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Gas- and Liquid-Phase Reaction of Free Phenylium Cation with Methanol

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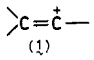
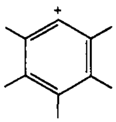
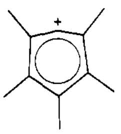
Abstract: A nuclear technique based on the spontaneous decay of multitritiated precursors that allows the generation of free carbonium ions of exactly the same nature in different environments has been employed for generating [p-^{3}H]phenylium ion from [1,4-$^3H_2$]benzene and for investigating its reactivity and selectivity toward methanol both in the gas phase at various pressures (5–65 torr) and in the liquid phase. The differences between the reactivity pattern of phenylium cation under different experimental conditions can be regarded as due to several factors, including the different efficiency of collisional stabilization of the excited reaction intermediates in the two media and the competition between the phenylium ion attack on the CH_3OH and the relaxation period of the CH_3OH dipole orientation, in both the gas and liquid phase at room temperature. The mechanism of the major competitive processes involving [p-^{3}H]phenylium ion in the presence of methanol, i.e., CH_3OH phenylation vs. phenylium ion automerization, is discussed in light of theoretical predictions and compared with related mass spectrometric and condensed-phase investigation. The results are in favor of the existence of a nucleogenic phenylium ion with a singlet-state electronic configuration, which tends to internally solvate its positive charge by a relatively fast ($k = 10^7$–10^8 s^{-1}) automerization process involving consecutive 1,2-hydrogen shifts.

Few members of the family of unsaturated carbenium ions (**1**) arouse so widespread an interest as the phenylium ion (**2**) since


(1)


(2)

Water's proposal of its intermediacy in the decomposition of benzenediazonium salts.[1] Singlet phenylium ion (**2**) has, in fact, the unique feature of having a nominally vacant sp^2 orbital orthogonal to the π system of the aromatic ring. It follows that the general tendency of vacant orbitals of cations to acquire the maximum degree of p character, expressed in **1** by the linear geometry about the electron-deficient carbon,[2] would contrast in **2** with the ensuing loss of aromaticity and increase in ring strain. A compromise between these opposing factors may involve considerable flattening of the C–C$^+$–C angle in the phenylium ion, allowing charge delocalization from the empty sp^2 orbital to the σ and π framework of the ring (structure **3**). Alternatively, it can imply simple transfer of a π electron from the benzene ring into the sp^2 vacant orbital, giving the ground-state phenylium cation with a triplet biradical configuration (i.e., **4**), if spin inversion accompanies the electron transfer. In all cases, a certain tendency of phenylium ion to isomerize to cyclic (e.g., **5**–**7**) and open-chain structures, where the positive charge can be much more easily accommodated, cannot be excluded a priori.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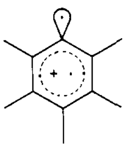
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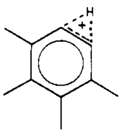
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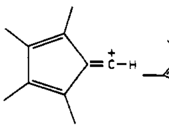
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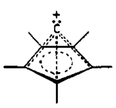
(7)

A considerable theoretical effort has been devoted to the assessment of the relative stabilities of singlet (**2** and **3**) and triplet (**4**) phenylium ion. While ab initio and semiempirical MO calculations agree in predicting the highly distorted singlet-state configuration **3** for the ground-state phenylium cation,[3] a high uncertainty is attached to the nature of the nearest higher energy states and their energetics.

Besides, multiplicities of the ground and low-lying excited states of unsubstituted phenylium ion have not been experimentally determined, and it is, therefore, difficult to evaluate the validity of theoretical predictions.[4] As a matter of fact, a variety of experimental evidence points to the intermediacy of a singlet "phenylium ion" in the decomposition of benzenediazonium salts in solution,[3d,5] on the grounds of its chemical behavior toward suitable acceptors. However, the question arises as to whether such behavior reflects the actual formation of an inherently stable singlet phenylium ion or whether it ensues from profound environmental effects, such as solvation, ion–ion and ion–molecule (N_2) pairing, etc., on the *incipient* phenylium cation.[6] In this case, in fact, extensive electrostatic interaction with the surroundings may relieve the unfavorable situation associated with the vacant sp^2 orbital in phenylium ion, thus favoring its formation in a singlet-state electronic configuration and preventing relaxation to more stable states by fast reaction with the nucleophiles present in the solvolytic system.[7]

Similar environmental factors may play an important role in preventing extensive isomerization of "phenylium ion" in the condensed phase as well. It is, in fact, well recognized that gaseous $C_6H_5^+$ ion, when generated in the ion source of a mass spectrometer by electron impact on iodobenzene, undergoes complete randomization of its five hydrogens with respect to all carbon

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(6) Gamba, A.; Simonetta, M.; Suffritti, G.; Szele, I.; Zollinger, H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 493–499.

(7) In dediazoniations of arenediazonium salts in condensed phase, many observations indicate that small changes in the reaction environment may change the mechanism and the products drastically. See, for instance: (a) Zollinger, H. *Acc. Chem. Res.* **1973**, *6*, 335–341. (b) Burri, P.; Loewenschuss, H.; Zollinger, H.; Zwolinski, G. K. *Helv. Chim. Acta* **1974**, *57*, 395–402. (c) Szele, I.; Zollinger, H. *J. Am. Chem. Soc.* **1978**, *100*, 2811–2815. (d) *Helv. Chim. Acta* **1978**, *61*, 1721–1729. (e) Bunnett, J. F.; Yijima, C. *J. Org. Chem.* **1977**, *42*, 639–643. (f) Broxton, T. J.; Bunnett, J. F.; Paik, C. H. *Ibid.* **1977**, *42*, 643–649.

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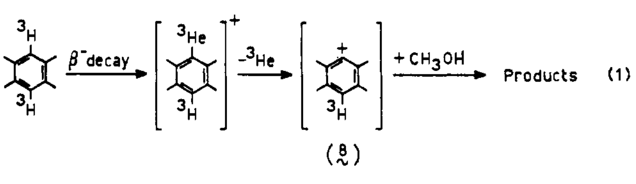
atoms before fragmenting to $C_4H_3^+$ ion.[8] One problem is that the $C_6H_5^+$ species produced here may not have the phenylium cation structure at all. On the other hand, when phenylium ions are actually formed in the gas phase by H_2 or CH_4 chemical ionization (CI) of suitable precursors, their energy content is not large enough to promote significant fragmentation,[9] and, therefore, no direct information on possible interconverting $C_6H_5^+$ structures can be achieved.

In this context, it would be highly desirable to generate a free, unsolvated phenylium ion under conditions where its electronic state and any structural interconversions can be investigated without complicating interferences from the environment. We believe that a simple and convenient way for attaining such conditions is to generate a free, unsolvated phenylium cation by using a nuclear technique, based on the spontaneous β^- decay of suitably multitritiated benzenes.[10] This general procedure, whose principles and applications have been recently reviewed,[11,12] allows one to produce in any system of interest positively charged species whose structure and energetics are a priori known and whose fate can be followed owing to the presence of residual radioactive labels. In addition, since the β^- decay of tritium takes place in a time very short on the chemical reactivity scale, the *same* positive ion is generated, independently of the environment, without being accompanied by any massive counterion, its charge being balanced by a far removed β^- particle.

