with **1** the guests bearing anionic residues take a more highly favored position in the aromatic guest plane than the guests of comparable substitution pattern bearing nonionic residues.

Acknowledgment. We thank Prof. H. A. Staab for helpful discussions and the generous support of this work.

Registry No. **1**, 86765-98-2; **1·2**, 93254-45-6; **1·4**, 93254-44-5; **1**–naphthalene, 93254-50-3; **1**–1,5-dimethylnaphthalene, 93254-46-7; **1**–2,6-dimethylnaphthalene, 93254-47-8; **1**–durene, 93254-52-5; **1**–1,5-naphthalenedisulfonate, 93254-57-0; **1**–2,6-naphthalenedisulfonate, 93254-56-9; **1**–1-naphthalenesulfonate, 93254-59-2; **1**–2-naphthalenesulfonate, 93254-58-1; **1**–*p*-toluenesulfonate, 93254-61-6; **2**, 129-00-0; **4**, 206-44-0; naphthalene, 91-20-3; 1,5-dimethylnaphthalene, 571-61-9; 2,6-dimethylnaphthalene, 581-42-0; durene, 95-93-2; disodium 1,5-naphthalenedisulfonate, 1655-29-4; disodium 2,6-naphthalenedisulfonate, 1655-45-4; sodium 1-naphthalenesulfonate, 130-14-3; sodium 2-naphthalenesulfonate, 532-02-5; sodium *p*-toluenesulfonate, 657-84-1.

Structure and Reactivity of $C_7H_7^+$ Ions from the Decay of Tritiated Toluenes. 1. Reactions of Free Tolyl Ions with Methanol in the Gas and Liquid Phases

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Abstract: Labeled tolyl cations from the decay of ring-multitritiated toluene have been allowed to react with methanol in the liquid and the gas phases, at pressures ranging from 6 to 100 torr, yielding methyl tolyl ethers as the major products, without appreciable formation of benzyl methyl ether. The isomeric composition of the products from the gaseous systems depends on the pressure, the percentage of *o*-tolyl ether increasing at the expense of the para isomer as the methanol pressure is reduced. The results show that the three tolyl ions exist as distinct species in the dilute gas state. When formed in a sufficiently excited state, as from the β decay of a ^3H atom in toluene, they undergo appreciable interconversion, without detectable isomerization to the benzyl cation, at least within the pressure range accessible to the decay technique.

Interest in gaseous $C_7H_7^+$ ions has not declined since 1957, when the suggestion was first advanced that tropylium ions are formed from toluene and cycloheptatriene under electron impact.[1] Indeed, problems related to the structure and the reactivity of $C_7H_7^+$ isomers have been actively investigated by mass spectrometry and have represented a classic test for all major diagnostic techniques developed in the last quarter of a century, including the study of the fragmentation pattern of selectively labeled precursors,[2–9] ICR spectrometry,[10–14] collision activation spectrometry,[15–18] equilibrium measurements in high-pressure ion sources,[19,20] chemical ionization mass spectrometry,[21,22] and the analysis of the charged products of relevant ion–molecule reactions.[23,24] As a result of such a vigorous and sustained effort, a large body of experimental data is currently available, almost exclusively derived from mass spectrometric studies.[25] Unavoidably, the picture obtained by the application of a single, if powerful, technique is incomplete, owing especially to the recognized[26] difficulties encountered when applying purely mass spectrometric procedures to positive structural identification of isomeric ions and their mixtures. Among other consequences, this state of affairs has largely deprived the theoretical approach to the structure and the stability of gaseous $C_7H_7^+$ isomers[26,27] of the usual correlation with pertinent experimental data, particularly useful for the calibration of semiempirical methods.

