liquid phase, the excited intermediate **1** may be efficiently quenched by fast collisional

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(16) (a) Sustmann, R.; Williams, J. E., Jr.; Dewar, J. M. S.; Allen, L. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1969**, *91*, 5350. (b) Hopkins, A. C.; Yates, K.; Csizmadia, I. G. *J. Chem. Phys.* **1971**, *55*, 3835.

(17) The $\Delta H_f°$ of a vibrationally ground-state phenylium ion has been calculated to be 244.8 kcal mol⁻¹ (Castenmiller, W. A.; Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 207. Tasaka, M.; Ogata, M.; Ichikawa, H. *J. Am. Chem. Soc.* **1981**, *103*, 1885).

(18) According to ab initio calculations (Schleyer, P. v. R.; Kos, A. J.; Raghavachari, K. *J. Chem. Soc., Chem. Commun.* **1983**, 1296), the $\Delta H_f°$ of a phenylium ion with the geometry of benzene is ca. 32 kcal mol⁻¹ higher than that of a vibrationally ground-state phenylium ion. Thus, the maximum formation enthalpy availabile to a nucleogenic phenylium ion is computed to be ca. 277 kcal mol⁻¹, which is in satisfactory agreement with the experimental value $(\Delta H_f° = 266-270$ kcal mol⁻¹: Rosenstock, H. M.; Larkins, J. T.; Walker, J. A. *Int. J. Mass. Spectrom. Ion Phys.* **1973**, *11*, 309) derived from the ionization potential of the phenyl radical.

$$C_2H_3^+ \cdot \quad + \quad \text{⟶} \quad \mathbf{1} \qquad (8)$$
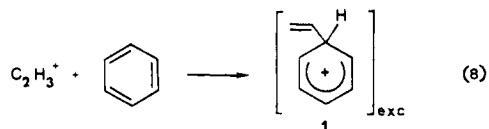
deactivation processes typical of the condensed environment. Rapid deprotonation of **1** by benzene provides a direct route to styrene.[2] In the gas phase, where collisional quenching is much less efficient, the excited intermediate **1** can undergo unimolecular fragmentation and extensive isomerization via hydrogen shifts to the ring positions[19] and to the unsaturated side chain to give eventually the thermodynamically most stable isomer among the conceivable structures **1–5** of eq 9.[20] Neutralization of inter-

$$\qquad\qquad\qquad\qquad\qquad (9)$$

2   **1**   **3**   **4**   **5**
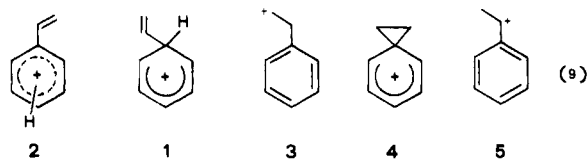
mediates **1–5** by fast proton transfer to a suitable acceptor B gives rise directly to labeled styrene (eq 10).

$$(1-5) \quad \xrightarrow[-BH^+]{+B} \quad \text{A} \qquad (10)$$
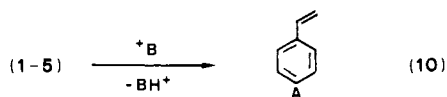
When CH_3OH is added to the decay systems, process 10 undergoes competition by the reaction of ions **1–5** with methanol. While **1** and **2** undergo exclusively proton transfer to the alcohol, intermediates **3–5** are expected to react with a methanol molecule to give the isomeric oxonium ions **6** and **7** (eq 11), which eventually lose a proton to a base (e.g., $N(CH_3)_3$) yielding the corresponding neutral methoxyphenylethane. The α-methoxyphenylethane

$$(3 \text{ and } 4) \quad \xrightarrow{+CH_3OH} \quad \begin{bmatrix} \mathbf{(6)} \end{bmatrix} \quad \xrightarrow[-BH^+]{+B} \quad \mathbf{(C)} \qquad (11a)$$