For the specific purposes of the present study, we decided to use $[p\text{-}^3H_2]$benzene, as the natural precursor of $[p\text{-}^3H]$phenylium cation (**8**) (eq 1). Generation of a phenylium ion such as (**8**),

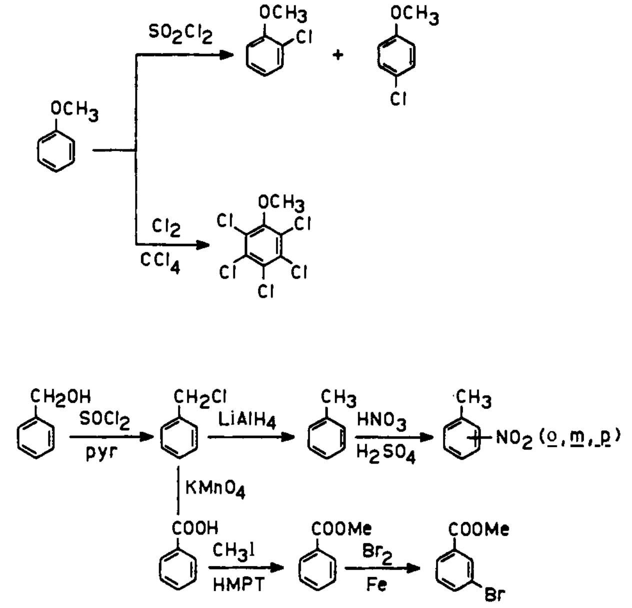


where a precise relationship between the positive charge and the residual ^3H label exists, and investigation of its reactivity and selectivity toward a suitable acceptor such as CH_3OH[13] under greatly different experimental conditions are expected to give insight into the electronic and reactivity features of an entirely free phenylium ion and to provide direct information on its inherent tendency to undergo rearrangement.

Experimental Section

Materials. The preparation, purification, and isotopic analysis of the $[1,4\text{-}^3H_2]$benzene sample used as a source of the decay ions have been described elsewhere.[14] The activity distribution, measured by 213.47-MHz FT ^3H NMR analysis, corresponded to ca. 56% $[1,4\text{-}^3H_2]$benzene and ca. 44% $[^3H]$benzene. Methanol and the aromatic compounds used as carriers or as standards in the gas chromatographic analyses were research grade chemicals from Merck and were used without further purification.

Scheme I



Growth of Decay Products. The gaseous samples were prepared by conventional vacuum techniques, introducing the $[1,4\text{-}^3H_2]$benzene mixture ($\sim$1 mCi), diluted with inactive benzene to a specific activity of 93 mCi mmol^{-1}, into evacuated and carefully outgassed 200-mL Pyrex vessels containing a measured amount of methanol together with O_2 (4 torr), used as a radical scavenger. The vessels were, therefore, sealed off and stored in the dark, at room temperature, for 3.5–10.0 months.

The liquid samples were prepared according to the following procedure: ca. 1 mCi of the $[1,4\text{-}^3H_2]$benzene mixture (specific activity: 93 mCi mmol^{-1}) was introduced into carefully evacuated and outgassed Pyrex vials (5 mL) equipped with a long capillary arm closed by a fragile tip. Each vial was sealed off from the vacuum line, and its capillary arm was introduced into a cylindrical vessel containing at the bottom a layer of purified mercury and filled with ca. 7 mL of methanol, which had been previously outgassed and washed with O_2. The fragile tip of the capillary arm was then broken under the level of methanol, which was consequently forced into the evacuated vial. When only a small bubble of gas was left at the top of the vial, the capillary arm was lowered further into the mercury. After a few hours, the vial was entirely filled by methanol, except for the lower portion of the capillary, where the mercury has risen, acting as a mobile seal. The vials were stored in the dark, at room temperature, for ca. 3.5–5.0 months.

Analysis of Products. Two distinct procedures were followed for the analysis of tritiated products from the decay systems. Aliquot portions of the homogeneous samples were subjected to radiogas chromatographic analysis with the main purpose of estimating the absolute yields. A C. Erba Model C gas chromatograph, equipped with a hot-wire detector in series with a 10-mL internal-flow proportional counter, heated at 160 °C, was used for the analyses. The GLC separations were carried out with helium as a carrier gas, the activity of the effluents being monitored by employing a CH_4/He 1:1 counting gas mixture, obtained by adding a methane makeup flow to the outlet of the hot-wire detector.

In most cases, the reaction vessels were opened and their contents diluted with precisely known amounts of inactive carriers of interest. After being thoroughly mixed, the samples were subjected to a preparative gas chromatographic separation to resolve and purify each individual component. The recovered fractions were again subjected to repeated separation and purification steps by preparative GLC, until a constant value of the specific activity of each component, measured by liquid scintillation counting (Tri-Carb 460 C, Packard Instrument Co.), was reached. The yield of each labeled product was deduced from the ratio of its activity to the total activity of the $[^3H]$phenylium ions formed within the system during the storage period, as calculated from the initial activity of $[1,4\text{-}^3H_2]$benzene and its known decay rate. The gas chro-

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[8] Dickinson, R.; Williams, D. H.; *J. Chem. Soc. B* **1971**, 249–251.

[9] (a) Leung, H. W.; Harrison, A. G. *J. Am. Chem. Soc.* **1979**, *101*, 3168–3173. (b) Speranza, M.; Sefcik, M. D.; Henis, J. M. S.; Gaspar, P. P. *Ibid.* **1977**, *99*, 5583–5589. (c) Bohme, D. K.; Stone, J. A.; Mason, R. S.; Stradling, R. S.; Jennings, K. R. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *37*, 283–296.

[10] (a) Speranza, M. *Tetrahedron Lett.* **1980**, *21*, 1983–1986. (b) Nefedov, V. D.; Sinotova, E. N.; Korsakov, M. V.; Alekseev, E. G. *Radiokhimiya* **1973**, *15*, 635–636. (c) Nefedov, V. D.; Sinotova, E. N.; Korsakov, M. V.; Shishkunov, V. A. *Zh. Org. Khim.* **1975**, *11*, 2350–2351. (d) Nefedov, V. A.; Sinotova, E. N.; Shishkunov, V. A. *Ibid.* **1976**, *12*, 1495–1498. (e) *Ibid.* 1351–1355. (f) Nefedov, V. D.; Sinotova, E. N.; Balakin, I. M. *Ibid.* **1980**, *16*, 458–459.

[11] For a discussion of the principles of the decay technique, see: (a) Cacace, F. In "Hot Atom Chemistry Status Report"; International Atomic Energy Agency: Vienna, 1975; p. 229. (b) Cacace, F. *Adv. Phys. Org. Chem.* **1970**, *8*, 79–149.

[12] For a review of the most recent applications, cf.: (a) Cacace, F. In "Interactions between Ions and Molecules"; Ausloos, P., Ed.; Plenum Press: New York, 1975. (b) Akulov, G. P. *Usp. Khim.* **1976**, *45*, 1970–1999. (c) Cacace, F. In "Kinetics of Ion-Molecule Reactions"; Ausloos, P., Ed.; Plenum Press: New York, 1979.

[13] The choice of CH_3OH, as acceptor of nucleogenic phenylium ion, was guided by the fact that a variety of kinetic and mechanistic studies on the decomposition of benzenediazonium salts has been carried out in methanolic solutions under largely different environmental conditions. (cf. ref 5b, 7e, *f*). See also: (a) Bunnett, J. F.; Takayama, H. *J. Org. Chem.* **1968**, *33*, 1924–1928. (b) *J. Am. Chem. Soc.* **1968**, *90*, 5173–5178. (c) Broxton, T. J.; Bunnett, J. F. *Nouv. J. Chim.* **1979**, *3*, 133–138. (d) Packer, J. E.; Heighway, C. J.; Miller, H. M.; Dobson, B. C. *Aust. J. Chem.* **1980**, *33*, 965–977.

[14] Angelini, G.; Speranza, M.; Segre, A. L.; Altman, L. J. *J. Org. Chem.* **1980**, *46*, 3291–3295.