In the attempt to widen the experimental approach to the problem, it was decided to undertake a study of the $C_7H_7^+$ isomers by using the method based on the β^- decay of ^3H atoms in suitably labeled toluenes. The decay technique, whose principles and applications have been reviewed,[28] is experimentally laborious, since it requires the preparation of precursors containing two or more ^3H atoms *in the same molecule.* However, it allows the introduction of free cations of specified structure into any system of interest, irrespective of its aggregation state, and to follow their reactions, owing to the presence of the residual radioactive atom(s). The unique features of the decay technique have been exploited

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Table I. Radioactive Products from the Decay of Ring-Tritiated Toluene in Liquid and Gaseous Methanol

system composition	temp, °C	absolute yield, %	isomeric composition of methyl tolyl ethers[b]		
			Ortho (%)	Meta (%)	Para (%)
liquid,[a] mole fraction of toluene = 0.038%	25	50 ± 5	33.0 ± 0.5	45.6 ± 0.8	21.4 ± 0.8
liquid,[a] mole fraction of toluene = 0.038%	−20	52 ± 4	33.6 ± 0.5	44.9 ± 0.3	21.5 ± 0.6
gas,[c] toluene, 1.0 torr; MeOH, 100 torr	25	69 ± 5	36.5 ± 0.6	46.1 ± 0.5	17.4 ± 0.3
gas,[c] toluene, 1.0 torr; MeOH, 20 torr	25	62 ± 5	40.1 ± 0.6	45.5 ± 0.2	14.4 ± 0.3
gas,[c] toluene, 1.0 torr; MeOH, 6.0 torr	25	59 ± 8	42.3 ± 0.5	45.5 ± 0.3	12.2 ± 0.2

[a] Methanol was saturated with O_2 at room temperature; toluene activity = 0.6 mCi. [b] No other cyclic products detected, see text. [c] Activity of toluene = 0.8–1.0 mCi. Oxygen was present as a radical scavenger.

to contrast the reactivity of free tolyl ions in gaseous and liquid systems. The interest of the latter is not restricted to comparison purposes, since the technique outlined in this paper could represent a useful tool for the study of the solution chemistry of arylium ions, so far severely hampered by the lack of convenient routes to the charged reagents. The decay technique has been applied by one of the authors (M.S.) to the study of the structure, and the automerization of free phenylium cations.[29-31] This study concerns the tolyl ions from the decay of toluene containing several ^3H atoms in the ring, while the reactivity of the benzyl cation from the decay of $C_6H_5C^3H_3$ will be illustrated in a forthcoming paper.

Experimental Section

Materials. The preparation of toluene, containing at least two ^3H atoms in the aromatic ring of the same molecule, was carried out according to an established procedure,[32] based on the cyclization of a 1:10 propyne/$^3H_2$–acetylene mixture over a K_2CrO_4-promoted silica–alumina catalyst at room temperature. The crude reaction product was diluted with inactive toluene and purified by preparative GLC, using a 2-m-long, 4-mm-i.d. column, packed with DC 200 Silicone Oil, 20% w/w on silanized Chromosorb W, operated at 110 °C. The purified fraction, further diluted to a specific activity of ca. 0.3 mCi mg^{-1}, was subjected to radio GLC, using the same apparatus and columns employed for the analysis of the decay products, in order to exclude the presence of any tritiated impurities. The intramolecular distribution of ^3H, deduced from the decrease of the molar activity following the substitution of the H atoms bound to different positions with inactive groups, was α = 0% (0%), ortho 33% (25%), meta 45% (50%), para 22% (25%), with a standard deviation of ±2%. The figures given in parentheses are the theoretical percentages, calculated by assuming that no ^3H scrambling occurs in the reaction of $C_2{}^3H_2$ with inactive propyne. The procedures employed for the preparation of the derivatives *o*- and *p*-nitrotoluene, α-chlorotoluene, benzoic acid, methyl benzoate, and methyl *m*-bromobenzoate as well as the gas chromatographic procedures for their purification have been described.[32]

Growth of the Decay Products. The procedure followed to prepare the gaseous and liquid samples were analogous to those described elsewhere.[30] The gaseous systems were prepared by introducing fragile ampules, containing ca. 0.8 mCi of purified toluene and MeOH into a carefully outgassed and evacuated 500-mL Pyrex vessel, equipped with a break-seal tip. The required amount of O_2 (used as a radical scavenger) was then added by standard vacuum techniques, and the vessel was sealed off. The toluene and MeOH ampules were then broken and the contents of the vessel were allowed to come to room temperature and to mix. The vessels were stored in the dark at 25 °C for periods of 6–8 months.

