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REACTIONS OF PHENYLIUM IONS WITH GASEOUS HYDROCARBONS. 1. METHANE, ETHANE, AND PROPANE.

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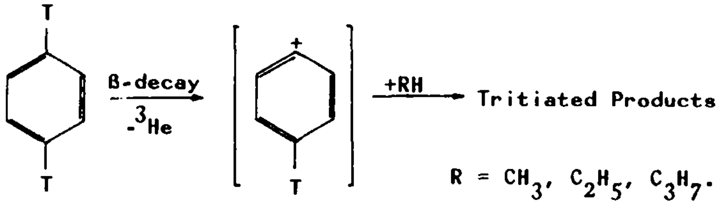
Abstract – The reaction of free tritiated phenylium ion, generated from nuclear decay of $[1,4\text{-}T_2]$-benzene in the presence of simple gaseous hydrocarbons RH (R = CH_3, C_2H_5, C_3H_7; partial pressure: 10-100 torr), yields predominantly the corresponding tritiated C_6H_5R products. The effects of gaseous nucleophilic acceptors (NuH = NH_3, CH_3OH) on the reaction with CH_4 were also investigated. Phenylium ion confirms its exceedingly high reactivity even toward pure σ-type substrates, as well as its considerable site selectivity, demonstrated by the distinct preference for the C-H bonds of the substrate. The stability features of the ionic intermediates from addition of phenylium ion with RH have been evaluated, as well as their fragmentation and isomerization mechanisms. The behaviour of phenylium ion toward simple aliphatic hydrocarbons in the gas phase (10-100 torr) is discussed and compared with previous mechanistic hypotheses from ICR mass spectrometric studies, carried out at much lower pressures (10^{-5} torr).

Spontaneous ß decay of tritium atom in tritiated compounds affords a convenient means to produce free carbocations of defined structure into any system of interest and to study their reactions by tracer techniques.[1] The method was recently applied to gather otherwise inaccessible information about unimolecular automerization of a gaseous phenylium ion 1, generated from decay in $[1,4\text{-}T_2]$-benzene (eq. 1), and its reactivity properties toward n-type acceptors.[2] The relevant data are consistent with a highly reactive phenylium ion with a distinct affinity for the n-centre of the substrate molecule. Our investigation has been now extended to establish the reactivity and the site selectivity of the decay phenylium ion toward substrates containing exclusively σ bonds. At the present level, the study has been restricted to the simplest members of the aliphatic hydrocarbons class, i.e. methane, ethane, and propane. We expect that this study will allow us to gather insight into the sensitivity of these simple hydrocarbons to electrophilic attack of a defined carbocation (the phenylium ion) in the gas phase, under conditions excluding interference of environmental effects (solvation, ion-pairing, etc.). It is thereby hoped to provide a reactivity model for phenylium ion toward simple hydrocarbons and a stability scale for the ensuing ionic adducts, under different experimental conditions.



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EXPERIMENTAL.

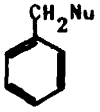
The key substrate for the nuclear-decay experiments, $[1,4\text{-}T_2]$-benzene, was prepared, purified, and analyzed using a previously described procedure.[3] The decay samples were prepared by introducing sealed glass capillaries containing ca. 1 mCi of tritiated benzene (specific activity: 90 mCi $mmol^{-1}$) into 300-mL Pyrex ampoules. The ampoules were then connected to a vacuum line and thoroughly degassed. The gaseous hydrocarbon substrate was then introduced, together with minor amounts of a nucleophilic additive (NuH = NH_3 or CH_3OH) and of oxygen (4 torr), which was used as a scavenger of the radical species that could be formed by the passage of the ß-particle from the nuclear decay of the tritiated benzene through the gaseous mixture. The decay mixtures were then stored for 12-14 months in the dark at room temperature. The vessels were then opened under airtight conditions and their content analyzed by radio glc, using a C. Erba Fractovap 4200 gas chromatograph equipped with a high-sensitivity hot-wire detector, coupled in series with a Berthold proportional counter tube, kept at 180°C.