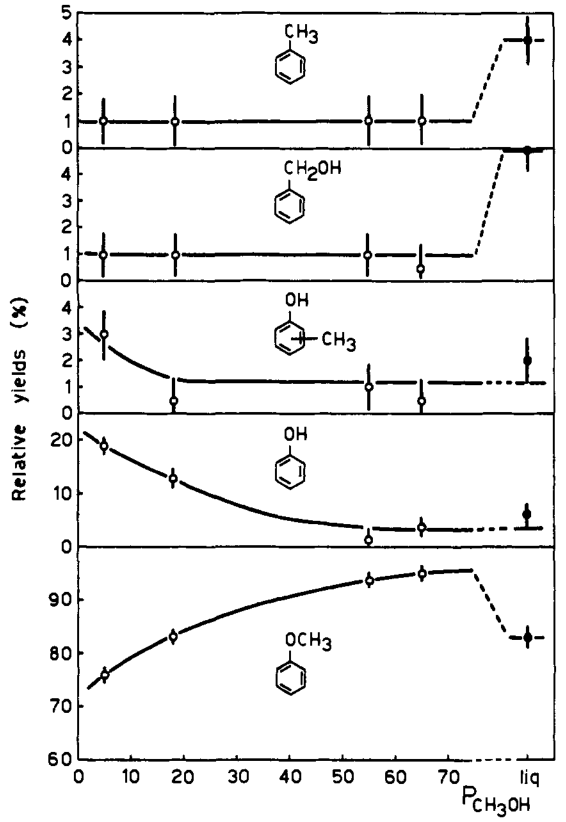


Figure 1. Relative distribution of the tritiated aromatic products in the gas (open circles) and liquid (solid circles) phase.

matographic analyses were carried out with the following columns: (a) Bentone 34–silicone oil E 301 (10 and 20%, respectively, on Chromosorb W, 5 m, 120 °C); (b) Bentone 34–diisodecyl phthalate (1:1 on Chromosorb W, 5 m, 140 °C).

Degradation of Tritiated Products. The tritium distribution within the tritiated products recovered from the decay samples was determined by a procedure based on the replacement of a ^{3}H of the product by an inactive substituent, followed by the measurement of the corresponding decrease of the molar activity.[15] The reactions employed for tritiated product degradation are shown in Scheme I. The purification of the reaction products was achieved by preparative GLC with the following columns: Bentone 34–diisodecyl phthalate 1:1 (on Chromosorb W, 3 m, 125 °C) for chloroanisoles; silicone oil 550 (20% on Chromosorb W, 4 m, 110 °C) for benzyl chloride; Bentone 34–silicone oil SE 30 1:1 (on Chromosorb W, 4 m, 160 °C) for toluene and nitrotoluenes; silicone oil E 301 (20% on Chromosorb W, 3.5 m, 140 °C) for methyl benzoate and methyl *m*-bromobenzoate.

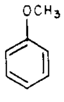
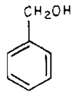
Results

The relative yields of the tritiated aromatic products from the attack of tritiated phenylium ion (**8**) on gaseous and liquid methanol are illustrated in Figure 1 as a function of the experimental conditions.

The absolute yields, expressed by the ratio of the total activity of the end products to the activity originally contained in the nuclear decay produced (nucleogenic) phenylium ion, can be calculated from the initial activity and the isotopic composition of the tritiated benzene sample, the decay rate of the tritium, the abundance (72%) of the phenylium ion among the decay fragments, and the absolute counting efficiency of the detector employed.

These admittedly crude calculations show that the aromatic products recovered in the liquid samples account for ca. 86 ± 6% of the activity contained in the decay ions, whereas the absolute overall yield of the same products formed in the gaseous samples is lower and further decreases upon lowering the system pressure (absolute yield (P_{CH_3OH}, torr): 72 ± 5% (65); 70 ± 5% (55); 65 ± 6% (18); 40 ± 12% (5)). Such decrease is counterbalanced by a considerable increase of the yield of low-boiling tritiated products, invariably accompanying formation of the aromatic derivatives. In general, it has been observed that the combined activity of the aromatic and of the low-boiling fraction of the sample accounts for ca. 80–90% of the theoretical yield, the remainder being presumably provided by some high-boiling labeled materials (e.g., oligomers, polymers, etc.) or, more likely, by the formation of $C_6H_5{}^3H$, whose activity cannot be discriminated from that contained in the undecayed [1,4-$^3H_2$]benzene.

Table I. Tritium Atom Distribution in Anisole and Benzyl Alcohol (T = 25 °C)

tritiated product	gas-phase experiments,[a] %, at P_{CH_3OH}, torr 5	18	55	65	liquid CH_3OH,[b] %
	0	0	0	0	0
	7.5	7.7	5.9	5.5	0
	20.9	16.6	16.0	14.5	0
	71.6	75.7	78.1	80.0	100
	nd[c]	nd[c]	nd[c]	nd[c]	0
					2
					13
					85

[a] P_{O_2} = 4 torr. [b] Liquid CH_3OH saturated with O_2. [c] nd = not determined, owing to the prohibitively low absolute yields of benzyl alcohol recovered in gas-phase decay runs.

Inspection of Figure 1 reveals that the most abundant labeled product formed is invariably anisole (76–94%), accompanied by much lower amounts of phenol, isomeric cresols, benzyl alcohol, and toluene. Their relative distribution in the gaseous samples is greatly affected by the partial pressure of CH_3OH (P_{CH_3OH}). In particular, a monotonic increase of the relative yield of anisole with P_{CH_3OH} is observed (from 76%, at P_{CH_3OH} = 5 torr, to 94%, at P_{CH_3OH} = 65 torr), coupled with a parallel decrease of the yield of phenol and cresols. In the liquid samples, the relative yield of anisole amounts to a value (ca. 83%), lower than that observed in the gas phase at P_{CH_3OH} = 65 torr, which is counterbalanced by higher amounts of the accompanying benzyl alcohol and toluene.[16]

Systematic degradation of the anisole produced in all samples showed consistently that the tritium atom distribution within the molecule is appreciably affected by the experimental conditions, as illustrated in Table I. Thus, while the tritium atom is exclusively retained in the para position of the anisole recovered from the liquid samples, a considerable tritium reshuffling is observed in the anisole from the gaseous systems, whose extent appreciably increases at low methanol pressures.

Discussion

Decay vs. Radiolysis as a Source of Tritiated Products. The experimental conditions chosen for the present study, in particular the low level of the specific activity of the gaseous (0.5–9 mCi mmol^{-1}) and liquid (ca. 6 × 10^{-3} mCi mmol^{-1}) samples, ensure that the formation of the labeled products must be traced to the reactions of the tritiated decay ions without any appreciable contribution from the radiolytic processes promoted by the β particles of tritium. In fact, even in the most critical case, i.e., in gaseous CH_3OH at the lowest pressure (5 torr), the extremely low molar fraction of [1,4-$^3H_2$]benzene (and [^{3}H]benzene) makes

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(15) Blank degradations carried out on suitably deuterated precusors excluded the occurrence of D shifts within the deuterated compounds to an extent exceeding the experimental uncertainty, under the substitution conditions.

(16) The relative product yield distributions concerning the runs in liquid CH_3OH and in gaseous CH_3OH at 18 torr are somewhat different from those reported in a preliminary communication (ref 10a). This discrepancy is due to the fact that the early [1,4-$^3H_2$]benzene samples used contained trace amounts of tritiated biphenyl, which is formed from the condensation of the decay-formed [p-^{3}H]phenylium ion with the C_6H_6 carrier and accumulates during storage of [1,4-$^3H_2$]benzene (ref 10b). The results of the present investigation refer, instead, to decay systems containing [1,4-$^3H_2$]benzene freshly purified by preparative GLC in order to eliminate dimerization products.