The liquid systems were prepared by introducing tritiated toluene into carefully cleaned and dried Pyrex vials, equipped with a long capillary arm, closed by a fragile tip, and connected to a vacuum line. Each vial was cooled to the liquid nitrogen temperature, evacuated, and sealed off from the line. The capillary arm was then introduced into a cylindrical vessel, containing at the bottom a layer of purified mercury and ca. 7 mL of methanol, which had been previously outgassed and saturated with O_2. The fragile tip of the capillary arm was broken under the level of methanol that was consequently drawn into the evacuated vial. When but a small bubble of gas was left at the top of the vial, the capillary arm was further lowered into the mercury layer. After a few hours, the vial was entirely filled with methanol, except for the lower portion of the capillary where mercury had risen, acting as a mobile seal. The vials were stored in the dark at two different temperatures (25 and −20 °C) for periods ranging from 6 to 8 months.

Radiochemical Analysis of Products. The apparatus used consisted of a Model C C.Erba gas chromatograph, equipped with a hot-wire detector and connected to a 80-mL internal flow proportional counter (Berthold Laboratorium A.G.) heated at 160 °C. Helium was used as the carrier gas, and the effluents were diluted with a precisely metered stream of methane, in order to obtain a 1:1 v/v mixture as the counting gas.

In most cases, the storage vessels were cooled to −196 °C and opened, and their contents were diluted with known amounts of inactive carriers and subjected to radio GLC after thorough mixing. Control analyses, carried out by omitting the addition of carriers, gave the same results within the experimental errors.

The identity of the radioactive products was established by comparing their retention volumes with those of authentic samples on at least two columns. The yield of the products was deduced from the ratio of the activity under their individual elution peaks to the total activity of the labeled $C_7H_7^+$ decay ions. The latter was calculated from the initial activity of toluene, its isotopic composition, the known decay rate of ^3H, and the elapsed time. The following columns were used: (i) a 5-m-long, 4-mm-i.d., stainless-steel column, packed with Bentone 34 (1.75%) + SP 1200 (5%, w/w) on 80/100 mesh Chromosorb W; (ii) a 4.5-m-long, 4-mm-i.d., stainless-steel column, packed with Bentone 34 (5%) + SP 1200 (5%, w/w) on 60/80 mesh, acid-washed Chromosorb W; (iii) a 4.5-m-long, $^1/_8$-in.-i.d., stainless-steel column, packed with E 301 silicone oil (25%) on 60/80 mesh acid-washed Chromosorb W.

Radiolytic Experiments. Weighed amounts of *p*-cresol (GLC standard from Polyscience Co.) calculated to give a 0.1–0.2 torr pressure at 37 °C were introduced into carefully evacuated and outgassed Pyrex bulbs together with MeF (50 torr) and O_2 (2 torr). The bulbs were sealed off and irradiated at 37 °C in a 220 Gammacell from Nuclear Canada Ltd. to a total dose of 2 MRad at a dose rate of ca. 0.5 MRad h^{-1}. The products were analyzed by GLC on the previously listed columns, and their identity was confirmed by GLC/MS, using a Hewlett-Packard Model 5982 A spectrometer or a ZAB-2F spectrometer from Micromass Ltd.

Results

The only aromatic products from the reaction of the decay ions with liquid and gaseous methanol are isomeric methyl tolyl ethers, whose yields and proportions are given in Table I. The isomeric composition of methyl tolyl ethers from the liquid systems corresponds, within experimental errors, to that expected from the known ^3H distribution within the molecule of parent toluene, without any appreciable isomerization.

No cyclic products other than tolyl ethers could be detected, despite a specific search for tritiated methyl benzyl ether, 3-methoxycycloheptatriene, and 7-methoxycycloheptatriene. The sensitivity of the radiometric technique employed sets an upper limit corresponding to less than 1% for the yields of the undetected products.

The combined yields of the methyl tolyl ethers account for 50 to 70% of the decay ions produced, the balance being provided by gaseous and low-boiling products with low retention volumes in radio GLC, and especially by the activity of methanol, arising presumably from the equilibration of MeOH with some tritiated product(s), e.g., water, containing labile ^3H atoms. The combined activity of gases, low-boiling products, methanol, and methyl tolyl

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ethers corresponds approximately to the expected activity of the decay ions formed within the various systems during the growth period.