$$(5) \quad \xrightarrow{+CH_3OH} \quad \begin{bmatrix} \mathbf{(7)} \end{bmatrix} \quad \xrightarrow[-BH^+]{+B} \quad \mathbf{(B)} \qquad (11b)$$

isomer B is the only tritiated aromatic ether recovered together with styrene from all the $C_2H_3^+$–C_6H_6 decay systems containing CH_3OH. This fact lends support to the view that either structures **3** and **4** are not easily accessible to the primary vinylation intermediate **1** or, otherwise, they rearrange further to a thermodynamically more stable intermediate, namely the α-methylbenzyl ion **5**, before addition to CH_3OH.

Phenylium Ion Attack on Ethylene. To verify the latter possibility, excited ethylenebenzenium ion **4** was primarily produced from the reaction of a nucleogenic phenylium ion with ethylene.[21] The reactivity of the intermediate thus obtained under conditions similar to those employed in the vinyl cation decay systems has

been deduced from the distribution of the tritiated products formed. The high yield of α-methoxyphenylethane B (82%), which contrasts with the complete absence of the β-isomer C, spells in favor of an ethylenebenzenium ion **4** rapidly rearranging to the thermodynamically more stable isomer **5**, before being trapped by CH_3OH. This conclusion is valid a fortiori for an ethylenebenzenium ion **4**, conceivably formed from the vinyl cation attack on benzene, a process significantly more exothermic than the ionic phenylation of ethylene (Figure 2). Therefore, the results from the phenylium ion attack on ethylene in the presence of CH_3OH strongly suggest that the α-methylbenzyl ion **5**, rather then the ethylenebenzenium ion **4**, is thermodynamically most stable among the $C_8H_9^+$ isomers accessible to both the ionic vinylation of benzene and the ionic phenylation of ethylene, in contrast to theoretical predictions.[22]

However, the results provide no conclusive evidence on the actual formation of the ethylenebenzenium ion **4** (or the β-phenylethyl cation **3**) from the vinyl cation attack on benzene, since, in principle, stable α-methylbenzyl cations **5** may directly arise from **1** by 1,3-hydrogen shift from the ipso position of the ring to the β side-chain carbon.

Fourier Transform ICR Mass Spectrometric Experiments. Detailed information on the nature and the behavior of the primary adducts from vinyl cation attack on benzene stems from the analysis of the FT–ICR mass spectrometric data of Table II. Under the low-pressure conditions (ca. 10^{-6} torr) typical of the ICR experiments, the excited $C_8H_9^+$ intermediates formed cannot be efficiently quenched by nonreactive collisions and therefore undergo extensive fragmentation which prevents their detection. Three main reaction channels are open to the $C_8H_9^+$ adduct, namely charge exchange reaction 2, proton transfer 5, and addition–elimination process 6. All of them involve appreciable hydrogen atom scrambling, as shown by the results obtained with deuterated benzene.

The relative distribution of the $C_6X_7^+$ (X = H, D) ions, obtained from the $C_2H_3^+$ ion attack on C_6D_6 (Table II), seems to exclude their formation from a σ-bonded "addition complex" $C_8X_9^+$, wherein preliminary hydrogen randomization has completely or partially occurred.[23] Rather, an exothermic proton transfer from $C_2H_3^+$ to C_6D_6 may be responsible for the formation of the major product, $C_6D_6H^+$ (52%), whereas the occurrence of $C_6D_5H_2^+$ (16%) and $C_6D_4H_3^+$ (4%) can be accounted for by consecutive hydrogen atom transfers within the encounter complex from $C_2H_3^+$ and C_6D_6. The hydrogen scrambling may formally proceed either by consecutive proton shifts (eq 12) or via hydride ion transfers (eq 13).