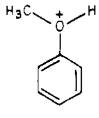
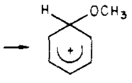
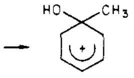
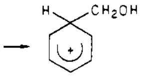
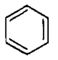
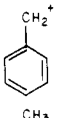
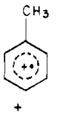
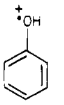
their radiolysis entirely negligible as a source of the tritiated products in comparison with the reactions of the decay ions. The relative efficiency of the two labeling channels is calculated to be ca. 1:10^4. This view is supported by the observation that the combined activity of the tritiated products from both the gaseous and the liquid systems accounts for over 80% of the decay ion activity, despite the substantially different level of specific activity. This, in fact, would undoubtedly cause a measurable change of the yields of the tritiated products should radiolytic processes appreciably contribute to their formation. However, these considerations are valid only at sufficiently low levels of tritiated benzene, i.e., at sufficiently low values of its specific activity.

In this respect, a certain degree of uncertainty is attached to some results obtained by Nefedov and co-workers in related decay systems,[10b,f] where the specific activity levels of the multitritiated benzene precursors exceed ours by a factor of at least 10^2, and autoradiolysis of tritiated benzene may account for a significant fraction of the labeled products.

Nature of the Reagent. The decay-induced fragmentation pattern of $C_6H_5{}^3H$ has been studied at low pressure with a specially designed mass spectrometer by Carlson,[17] who reported the following abundances for the major decay ions: $C_6H_5^+$, 72.0%; $C_6H_5^+$, 2.5%; C_6H^+, 1.3%; $C_4H_3^+$, 2.6%; $C_4H_2^+$, 3.4%; C_4H^+, 3.6%; $C_3H_2^+$, 2.7%; C_3H^+, 3.4%, C_3^+, 1.2%. These results are consistent with the conclusions of theoretical studies on the molecular excitation caused by β decay of a constituent atom in related systems,[18] showing that the primary daughter ions, $[C_6H_5{}^3He]^+$, are mainly formed in their electronic ground state and dissociate immediately into ^3He and a phenylium cation. A minor fraction (28%) of the decay ions, instead, receives large excitation energies, mostly due to the β-electron–antineutrino recoil and to the electron cloud "shaking"[19] as the β particle leaves the tritium atom, which cause their further extensive fragmentation. Given the specific distribution of excitation energy, which is either very large or negligible, the fragmentation pattern measured at 3×10^{-6} mmHg can be reasonably used to describe the decay of tritiated benzene in gases at much higher pressures or even in liquid systems, since collisional deactivation can hardly moderate the decomposition of the fraction of daughter ions formed in highly excited states (up to 30 eV). For the same reason, isotopic effects can reasonably be disregarded in the dissociation of the decay ions, and the fragmentation pattern established for $C_6H_5{}^3H$ can be extended to $[1,4\text{-}{}^3H_2]$benzene. From these assumptions, it can be concluded that $[^3H]$phenylium ion **8** represents the major source of the tritiated products identified in the decay systems, with only minor contribution from other radioactive decay fragments.

While the mass spectrometric and the theoretical studies quoted above[17,18] indicate that **8** is formed in its electronic ground state, no evidence is provided concerning the level of vibrational excitation, associated inter alia with the relaxation from the regular hexagonal structure of the $[1,4\text{-}{}^3H_2]$benzene precursor to the conceivably different structure of the ground-state phenylium cation, for instance **3** (see Dill et al.).[3e] In particular, no information is available as to the fraction of energy carried away by the receding ^3He atom, associated in turn with the timing of the ^3He departure from the daughter $[p\text{-}{}^3H,{}^3He\text{-}C_6H_4]^+$ species. In the extreme hypothesis of an adiabatic process, the calculation of Dill et al.[3e] sets an upper limit of ca. 25 kcal mol^{-1} to the vibrational excitation energy of the decay phenylium ion.

Table II. Energetics of Several Relevant Reactions of Phenylium Ion with CH_3OH[a]

	process			ΔH°, kcal mol^{-1}	
				b	*c*
i	$C_6H_5^+ + CH_3OH$	→ 		−66[d]	−41[d]
ii		→ 		exothermic[e]	
iii		→ 		exothermic[f]	
iv		→ 		exothermic[e]	
v		→ 	+ $^+CH_2OH$	−32	−7
vi		→ 	+ $\cdot CH_2OH$	+2	+27
vii		→ 	+ H_2O	−68	−43
viii		→ 	+ $\cdot OH$	+2	+27
ix		→ 	+ $\cdot CH_3$	−16	+9

[a] Other conceivable processes calculated to be endothermic by more than 15 kcal mol^{-1}. The $\Delta H_f°$'s of the ions and of the neutrals used for these calculations have been taken from the following: (a) Field, F. H.; Franklin, J. L. "Electron Impact Phenomena"; Academic Press: New York, 1970. (b) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. "The Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1969. (c) Vedeneyev, V. I.; Gurvich, L. V.; Kondrat'yev, V. N.; Medvedev, V. A.; Frankevich, Ye. L. "Bond Energies, Ionization Potentials and Electron Affinities"; Edward Arnold Publishers, Ltd: London, 1966. [b] ΔH°'s calculated by using the experimental $\Delta H_f° = 270$ kcal mol^{-1} for $C_6H_5^+$. [c] ΔH°'s calculated by using the theoretical $\Delta H_f° = 245$ kcal mol^{-1} for $C_6H_5^+$. [d] Calculated by using $\Delta H_f° = 156$ kcal mol^{-1} for the oxygen-protonated anisole (Catalan, J.; Yanez, M *J. Am. Chem. Soc.* 1979, *101*, 3490–3492. [e] Proton affinity (PA) for the ipso position of anisole (eq ii) and of benzyl alcohol (eq iv) assumed equal to that of toluene (PA = 179 kcal mol^{-1}) (Devlin, J. L., III; Wolf, J. F.; Taft, R. W.; Hehre, W. J. *Ibid.* 1979, *98*, 1990–1992). [f] From eq viii and ix, by considering that radical–radical recombination is generally several tens of kilocalories permole exothermic.

Energetics of Phenylium Ion Attack on Methanol. The calculated difference in energy (~25 kcal mol^{-1}) between a benzene-like structure for **8** and the vibrational ground-state structure **3** accounts for the deviation between the calculated heat of formation of phenylium ion ($\Delta H_f° = 244.8$ kcal mol^{-1})[20] and the experimental value derived from the ionization potential of phenyl radical ($\Delta H_f° = 266$–270 kcal mol^{-1}).[21] In fact, ionization of phenyl radical by electron or photon impact is a vertical process, and therefore the experimental heat of formation of $C_6H_5^+$ measured by this method refers to an ion with the same structure of the radical precursors and, hence, with excess vibrational energy (~25 kcal mol^{-1}). The structure of the phenylium ion formed by the decay method may range from that of the benzene precursor to

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(17) Carlson, T. A. *J. Chem. Phys.* **1960**, *32*, 1234–1239.

(18) (a) Ikuta, S.; Okuno, K.; Yoshihara, T.; Shiokawa, T. *Radiochem. Radioanal. Lett.* **1975**, *23*, 213–219. (b) Okuno, K.; Yoshihara, K.; Shiokawa, T. *Radiochim. Acta* **1978**, *25*, 21–25.

(19) The β^- particle possesses high energy and leaves the atom in a time short relative to periods of orbital electron motion (0.1–0.01 of a period). This suddenly changes the nuclear charge and consequently perturbs the electrostatic environment of the surrounding cloud of electrons. Usually the cloud of electrons will contract adiabatically to accommodate itself to the increased nuclear charge, but sometimes excited electronic states or ionization ("shake off") may result (cf.: Wexler, S. In "Actions Chimiques et Biologiques des Radiations"; Huitième Série, Masson & C., Ed., Paris, 1965).