The results most relevant to the specific purpose of this study can be itemized as follows: (i) the absence of benzyl methyl ether and cycloheptatriene derivatives, as well as of diphenyl- and diphenylmethane derivatives, among the tritiated products from both liquid and gaseous systems; (ii) the dependence of the isomeric composition of methyl tolyl ethers from the gaseous systems on the methanol pressure. As the latter is decreased, the proportions of *o*-tolyl ether increase at the expense of the para isomer, while the percentage of *m*-tolyl ether remains nearly constant. The trend is illustrated in Figure 1, where the isomeric composition of products is plotted vs. the interval between collisions in gaseous methanol at the different pressures investigated.

Discussion

The Reagent. Under the conditions prevailing in the present study, the labeled decay ions are the only significant source of *tritiated* products,[33] and a concise outline of their formation process is relevant to the subsequent discussion. The decay-induced fragmentation of isomeric tolyl tritides has been investigated with mass spectrometric techniques.[34] The results of the experiments carried out at low pressures ($<10^{-5}$ torr) show that ca. 80% of the decay events lead to formation of stable $C_7H_7^+$ ions, that survive undissociated for more than 10^{-5} s. The abundance of $C_7H_7\,{}^3He^+$ ions is negligible (<0.6%), while ca. 20% of the nuclear events cause profound molecular disruption, giving a number of fragments ($C_5H_5^+$, $C_5H_3^+$, $C_5H_2^+$, $C_4H_3^+$, $C_4H_2^+$, $C_3H_3^+$, $C_3H_2^+$, C_3H^+, etc.) in low individual yields. The experimental results are consistent with the theoretical treatment of the molecular consequences of β^- decay, which predicts that over 80% of the $C_7H_7{}^3He^+$ primary daughter ions are formed in the ground electronic state, receiving no appreciable recoil energy from the emission of the β particle and the antineutrino. The remaining fraction (ca. 20%) is formed in highly excited states (>20 eV), owing especially to the "shaking" of the electron cloud, feeling the sudden increase of the nuclear charge.[35] The quantitative loss of ^3He is easily accommodated by the known repulsive nature of the potential energy curve of the C–He bond, which is expected to undergo immediate fission.[36]

Given the unique distribution of excitation energies, either negligible or very large, the fragmentation pattern measured at low pressures can be reasonably extended to gases at higher pressures, or even to the liquid systems, since collisional stabilization can hardly be expected to prevent dissociation of those ions that receive very high energies in the decay event.

The above considerations suggest that $C_7X_7^+$ ions (X = ^3H, H), formed in their ground state from ca. 80% of the nuclear transitions, yield eventually the observed tritiated tolyl methyl ethers, while the fragments from the highly excited daughter ions (ca. 20%) are the source of the gaseous and low-boiling products.

Indeed, there is a reasonable agreement between the measured yields of the aromatic products and those expected from the low-pressure mass spectrometric data.

As to the internal energy of the $C_7X_7^+$ ions from the decay, their formation entails an inherent cause of vibrational excitation even in those cases (over 80%) where the electron-cloud "shaking" and the β recoil effects are negligible. In fact, the sudden nuclear transient generates $C_7X_7^+$ ions having a regular hexagonal ring, reminescent of that of the parent C_7X_8 molecule, energetically unfavorable with respect to the highly distorted ring that, according to theoretical calculations, characterizes ground-state tolyl ions.[37]

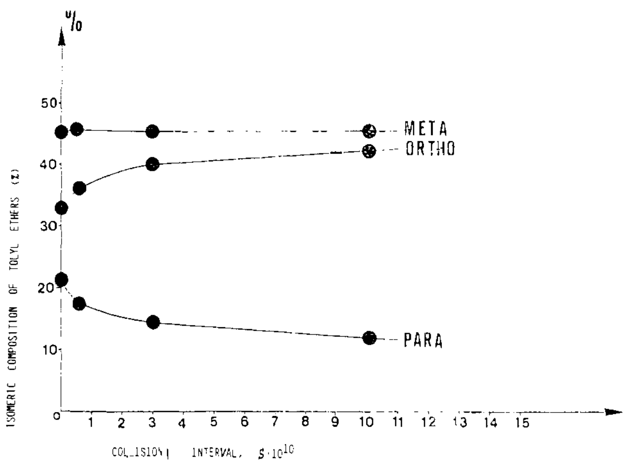
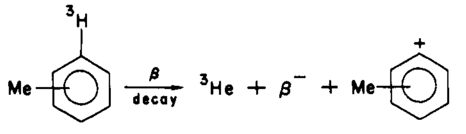


Figure 1. Dependence of the isomeric composition of methyl tolyl ethers on the interval between collisions in gaseous methanol. The latter has been calculated according to the ADO model (ref 50) for the different methanol pressures investigated.