$$[C_2H_3^+ \cdot C_6D_6] \; \rightleftarrows \; [C_2H_2 \cdot C_6D_6H^+] \; \rightleftarrows \; [C_2H_2D^+ \cdot C_6D_5H] \; \rightleftarrows$$
$$\mathbf{8}$$
$$[C_2HD \cdot C_6D_5H_2^+] \quad (12)$$

$$[C_2H_3^+ \cdot C_6D_6] \; \rightleftarrows \; [C_2H_3D \cdot C_6D_5^+] \; \rightleftarrows \; [C_2H_2D^+ \cdot C_6D_5H] \; \rightleftarrows$$
$$\mathbf{9}$$
$$[C_2HD \cdot C_6D_5H_2^+] \quad (13)$$

A hint to the scrambling mechanism is provided by the FT–ICR results concerning the ionic phenylation of ethylene by $C_6D_5^+$. Here, an extensive hydrogen atom rearrangement is observed, leading to almost equal proportions of $C_6D_4H^+$, $C_6D_3H_2^+$, and $C_6D_2H_3^+$, prior to the formation of $C_6X_7^+$ and $C_8X_7^+$ (X = H, D). It should be noted that all the above processes are nearly thermoneutral (Figure 2) and, therefore, may proceed via longlived $[C_6H_5^+ \cdot C_2H_4]$ collision complexes, where extensive hydrogen shuffling may occur prior to covalent bonding to produce $C_6X_7^+$ and $C_8X_7^+$ ions.[24]

(19) (a) Brouwer, D. M.; Mackor, E. L.; Mac Lean, C. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1970; Vol. 2. (b) Brouwer, D. M. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 611. (c) Olah, G. A.; Mo, Y. K. *J. Am. Chem. Soc.* **1972**, *94*, 9241. (d) Perez, G. *J. Phys. Chem.* **1976**, *80*, 2983.
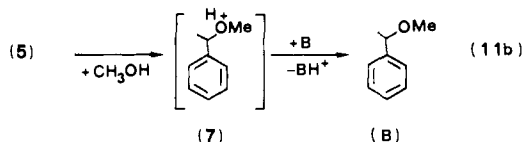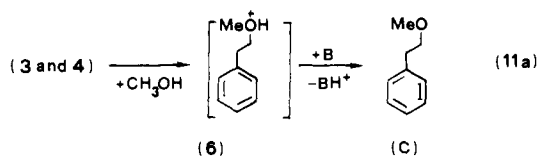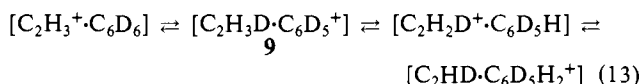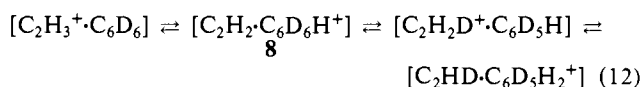
(20) (a) Fornarini, S.; Speranza, M.; Attinà, M.; Cacace, F.; Giacomello, P. *J. Am. Chem. Soc.* **1984**, *106*, 2498. (b) Lay, J. O., Jr.; Gross, M. L. *Ibid.* **1983**, *105*, 3445. (c) Harrison, A. G.; Houriet, R.; Tidwell, T. T. *J. Org. Chem.* **1984**, *49*, 1302.

(21) Colosimo, M.; Speranza, M.; Cacace, F.; Ciranni, G. *Tetrahedron* **1984**, *40*, 4873.

(22) Semiempirical MINDO/2 calculations predict **4** ($\Delta H_f° = 193$ kcal mol^{-1}: Scholler, W. W. *J. Chem. Soc., Chem. Commun.* **1974**, 872) to be more stable than **5** ($\Delta H_f° = 197$ kcal mol^{-1}: Aue, D. H.; Bowers, M. T. In "Gas-Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979). On these grounds, the energy levels concerning species **4** and **5** in Figure 2 were reported.

(23) (a) Nibbering, N. M. M.; De Boer, Th. J. *Org. Mass Spectrom.* **1969**, *2*, 157. (b) Venema, A.; Nibbering, N. M. M.; De Boer, Th. J. *Ibid.* **1970**, *3*, 1589.