(20) (a) Castenmiller, W. A.; Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, 207–213. (b) Tasaka, M.; Ogata, M.; Ichikawa, H. *J. Am. Chem. Soc.* **1981**, *103*, 1885–1891.

(21) Rosenstock, H. M.; Larkins, J. T.; Walker, J. A. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *11*, 309–328.

that of a vibrational ground-state $C_6H_5^+$ ion, and therefore the actual enthalpy of formation of the ion (**8**) in the decay system may span from ca. 245 and 270 kcal mol^{-1}.

Several exothermic reaction channels are available to the tritiated phenylium ion in its attack on methanol, as illustrated in Table II, where the approximate $\Delta H°$ values for the relevant gas-phase processes are also reported. Of course, the calculated $\Delta H°$ values are much less cogent if referred to processes occurring in the liquid systems, where ion solvation might intervene. However, it can be safely concluded that all the addition steps (i–iv) are thermochemically allowed in the decay systems. Conceivably, there are at least two "blind" (i.e., not leading to identifiable labeled products, other than the tritiated precursors) reaction channels (v and vi), allowed on thermochemical grounds,[22] which could account for the activity loss (10–20%) observed in all systems. Channels viii and ix may contribute, together with reaction iii, to the formation of tritiated toluene and phenol, respectively. Finally, no products (e.g. benzyl methyl ether) that could support the occurrence of channel vii were found in both the gaseous and the liquid decay samples.

Phenylium Ion in Liquid Methanol. In the discussion of $[^3H]$phenylium ion attack on methanol, it is convenient to consider first the liquid-phase reaction, whose features appear to fit into the familiar picture of conventional benzenediazonium salt decomposition in liquid methanol.[5] In both systems, in fact, the predominant product is anisole, whose formation is primarily[23] ascribed to the exothermic attack of a *singlet* phenylium ion on the oxygen lone pairs of methanol, with formation of a methylphenyloxonium ion (**9** in step i of Scheme II). Intermediate **9**, excited by the exothermicity of its formation process, may undergo fragmentation (e.g., eq ix of Table II) and/or isomerization (eq x, Scheme II) unless efficiently quenched by fast collisional deactivation (eq xi) typical of the liquid environment. Deprotonation of intermediate **9** by any base B contained in the system, including primarily the CH_3OH itself,[24] provides a direct route to anisole (step xii). Alternatively, the excited species **9** may undergo a thermoneutral nucleophilic displacement on its methyl group by CH_3OH with formation of tritiated phenol (step xiii). Apart from the fragmentation path ix of Table II, an alternative route to phenol would involve the phenylium ion attack on the C–O bond of methanol, giving the σ complex **10** (eq iii of Scheme II), and the subsequent nucleophilic displacement by CH_3OH (eq xiv). Occurrence of species **10** in the attack of phenylium ion on methanol might be supported by the presence of small but appreciable yields of isomeric cresols among the recovered products, whose formation can involve insertion of the phenylium ion into the C–O bond of CH_3OH and subsequent isomerization (step xv), or, less likely, intramolecular methyl-group transfer within **9** (eq x).[25b]

In the framework of this model, it is interesting to note that, in spite of the more favorable thermochemistry of process xiii, neutralization of **9** by proton transfer (eq xii) is much more efficient than step xiii, in the liquid phase.[24] A rationale for such behavior can be found in the fact that the thermoneutral nucleophilic displacement xiii is likely to involve a substantial activation barrier, which makes it a relatively slow process.[25]

Despite the relatively minor yields of benzyl alcohol recovered in the decay systems, the mechanism of formation of this product deserves special consideration, since it can provide some additional information on the electronic configuration of the nucleogenic phenylium ion. In fact, benzyl alcohol formation may be traced to the insertion of singlet phenylium ions into one of the C–H bonds of methanol leading to $\mathbf{11}_p$ (eq iv), which subsequently undergoes deprotonation by other methanol molecules (eq xvi). A mechanism of this sort finds strong support in the gas-phase addition of a phenylium ion, generated in an ICR source, with D_2 or CH_4 molecules, which is undoubtedly a one-step process.[26] Nevertheless, a different origin of benzyl alcohol can be traced to the biradical triplet-state structure, proposed as the alternative configuration for phenylium ion. In analogy with the general behavior of triplet carbenic species, triplet phenylium ion is expected to abstract a H atom of CH_3OH, giving the benzene radical cation **12** (eq xvii), where the original relationship between the tritium atom and the vacant σ orbital is lost. In the liquid CH_3OH cage, **12** has a high probability to recombine with the $\cdot CH_2OH$ fragment (eq xviii), producing a $\mathbf{11}_{random}$ intermediate, which differs from that of eq iv by the complete scrambling of the ^3H label. In light of these considerations, the electronic configuration of phenylium ion can be therefore inferred from the ^3H atom distribution in the labeled benzyl alcohol. The extensive retention of tritium in the para position of benzyl alcohol (Table I) supports its origin from a *singlet* phenylium ion, in full agreement with the conclusion reached on the grounds of the tritiated product distribution.

Phenylium Ion in Gaseous Methanol. Analysis of Figure 1 reveals that the product distribution from the gas-phase runs is somewhat different from that of the experiments in liquid methanol. Furthermore, the relative product distribution observed in the gas phase is rather sensitive to the partial pressure of methanol. In particular, the relative yield of anisole appreciably decreases with P_{CH_3OH} to an extent that is mostly counterbalanced by an increase of the phenol and cresol relative yields, while both benzyl alcohol and toluene maintain their relative yield (~1%) constant. These trends are satisfactorily explained upon consideration that, in contrast with the high efficiency of collisional deactivation in liquid methanol, the site selectivity of phenylium ion toward CH_3OH is distorted, in the gas phase, by the occurrence of other high activation energy processes, such as the nucleophilic displacements xiii and xiv, by the isomerization processes x and xv, and by the fragmentation reactions of Table II, whose significance is exhalted at low CH_3OH pressure (5 torr). In this connection, it is conceivable that the relative product distribution, measured at the highest CH_3OH pressure used (65 torr), namely under conditions where the extent of the above high-energy secondary processes is more limited, represents the lower limit of the site selectivity of singlet phenylium ion toward CH_3OH *in the gas phase*. Despite the likely occurrence of residual fragmentation and isomerization processes, this limit indicates that, in the gas phase, the highly reactive phenylium ion[26] displays a remarkable selectivity toward the n center of CH_3OH (94%), with respect to the other nucleophilic (σ-type) centers of the molecule.

Comparison of the product distribution obtained at P_{CH_3OH} = 65 torr with that from the liquid samples discloses an intriguing pecularity. It should be pointed out, in fact, that in the liquid methanol, the absolute yield of toluene (3.4%), which mostly arises from the dissociative process viii (Table II) is invariably *greater* than that measured in gas phase (0.4–0.7%), where its formation is expected to be favored. This behavior may reflect the preferential solvation of benzene by the methyl moiety of the solvent in liquid methanol.[27] Following the almost instantaneous decay event, rotational relaxation of the methanol molecules formerly

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[22] With the level of uncertainty (2–3 kcal mol^{-1}) in evaluating the heats of formation of the species involved taken into account, processes vi and viii can be considered thermoneutral, if induced by attack of a vibrationally excited phenylium ion (ΔH_f = 270 kcal mol^{-1}) on CH_3OH.

[23] Another conceivable route to anisole would involve insertion of phenylium ion into the O–H bond of CH_3OH leading to ipso protonated anisole (eq ii). However, the extent of such process should not diverge much from that of similar insertions into the C–O and C–H bonds of methanol, which, on the basis of the product distribution, represent only minor reaction channels.