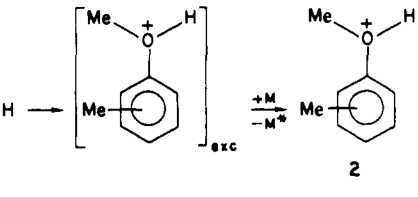
While specific data on the corresponding deformation energy are not available for the tolyl ions, a reasonable estimate is represented by the value (32 kcal mol^{-1}) calculated for the correspondingly deformed phenylium ion, for which a similar structural relaxation is predicted.[38] In this view, 32 kcal mol^{-1} represents the excess vibrational energy of the tolyl ions from the decay of tritiated toluene, following the relaxation of their regular hexagonal ring into the more stable deformed geometry.

Reaction in Liquid Methanol. It is suggested that formation of tritiated tolyl ethers from the decay of multilabeled toluene in liquid methanol occurs via the reactions illustrated by the following equations, where indication of the undecayed ^3H atoms of the daughter ions is omitted for the sake of clarity.



1

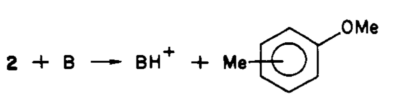
(1)



2

(2)

Reaction 2 is exothermic, and its $\Delta H°$ value can be estimated[39] around −45 kcal mol^{-1}. Following collisional stabilization, very effective in the liquid system, oxonium ion **2** undergoes deprotonation to yield the observed tolyl ethers. As to the nature of base B, it should be noted that deprotonation of **2** by a single molecule of methanol would be endothermic.[40]



(3)

However, cooperative deprotonation

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(33) The extreme dilution of tritiated species makes radiolytic processes entirely negligible in comparison with β decay as a source of *tritiated* products. This of course is true only if the specific activity of the system is sufficiently low, as in the present study. At the much higher levels typical of earlier studies (cf.: (a) Nefedov, V. D.; Sinotova, E. N.; Korsakov, M. V.; Alekseev, E. G. *Radiokhimiya* **1973**, *15*, 635), radiolytic contribution may become significant, and it predominates under the conditions employed for labeling purposes (cf.: (b) Yang, K.; Gant, P. L. *J. Phys. Chem.* **1962**, *66*, 1619).

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(37) The C–C^+–C angle in the most stable structure of tolyl ions ranges from 144.9° to 148.8° according to the calculations of ref 26.

(38) (a) Schleyer, P. v. R.; Kos, A. J.; Ragavachari, K. *J. Chem. Soc., Chem. Commun.* **1983**, 1296. See also: (b) Dill, J. D.; Schleyer, P. v. R.; Binkley, J. S.; Seeger, R.; Pople, J. A.; Haselbach, E. *J. Am. Chem. Soc.* **1976**, *98*, 5428.

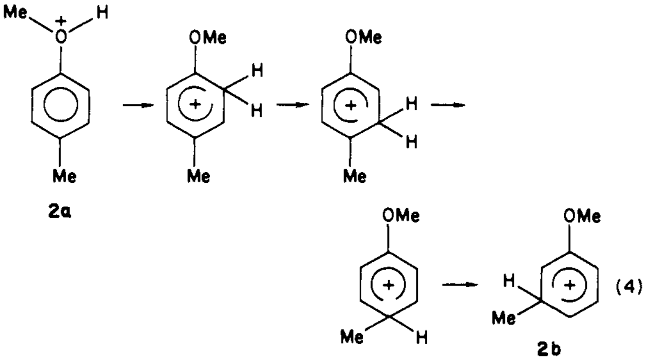
(39) This value has been calculated for the formation of *m*-tolyl methyl oxonium ion by using a $H_f°$ value of 236 kcal mol^{-1} for the *m*-tolyl ion (ref. 26) and by assuming that the PA of the oxygen atom of *m*-tolyl methyl ether is the same as in the anisole, i.e., 197 kcal mol^{-1}, cf.: (a) Reynolds, C. H.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1982**, *104*, 3244. The $H_f°$ value of *m*-tolyl methyl ether has been taken from the following: Cox, J. D.; Pilcher, G. "Thermodynamics of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

by several molecules of the alcohol is likely to occur in the liquid, and even in the gaseous systems within a ionic cluster. The isomeric composition of tritiated tolyl ethers formed in liquid methanol corresponds, within experimental errors, to that expected from the known ^3H distribution within the molecule of the parent toluene.