The tritiated products were identified by comparing their retention volumes with those of authentic specimens under identical chromatographic conditions, on two different columns: (i) Bentone 34-SP 1200, 1.75%:5% on 100/120 Supelcoport, 5m, at 80°C; (ii) Silicone Oil 550 10% on 80/100 Chromosorb W-AW, 5m, at temperatures ranging from 100 to 200°C.

RESULTS AND DISCUSSION.

The composition of the decay systems and the yields of the identified tritiated products are reported in the Table. The absolute yields of the listed aromatic products were obtained by comparing their overall activity with the maximum theoretical activity that may be incorporated in the products. This can be calculated from the initial activity and the isotopic composition of the tritiated benzene sample (54% $[1,4\text{-}T_2]$-benzene and 46% T-benzene),[3] the decay rate of the tritium, the abundance (72%) of the $C_6H_5^+$ structure retained after

TABLE. Product Yields from the Reaction of Tritiated Phenylium Ions with Simple Alkanes in the Gas Phase.

System Composition (torr) a)		Absolute Yields of Products (%) b)		
Alkane, RH	NuH			
R = CH_3, 15	-	12.3	-	-
R = CH_3, 20	NH_3 (2.0)	10.0	c)	<0.5
R = CH_3, 35	NH_3 (2.0)	23.5	c)	<0.5
R = CH_3, 25	NH_3 (4.0)	55.2	c)	<0.5
R = CH_3, 20	CH_3OH (2.6)	22.3	22.4	<0.5
R = CH_3, 20	CH_3OH (5.3)	12.3	34.4	<0.5
R = CH_3, 100	-	58.3	-	-
R = C_2H_5, 10	-	15.6	-	-
R = C_2H_5, 100	-	22.7	-	-
R = C_3H_7, 10	-	15.4 (R= iPr) d) 3.8 (R= nPr) d)	-	-
R = C_3H_7, 100	-	18.2 (R= iPr) 13.1 (R= nPr)	-	-

a) The systems contained, besides the substrates, 4 torr of O_2; b) The data represent the average of at least three independent analyses. Standard deviation of data *ca.* 10%; c) The aniline yields are not reported, being largely variable because of the presence of readily exchangeable NH_2 hydrogens; d) Also 2.4% of tritiated ethylbenzene formed.

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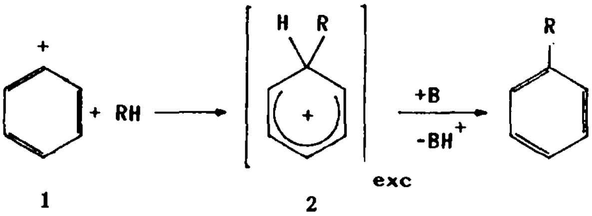
nuclear transition,[4] and the absolute counting efficiency of the detector employed. Analysis of the Table reveals that appreciable yields of toluene and ethylbenzene are exclusively formed from CH_4 and C_2H_6, respectively, while variable proportions of isomeric propylbenzenes are recovered in the C_3H_8 systems. The following discussion will be restricted to these labeled aromatic products, whose formation can be directly and exclusively related to the attack of the tritiated phenylium ion 1 on RH and to the stability of the ensuing ionic adducts, neglecting other labeled products (*e.g.* low-boiling compounds, T-benzene, etc.) accounting for most of the residual activity not reported in the Table, whose formation is due to secondary processes, such as unimolecular ion fragmentation or hydride-ion transfer between 1 and the hydrocarbon.