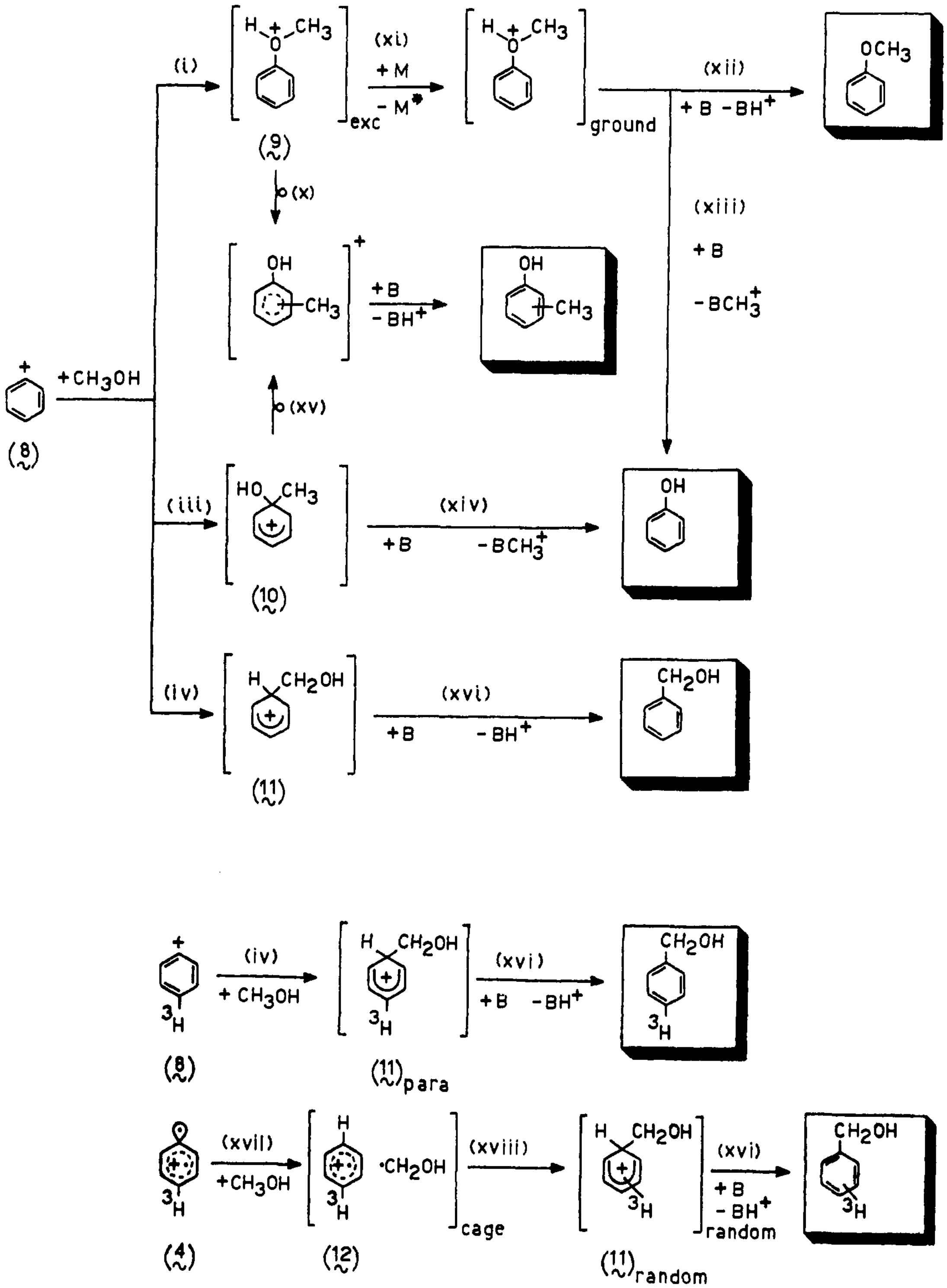
[24] Direct proton transfer from ground-state **9** to *one* molecule of CH_3OH (eq xii) is a process ca. 12 kcal mol^{-1} endothermic. However, in the liquid phase fast deprotonation of **9** can take place if the oxonium ion is in an excited state or if preliminary coordination of two or more CH_3OH molecules on the proton of **9** occurs (cf.: Grimsrud, E. P.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 7939–7943. Hiraoka, K.; Grimsrud, E. P.; Kebarle, P. *Ibid.* **1974**, *96*, 3359–3364).

[25] (a) Speranza, M.; Pepe, N.; Cipollini, R. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1179–1186. (b) Pepe, N.; Speranza, M. *Ibid.* **1981**, 1430–1436. (c) Speranza, M.; Angelini, G. *J. Am. Chem. Soc.* **1980**, *102*, 3115–3120. (d) *Ibid.* **1981**, *103*, 3792–3799. (e) *Ibid.* **1981**, *103*, 3800–3806. (f) Colosimo, M.; Bucci, R. *J. Phys. Chem.* **1979**, *83*, 1952–1957.

[26] Speranza, M.; Sefcik, M. D.; Henis, J. M. S.; Gaspar, P. P. *J. Am. Chem. Soc.* **1977**, *99*, 5583–5589.

[27] Irving, H. M. N. H.; Simpson, R. B. *J. Inorg. Nucl. Chem.* **1972**, *34*, 2241–2247.

Scheme II



solvating [1,4-$^3H_2$]benzene is probably too slow to form an organized solvent shell around the [^{3}H]phenylium ion by directing the oxygen atom, which represents the negative end of their dipole, toward the positive charge of the ion, before the reaction with the ion itself. Consequently, in liquid methanol, the probability of attack on the CH_3 moiety of the solvent by the highly reactive phenylium ion increases with respect to the gas phase, where the CH_3OH molecules have enough time to undergo rotational relaxation before reacting with the ion, yielding anisole as the major product.[28] Since reorientation times of the methanol molecules in pure liquid methanol can be calculated to be of the order of a few picoseconds,[29] it follows that the reaction of phenylium ion with the CH_3 group of methanol should occur within the same time scale.

Phenylium Ion Rearrangement. Analysis of Table I reveals that tritium label is completely retained in the para position of the tritiated anisole recovered in the liquid samples. Such complete retention corroborates the view that no atomic motion in [1,4-$^3H_2$]benzene occurs during the decay event[19] and rules out any conceivable ^{3}H shift in the daughter phenylium ion, before condensation with liquid methanol and deprotonation of the resulting intermediate to anisole. However, the picture in the gas-phase experiments, i.e., at much longer ion lifetimes, appears entirely

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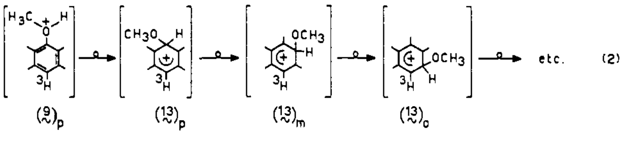
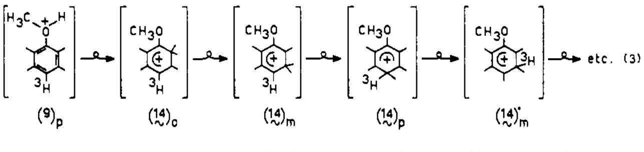
(28) Bowers, M. T.; Su, T. In "Interactions between Ions and Molecules", Ausloos, P. Ed.; Plenum Press: New York, 1975.

(29) O'Reilly, D. E.; Peterson, E. M. *J. Chem. Phys.* **1971**, *55*, 2155–2163.