It is therefore concluded that neither tolyl ions **1** nor oxonium ions **2** undergo appreciable isomerization when the reaction sequence 1 to 3 takes place in liquid methanol, consistent with the high efficiency of collisional stabilization processes typical of the condensed phase.

Reaction in Gaseous Methanol. The results of the gas-phase experiments differ from those obtained in liquid methanol in that the isomeric composition of tolyl ethers changes appreciably at low methanol pressures. This evidence suggests intramolecular isomerization of tolyl ions **1** and/or oxonium ions **2**.

It is relevant to the purposes of the discussion to rule out the latter process, which could conceivably occur via a sequence involving multiple proton and methyl shifts, e.g.

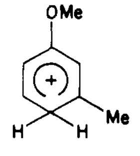


(4)

To this end, a specific experimental test has been carried out, preparing **2a** via an alternative route, i.e., the gas-phase methylation of *p*-cresol by radiolytically formed dimethylfluoronium ions

$$p\text{-}MeC_6H_4OH + Me_2F^+ \rightarrow MeF + \mathbf{2a} \nrightarrow \mathbf{2b} \quad (5)$$

The O-alkylated product obtained in MeF at 50 torr consisted exclusively of the para isomer, without detectable formation of *o*- and *m*-tolyl ethers, thus excluding occurrence of sequence 4. The latter appears quite unlikely on mechanistic grounds as well. First, skeletal isomerization requires an intramolecular methyl shift to occur in competition with a proton shift, whose activation energy is known to be much lower.[42] Furthermore, at the pressures prevailing in the present study, collisional deactivation is expected to prevent the occurrence of sequence 4, requiring multiple crossing of appreciable activation barriers. Finally, interconversion of arenium ions should proceed toward the most stable isomers, i.e., *m*-tolyl ethers protonated at positions 2, 4, or 6, e.g.



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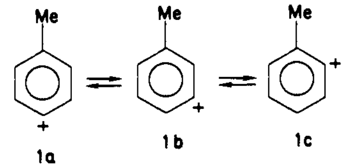
contrary to the experimentally observed trend, pointing to an increase of methyl *o*-tolyl ether at low pressures.

These considerations show that the observed changes of the isomeric composition of tolyl ethers can hardly be traced to rearrangement of the oxonium ions **2**[43] and must arise from isomerization of gaseous tolyl ions *before* their reaction with methanol.

Among the possible mechanisms, the most simple one involves 1,2 hydride shifts within tolyl ions vibrationally excited by relaxation of the regular hexagonal structure of their ring to the more stable highly deformed geometry (vide supra), i.e.



(6)

An analogous mechanism has been suggested for the automerization of gaseous phenylium ions from the decay of [1,4-$^3H_2$]benzene.[30,31]

Sequence 6 does not conflict with any of the experimental features. Indeed, it easily accommodates the observation that the product from **1b** remains nearly constant, while the product from **1c** increases and that from **1a** decreases, at low MeOH pressures. Such a trend can be rationalized by assuming an isomerization sequence **1a** → **1b** → **1c** via consecutive 1,2 hydride shifts probably on account of the higher stability of isomer **1c** (vide infra). The stationary concentration of **1b** would then be established, as a result of the comparable rates of steps **1a** → **1b** → **1c** within the (limited) conversion range observed.

An experimental feature most relevant to the discussion is that no tritiated products whose formation can be traced to benzyl ion could be detected, despite a specific search. Since it has been shown[44] that labeled benzyl cations react efficiently with gaseous methanol yielding tritiated benzyl methyl ether, one must conclude that tolyl ions capable of undergoing mutual interconversion do not rearrange into the benzyl structure, or at least that the rate of the process

$$\mathbf{1} \nrightarrow \underset{\mathbf{4}}{C_6H_5CH_2^+} \quad (7)$$

is substantially lower than that of reaction 6.