It follows that the activation barrier for the hydrogen scrambling within $[C_6D_5^+\cdot C_2H_4]$ must be relatively low if compared to that related to the formation of $C_6X_7^+$ and $C_8X_7^+$. Considering now the substantially higher energy content of the $C_2H_3^+-C_6D_6$ pair, if compared to the $C_6D_5^+-C_2H_4$ couple, it can be concluded that should a loosely bonded $[C_6D_5^+\cdot C_2H_3D]$ complex be a common intermediate in both processes, it would behave in the same way, namely dissociate to $C_6X_5^+$ and C_2X_4 (X = H, D). It is also likely that dissociation is preceded by partial hydrogen scrambling within the encounter complex. The fact that ICR spectra show no appreciable formation of $C_6X_5^+$ ions in the vinylation of benzene suggests that formation of $C_6D_5H_2^+$ and $C_6D_4H_3^+$ from $C_2H_3^+$ attack on C_6D_6 cannot occur via intermediate **9** (eq 13), but rather it involves other species, presumably **8**, which are direct precursors of $C_6X_7^+$ and whose formation process (eq 12) is likely characterized by an appreciably lower energy barrier. In this view, the fast hydrogen scrambling observed in the $C_6X_5^+$ ion after attack on ethylene cannot be traced to the intermediacy of a $[C_6D_5H\cdot C_2H_3^+]$ adduct, but rather it should proceed via more complicated and as yet unspecified mechanisms.
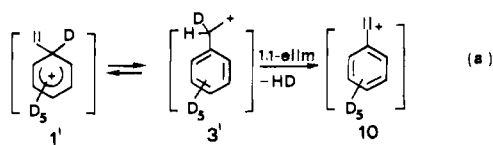
An additional reaction channel open to the vinyl cation–benzene adduct is the addition–elimination reaction 6 leading to $C_8H_7^+$. According to the above conclusions, the reaction is likely to proceed via a preliminary complex, undergoing partial hydrogen atom scrambling. The isotopic composition of the $C_8X_7^+$ (X = H, D) daughter species from $C_2H_3^+$ attack on C_6D_6 (eq 6′) confirms this view, although the relatively high intensity of $C_8D_5H_2^+$ (9%) indicates that a HD moiety is preferentially lost from the encounter complex. A similar behavior is frequently observed under ICR conditions in related addition–elimination processes, such as the CD_3^+ ion attack on benzene, where preferential loss of a HD molecule is observed, together with appreciable hydrogen scrambling within the parent addition complex.[4,25] On these grounds, it is suggested that formation of $C_8D_5H_2^+$ from $C_2H_3^+$ attack on C_6D_6 involves preferentially unimolecular loss of the ipso D and the adjacent side chain H of the excited intermediate **1** to give the 1-phenylvinyl cation **10**.[26]

Any conceivable rapid hydrogen randomization between the ring and the side chain or any carbon skeleton rearrangement

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(24) (a) Dewar, M. J. S.; Ford, G. P.; Reynolds, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 3162. (b) Ausloos, P.; Lias, S. G. *Ibid.* **1981**, *103*, 3641. (c) Ausloos, P.; Lias, S. G. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *58*, 165.
(25) Speranza, M., unpublished results.
(26) An additional possibility could be a fast isomerization of **1′** to the β-phenylethyl cation **3′**.

$$\left[\ \begin{array}{c} \text{D} \\ \bigcirc_{(+)} \\ \text{D}_5 \end{array}\ \right] \rightleftharpoons \left[\ \begin{array}{c} \text{H} \quad \text{D} \\ \bigcirc \\ \text{D}_5 \end{array}\ \right] \xrightarrow[-\text{HD}]{1,1\text{-elim}} \left[\ \begin{array}{c} \\ \bigcirc \\ \text{D}_5 \end{array}\ \right]^+ \qquad (\text{a})$$

$$\quad\quad\quad \mathbf{1'} \qquad\qquad\qquad \mathbf{3'} \qquad\qquad\qquad \mathbf{10}$$