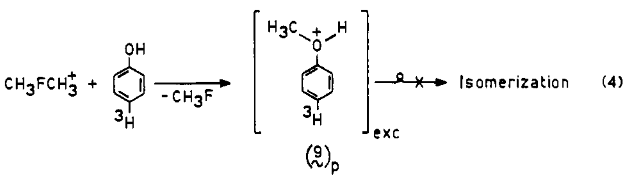
different. The anisole formed in the gaseous CH_3OH samples presents a significant scrambling of the ^3H label over the meta and ortho positions of the ring (ortho < meta < para), whose extent increases at low CH_3OH pressures.

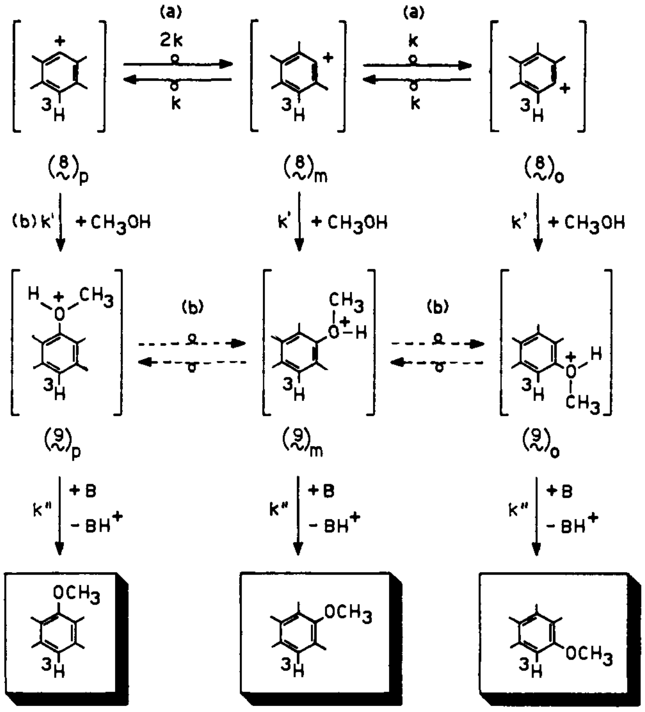
From a general standpoint, at least two different mechanistic pathways for ^3H scrambling observed in the gas-phase experiments can be conceived. Thus, the ^3H rearrangement can be though as proceeding within the [^3H]phenylium ion before condensation with CH_3OH (path a of Scheme III) or, alternatively, after the attack of the [*p*-^3H]phenylium ion on CH_3OH, i.e., within the intermediate precursor of the labeled anisole (path (b)). Several detailed mechanisms can be conceived for the **9** isomerization sequence b (eq 2 and 3).





For a test of the mechanistic hypothesis 2, *p*-dimethoxybenzene has been protonated with H_3^+ ions, generated from the γ radiolysis of H_2 gas, under conditions (P_{H_2} = 20 torr) resembling as much as possible the gas-phase decay experiments. *p*-Dimethoxybenzene is known to undergo exclusive O-protonation in superacid media,[30] and therefore a significant amount of O-protonated derivative, closely related to **9**,[23] is expected to be formed. The failure to detect any protonation-induced methoxy-group shift within the substrate, in spite of the marked exothermicity ($\Delta H° \simeq -85$ kcal mol^{-1} [31]) of the protonation process, argues against the occurrence of the isomerization sequence 2 to any significant extent. Several considerations exclude the isomerization mechanism 3, involving stepwise H migration over the ring of protonated anisole. First, the overall rate for the multiple H shifts (3) is computed, for closely related systems, to be slow if compared to the high collisional quenching of protonated anisole in the gas-phase decay systems[32] (P_{CH_3OH} = 5–65 torr). It is moreover to be noted that protium migration within **14** should be highly favored over that of ^3H on account of the accompanying kinetic isotope effect. Finally, the intramolecular hydrogen-atom transfer from the oxygen of **9** to the para position would require overcoming of multiple energy pseudobarriers, due to the higher energy levels of meta-protonated anisole **14**$_m$ and **14**$_m'$ with respect to the oxygen-, ortho- and para-protonated isomers **9**$_p$, **14**$_o$, and **14**$_p$.[30] Experimental support to these considerations was sought via an independent approach to gaseous para [^3H] intermediate **9**$_p$, involving oxygen methylation of [*p*-^3H]phenol[33] with the strong Lewis acid $CH_3FCH_3^+$ obtained in the dilute gas state from γ radiolysis of CH_3F (P_{CH_3F} = 20 torr),[25b] e.g.:





Scheme III

It should be noted that the excitation energy of **9**$_p$ from reaction 4 is comparable to that from eq 3.[34] However, the reaction environment is somewhat different, since replacement of CH_3OH with the much less basic CH_3F as the bulk constituent of the mixture is likely to favor ^3H scrambling within **9**$_p$. Nevertheless, without discounting such a difference, the results of the $CH_3FCH_3^+$ methylation experiments, yielding tritiated anisole as the major product without any detectable ^3H migration from the para position, provide strong evidence against the intramolecular isomerization process 3 as responsible of the ^3H scrambling observed in the anisole recovered from the gas-phase decay experiments. The same argument can be used for further corroborating the previous conclusions concerning mechanism 2.

Looking at mechanisms 2 and 3 as hardly realistic, phenylium ion isomerization *before* attack on CH_3OH (path (a) of Scheme III) appears the most plausible in accounting for the ^3H scrambling within the recovered tritiated anisole or, at least, as the only one not conflicting with the available evidence. Sequence a can be regarded as an example of phenylium ion automerization, if allowance for the ^3H atom is made, which leads to ^3H scrambling within the ion before its trapping by CH_3OH. The number density of the CH_3OH molecules in the gaseous systems determines the lifetime of the free phenylium ion and, therefore, the extent of its automerization. Accordingly, more extensive ^3H scrambling is observed in the anisole recovered in the gaseous systems at the lowest pressures, i.e., at the longest ion lifetimes, whereas, in the liquid phase, efficient collisional quenching and fast condensation of phenylium ion with CH_3OH prevent any appreciable phenylium ion automerization.

Kinetics of Phenylium Ion Automerization. The proposed phenylium ion automerization process finds quantitative support in the ^3H distribution within labeled anisole as a function of the phenylium ion lifetime, which, in turn, is related to the CH_3OH partial pressure in the gaseous systems. Kinetic treatment of the automerization reaction network of Scheme III gives the calculated automerization curves reported in Figure 2. The best fitting of these curves, representing the integrated rate equations, with the

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(30) Olah, G. A.; Mo, Y. K. *J. Org. Chem.* **1973**, *38*, 353–366.

(31) Calculation carried out by using a $\Delta H_f°(H_3^+)$ = 262 kcal mol^{-1}. (a) Ausloos, P.; Lias, S. G. *J. Chem. Phys.* **1964**, *40*, 3599–3605. (b) Aquilanti, V.; Giardini-Guidoni, A.; Volpi, G. G. *Trans. Faraday Soc.* **1968**, *64*, 3282–3287. (c) Cacace, F.; Cipollini, R.; Occhiucci, G. *J. Chem. Soc., Perkin Trans. 2* **1972**, 84–88.

(32) Brouwer, D. M.; Mc Lean, C.; Mackor, E. L. *Discuss. Faraday Soc.* **1965**, *39*, 121–129.

(33) [*p*-^3H]Phenol has been prepared through reaction of *p*-bromophenol with *n*-butyllithium in ether followed by addition of ^3H_2O according to the procedure described by Pedersen and Larsen (Pedersen, T.; Larsen, N. W. *J. Labelled Compd.* **1969**, *5*, 195–196).

(34) The exothermicity of the formation of **9**$_p$ by eq 4 ($-\Delta H° \simeq$ 30–50 kcal mol^{-1}, if $\Delta H_f°(CH_3FCH_3^+)$ = 161 ± 8 kcal mol^{-1} (ref 35)) is comparable to that of reaction i if a ground-state phenylium ion is involved ($-\Delta H°$ = 41 kcal mol^{-1}; cf. Table II).