Comparison with Theoretical Results. The energy barrier $E^{\ddagger}$ for 1,2 hydride shifts within phenylium ions has been calculated with different methods, together with the excess internal energy E^* of phenylium ions (as those from the decay of tritiated benzene) having a regular hexagonal ring instead of the highly deformed one which characterizes the most stable structure. The difference $\Delta E = E^{\ddagger} - E^*$ amounted to 52 kcal mol^{-1} according to STO-3G calculations[38b] and to 21 kcal mol^{-1} at the MINDO/3 level.[38a,45] Both values were large enough to justify the reluctance[38a,45] to concede that 1,2 hydride shifts can occur within the excited phenylium ions from the decay of tritiated benzene, as suggested by strong experimental evidence. Fortunately, the situation has been considerably eased by very recent, higher level calculations,[38a] whose results have reduced ΔE to slightly less than 8 kcal mol^{-1}

As to tolyl ions proper, the energy barrier $E^{\ddagger}$ for 1,2 hydride shifts, e.g., for **1b** → **1c**, was 38.9 kcal mol^{-1} according to MINDO/3 calculations,[26] i.e., some 5 kcal mol^{-1} *lower* than for $C_6H_5^+$. No theoretical data are currently available concerning the excess internal energy E^* of tolyl ions having a regular hexagonal ring, as those formed from the decay of tritiated toluene. Nevertheless, assuming for E^* the same value recently calculated for the equally deformed $C_6H_5^+$ ions,[38a] the difference ΔE with the energy barrier $E^{\ddagger}$ from the MINDO/3 approach[26] is only 6.6 kcal mol^{-1}. Such

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(40) The PA of CH_3OH is taken between 179 and 184 kcal mol^{-1}, cf.: Walder, R.; Franklin, J. L. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 85.

(41) Pepe, N.; Speranza, M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1430. The exothermicity of the analogous reaction with phenol has been estimated between 30 and 50 kcal mol^{-1}, see ref 30.

(42) According to Brouwer (Brouwer, D. M. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 611), the activation energy for methyl shifts is 20–23 kcal mol^{-1}, as compared to 11 kcal mol^{-1} for proton shifts, see: Brouwer, D. M.; Mac Lean, C.; Mackor, E. L. *Discuss. Faraday Soc.* **1965**, *39*, 121.

(43) A mechanism based on a sequence analogous to (4), suggested to account for the observed ^3H scrambling within anisole from the reaction of tritiated phenylium ions with methanol (ref 39a), has been ruled out by specific control experiments (ref 30) and by the conclusive observation that ^3H scrambling within the ring of the products persists even when methanol is replaced by a methyl halide as the trapping nucleophile (ref 31). The observation that the oxonium ions from the reaction of phenylium ions with methanol, whose excitation energy is quite comparable to that of **2**, fail to undergo ^3H scrambling within the ring, despite the *lower* barrier for proton shifts than for methyl shifts, provides additional evidence against sequence 4.

(44) Cacace, F.; Ciranni, G.; Sparapani, C.; Speranza, M., submitted for publication.

(45) Tosaka, M.; Ogata, M.; Ichikawa, H. *J. Am. Chem. Soc.* **1981**, *103*, 1885.

(46) Dewar, M. J. S.; Ford, G. P.; Reynolds, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 6162.

a difference is quite small,[47] if one takes into account the assumption made, the inherent accuracy of semiempirical methods, and especially the dramatic and constant decrease of the ΔE value following the application of greatly refined, and hence more trustworthy theroretical, calculations to the unsubstituted phenylium ion. It is difficult to assess, at the present time, whether mechanism 6, based on 1,2 hydride shifts, would be consistent with the results of higher level theoretical methods, as those recently applied to $C_6H_5^+$. In any event, the discrepancy, if any, should not be nearly as serious as with earlier semiempirical results.

As to the relative stability of tolyl ions, the order deduced from the MINDO/3 approach, i.e., para < meta < ortho, is not consistent with the experimental evidence from this study, pointing to an *increase* of the product deriving from **1c** and to a simultaneous *decrease* of the product from **1a** at low MeOH pressures.