If β-phenylethyl ion (**3′**) follows the fragmentation pattern of the unsubstituted ion, it would rapidly eliminate the geminal H and D atoms from the β carbon to give directly the phenyl-substituted vinyl cation **10** (Hvistendahl, G.; Williams, D. H. *J. Chem. Soc., Perkin Trans. 2* **1975**, 881). However, although formally possible, the elimination mechanism (a) is rather unlikely, since the β-phenylethyl ion is predicted to collapse to the ethylenebenzenium structure **4** without activation energy (ref 22). It follows that the α and β carbons of species **3′** would soon become indistinguishable and, hence, a H_2 molecule elimination should occur at least as efficiently as the HD loss, in contrast with the experimental FT–ICR evidence.

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within the vinylation adduct prior to a hydrogen molecule elimination would give a $C_8X_7^+$ (X = H, D) isotopic distribution other than that experimentally observed. It therefore can be concluded that the only conceivable unimolecular isomerization competing with the HD loss from the $[C_2H_3^+\cdot C_6D_6]$ adduct is $\mathbf{1} \rightleftharpoons \mathbf{2}$, namely the only process occurring via intramolecular ring-hydrogen transfers.

A final consideration concerns the lifetime of the excited intermediates **1** and **2** from the vinyl cation decay systems. No labeled products whose formation could be traced to the fragmentation of the $C_8H_7^+$ intermediate (i.e., phenylacetylene, methoxyphenylethylenes, diphenylethylenes, etc.) were observed. This fact lends support to the view that the primary vinylation adducts **1** and **2** survive unimolecular dissociation for at least 10^{-7} s, the time required for its interception by a nucleophile molecule in the decay systems. Such a lifetime entitles the ring-protonated styrenes **1** and **2** to the rank of fully legitimate ionic intermediates, necessarily corresponding to local minima on the $C_8H_9^+$ potential energy surface.

Conclusions. The present FT–ICR results show that the exothermic attack of a free vinyl cation on benzene leads to primary excited complexes, long lived enough to allow partial hydrogen atom scrambling, but eventually relaxing in σ-bonding intermediates, similar to the "Wheland complexes" involved in analogous solution-chemistry processes. The nuclear-decay results directly support this conclusion[2,4,27] by demonstrating, with the degree of confidence allowed by the actual isolation of the neutral products, that stable ring-protonated styrene structures **1** and **2** are primarily formed by vinyl cation attack on benzene. Such stable intermediates, whose lifetime exceeds 10^{-7} s, therefore should be included in the rich class of stable $C_8H_9^+$ isomers.[5b] In the gas phase, excited ions **1** and **2** tend to rearrange further to give eventually the most stable $C_8H_9^+$ structure accessible to the $[C_2H_3^+\cdot C_6H_6]$ complex, namely the α-methylbenzyl cation **5**. Whether such isomerization occurs directly or via the intermediacy of an ethylenebenzenium species **4** is at present uncertain. However, the decay results show, in partial agreement with previous conclusions,[5] that when an excited ethylenebenzenium ion **4** is generated in the gas phase by phenylium ion attack on ethylene, it readily rearranges to the more stable α-methylbenzyl cation **5**, even at relatively high pressures (up to ca. 60 torr). No evidence for additional isomerization pathways available to the **1–5** intermediates, including those leading to the thermodynamically most stable $C_8H_9^+$ isomer, i.e., the methyltropylium ion,[5c,e] arises from the present study. This conclusion is in complete agreement with that of previous investigations concerning related $C_7H_7^+$ ions.[28]

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(27) Cacace, F. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1129.
(28) (a) Cacace, F.; Ciranni, G.; Sparapani, C.; Speranza, M. *Radiochim. Acta* **1984**, *35*, 195. (b) Cacace, F.; Ciranni, G.; Sparapani, C.; Speranza, M. *J. Am. Chem. Soc.* **1984**, *106*, 8046.