(35) Beauchamp, J. L.; Holtz, D.; Woodgate, S. D.; Patt, S. L. *J. Am. Chem. Soc.* **1972**, *94*, 2798–2807.

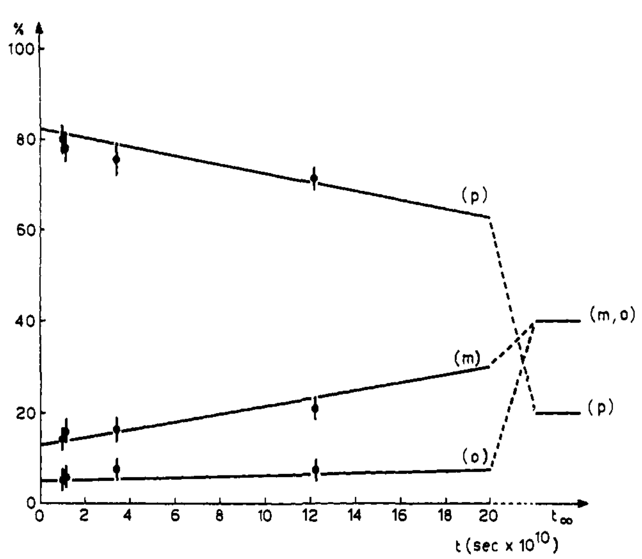

Figure 2. Phenylium ion automerization extent as a function of the partial pressure of CH_3OH. The curves represent the integrated rate equations from path a of Scheme III (relative yield of [^{3}H]phenylium ions: *p*: [*p*-^{3}H]$C_6H_4^+$; *m*: [*m*-^{3}H]$C_6H_4^+$; *o*: [*o*-^{3}H]$C_6H_4^+$). The solid circles denote the relative distribution of the corresponding isomeric [^{3}H]anisoles from the gas-phase decay runs.

experimental points is obtained for a phenylium ion automerization rate constant of the order of 10^7–10^8 s^{-1}.[36] This indicates that the vibrationally excited phenylium ion from the nuclear decay undergoes automerization in the gas phase via a relatively fast hydrogen scrambling that involves moderate activation barriers.[37] These findings are in full agreement with the complete hydrogen randomization occurring in a vibrationally excited $C_6H_5^+$ ion, when generated at much lower pressures in the ion source of a mass spectrometer by electron impact on suitable precursors.[8]

Interconverting Structures in Phenylium Ion Automerization. The structural features of the possible intermediate species involved in the phenylium ion automerization process of Scheme III are of fundamental interest. This is a relevant problem in mass spectrometric investigation,[8] which excited considerable theoretical interest as well. Among the conceivable structures that may be involved in the ^{3}H scrambling within [^{3}H]phenylium ion, species **5**–**7** appear the most plausible. Theoretical studies, in fact, place them in local energy minima of the phenylium ion automerization potential surface, lying 44–77 (**5**), 36–48 (**6**), and 25–67 (**7**) kcal mol^{-1} above the absolute energy minimum of singlet phenylium ion **3**, respectively.[3e,20,38] A substantial activation energy (69 kcal mol^{-1}), calculated for the **3** → **7** conversion,[20b] attenuated the temptation to formulate a phenylium ion automerization via the low-energy structure **7**.

Experimental evidence against intervention of **7** in phenylium ion automerization is provided by the para > meta > ortho ^{3}H distribution in tritiated anisole from the gas-phase decay experiments. These results are, in fact, at variance with the hypothetical intermediacy of the highly symmetrical pyramidal structure **7** that would rather cause an equal extent of ^{3}H scrambling on the ortho and meta position of the labeled anisole.

The choice is, therefore, restricted to structures **5** and **6**. Discrimination between them is not straightforward, although **5** implies phenylium automerization by H shifts, while **6** involves CH group scrambling, and therefore their intermediacy could in principle be experimentally tested by simultaneous C and H labeling. However, several observations speak in favor of structure **5** as the most likely intermediate in phenylium ion automerization, observed in the decay systems. As recently pointed out,[38] (**3** ⇄ **6** (as well as **3** ⇄ **7**) interconversion is symmetry forbidden, and hence, it is expected to require an appreciable extra activation barrier over the inherent endothermicity (~40 kcal mol^{-1}) involved in the **3** → **6** step.[20b] Such severe energetic requirements are hardly consistent with the relatively fast phenylium ion automerization, observed in the gas-phase decay experiments, which appears to involve a quite moderate activation barrier ($\Delta G^{\ddagger} \sim 10$ kcal mol^{-1}).

In conclusion, the present data suggest **5** as the most likely high-energy intermediate in the phenylium ion automerization observed in the decay systems, although theoretical calculations place it too high in energy with respect to **3** ($\Delta E \geq 44$ kcal mol^{-1}).[3e] However, it cannot be excluded that, under more drastic conditions (e.g., in the ion source of a mass spectrometer), fast phenylium ion automerization via hydrogen shifts (Scheme III) might be accompanied by slower automerization pathways involving intermediates **6** and/or **7**.

These conclusions find a counterpart in the condensed-phase experimental evidence of a remarkably large β-deuterium isotope effect in the thermal decomposition of benzenediazonium ion.[3d] This effect is ascribed to a significant contribution of ortho hydrogen hyperconjugation in the transition state linking benzenediazonium to phenylium ion. On these grounds, however, an appreciable vicinal hydrogen participation to the leaving N_2 molecule cannot be excluded, which is promoted by the need of internally "solvating" the partial positive charge in the incipient phenylium ion before intervention of the nucleophilic medium. Under longer lived conditions, as in the gas phase, such tendency may be regarded as the first step toward phenylium ion automerization.

Conclusions

A nuclear decay approach to the characterization of a free, unsolvated phenylium ion in the gas and condensed phase is illustrated in the present study. The reactivity and selectivity features of the nucleogenic phenylium ion toward a suitable acceptor (CH_3OH) are consistent with a singlet-state electronic configuration. No evidence for its interconversion to a triplet state or to open-chain isomeric structure has been obtained, in agreement with theoretical predictions. In the gas phase, nucleogenic phenylium ion tends to internally solvate its positive charge via a fast automerization reaction involving consecutive 1,2 hydrogen shifts. The proposed automerization process is consistent with related data obtained by mass spectrometric methods, whereas a discrepancy exists between the calculated and the experimental energy levels of the species **5** intermediate of the phenylium ion automerization reaction.

Note Added in Proof. The arguments used in the Discussion to rule out mechanism 3 reply to the points raised in: Dewar, M. J. S.; Reynolds, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 3244–3246, published during the editorial processing of the present paper.

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(36) It should be noted that representation of the integrated rate equations of Scheme III, path a, would give exponential concentration vs. time curves. In Figure 2, these curves appear as straight lines. This is due to the relatively short time span covered in the gas-phase experiments. Investigation of the phenylium ion automerization process at longer ion lifetimes implies use of a much lower CH_3OH partial pressure. Such conditions are impracticable, since the extent of undesired side reactions (ion fragmentation, reactions with impurities, reactions on the walls, etc.) may become significant.

(37) The phenylium ion automerization rate is comparable to that of the benzene radical ion and slightly lower than that of the isomerization of linear butyl ion to *s*- and *t*-$C_4H_9^+$. (cf. (a) Beynon, J. H.; Caprioli, R. M.; Perry, W. O.; Baitinger, W. E. *J. Am. Chem. Soc.* **1972**, *94*, 6928–6833. (b) Shold, D. M.; Ausloos, P. *Ibid.* **1978**, *100*, 7915–7919.)

(38) Krogh-Jespersen, K.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Org. Chem.* **1980**, *45*, 1608–1614.