On the other hand, the energy barrier of process 7, e.g., **1c** → **4** calculated at the MINDO/3 level, was 25 kcal mol^{-1}, considerably *lower* than of process 6, e.g., **1b** → **1c**, namely 38.9 kcal mol^{-1}. Consequently, excited tolyl ions **1b** were predicted to collapse directly to **4**, without being trapped as **1c**.[26] This view is at variance with the experimental results of this study, that provides positive evidence against occurrence of isomerization 7 of tolyl ions which instead appear capable of significant interconversion.

Independent evidence supports the view that the activation energy of process 7 exceeds the barrier calculated at the MINDO/3 level. In fact, tolyl ions formed in the mass spectrometer via the reaction of H_3^+ ions with *p*-fluorotoluene, whose exothermicity (−57 kcal mol^{-1}) is much larger than the calculated barrier, fail to isomerize into benzyl cations, despite the relatively low H_2 pressure (≤ 1 torr) and the high temperature (160 °C) prevailing in the ion source.[22]

Comparison with Mass Spectrometric Results. Once the differences existing in the time scale and the excitation mechanism typical of the two experimental approaches are taken into account, the results from the application of the decay technique to gaseous tolyl ions support, in general, the conclusions of pertinent mass spectrometric studies.

In fact, species tentatively identified as tolyl ions with use of indirect structural criteria based on the nature of their neutral precursors, or by diagnostic techniques such as collisional activation (CA), have been obtained in a state of high purity (>90%) by electron impact[15,17,18,48] or by chemical ionization[18,22,49] mass spectrometry.

These species appear to survive as long as 10^{-5} s without rearrangement to the benzyl or tropylium structure,[18] despite the excitation energy from their formation processes. In this connection, the present study provides "hard" confirmatory evidence, based on the actual isolation of structurally diagnostic products, for the occurrence of tolyl ions as distinct species in the dilute gas state. The different rate of processes 6 and 7, deduced from the decay experiments, is also consistent with the mass spectrometric evidence. First, the low rate of (7) explains the surprising stability of tolyl ions with respect to isomerization to benzyl, or tropylium cations, noted in mass spectrometric studies.[17,18] Furthermore, process 6, observed in the present study even at "high" pressures (6 to 100 torr), is expected to be much more efficient at the excitation levels and the low pressures typical of mass spectrometry, thus causing complete equilibration of tolyl ions **1** with sufficient internal energy to the most stable ortho isomer **1c** *well before* structural assay by CA. This could explain the observation that tolyl ions, irrespective of their precursor and therefore, presumably, of their *initial* isomeric composition, exhibit nearly identical CA spectra, which, however, are different from those of benzyl or tropylium ions, excluding rearrangement of **1** into either of these common structures.

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Registry No. 1a, 61837-10-3; **1b**, 61837-09-0; **1c**, 53272-68-7; **2a**, 37145-50-9; **2b**, 92014-29-4; MeF, 593-53-3; Me_2F^+, 64710-12-9; MeOH, 67-56-1; CH_3Ph-*ring*-^3H_x, 92077-38-8; *o*-MeC_6H_4OMe-*ring*-^3H_x, 92014-30-7; *m*-MeC_6H_4OMe-*ring*-^3H_x, 92014-31-8; *p*-MeC_6H_4OMe-*ring*-^3H_x, 92014-32-9; *p*-cresol, 106-44-5.

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Hückel Rules and Electron Correlation[†]

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Abstract: The possible effects of electron correlation on Hückel-type rules for cyclic π-electron systems are considered. General exact results are developed for a wide variety of models, including a range of degrees of electron correlation, for homo- or heteroannulenes or various distorted cycles, either of Hückel or Möbius type. The theorematic results confirm some general qualitative points of the Hückel-type rules and provide checks on approximate solutions to these various models.

1. History and Introduction

Cyclic π-electron systems and their special (often "aromatic") features have long been of much interest. Hückel's[1] celebrated *4n + 2 rule* provided a key step toward elucidating these features. As such, it has been acclaimed[2-4] one of the most fundamental rules of chemistry and has found[5-7] wide applicability among (organic) chemists. The original rule states that the planar monocyclic systems containing $(4n + 2)$ π-electrons are expected to exhibit aromatic stability. A later amendment states that the

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