Direct addition of phenylium to the C-H bonds of the hydrocarbon RH (R = CH_3, C_2H_5, and C_3H_7) is suggested to be a major channel leading to the aromatic products of the Table, via the formation of the corresponding arenium intermediate 2 (eq. 2), excited by the exothermicity of their formation process. In the case of RH = CH_4, reaction 2 is the only energetically allowed channel

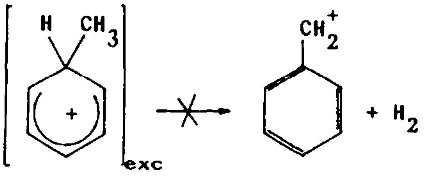


1 2 (2)

available to the decay phenylium ion ($\Delta H°$ = -60 kcal mol^{-1}),[5] whereas when RH = C_2H_6 or C_3H_8, process 2 may be accompanied by the corresponding hydride-ion transfer to give T-benzene.[6] Accordingly, a higher absolute yield of tritiated C_6H_5R is observed in the methane mixtures with respect to those with ethane or propane, under the same conditions (e.g. at $P_{(RH)}$ = 100 torr).

Unless stabilized by unreactive collisions with the hydrocarbon molecules, the excited intermediates 2 may undergo fragmentation to simpler species. In fact, the yield of tritiated aromatics increases with the partial pressure of the hydrocarbon, as well as with that of NH_3 or CH_3OH, which favours the neutralization step of sequence 2.

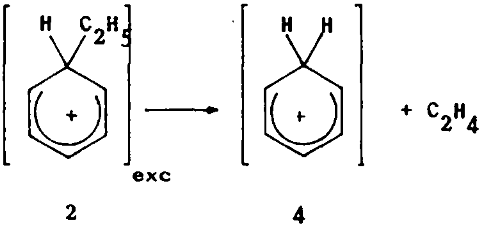
A plausible fragmentation pathway available to the excited species 2 from CH_4 (R = CH_3) involves loss of a H_2 molecule to give benzyl cation 3 (eq. 3).[7] As a matter of fact, previous low-pressure ICR investigation indicated that



2 3 (3)

a $C_7H_7^+$ fragment invariably accompanies formation of $C_7H_9^+$ from attack of phenylium ion on CH_4.[8] However, no information on the structure of the $C_7H_7^+$ species was available from that study. In the present decay experiments, occurrence of the fragmentation 3 to any significant extent can be safely excluded. In fact, neither benzylamine nor benzylmethylether could be recovered among the tritiated products from the CH_4 systems containing NH_3 and CH_3OH, respectively. Owing to the well-established reactivity of $C_7H_7^+$ toward amines[9] and alcohols,[10] it can be concluded that excited arenium ions from eq. 2 do not fragment to give benzyl cation 3 as well as other aromatic $C_7H_7^+$ isomers, or at least that, under the decay conditions, the rate of the fragmentation process 3 is substantially lower than those of alternative fission reactions (*e.g.* ring opening), not leading to aromatic products.

Low-pressure ICR investigation[8] established that an additional fragmentation process is available to the ionic adduct 2 from phenylium-ion attack on ethane, namely that involving loss of a C_2H_4 moiety with formation of a $C_6H_7^+$ fragment 4 (eq. 4).[11] Although occurrence of such fragmentation channel

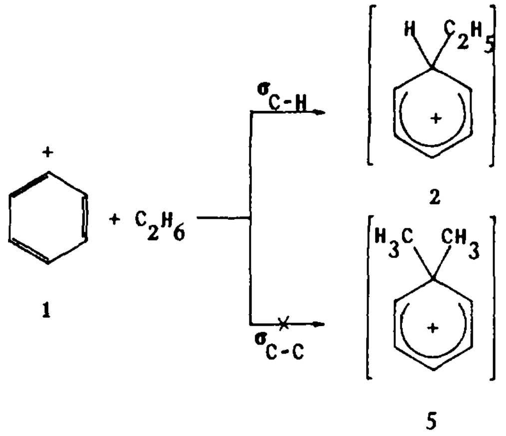


(4)

cannot be demonstrated by the present decay experiments, since it leads to tritiated benzene which is not discernible from the undecayed starting $[1.4\text{-}T_2]$-benzene, nevertheless it is supported by the comparatively lower absolute yields of aromatic products recovered in the RH = C_2H_6 and C_3H_8 systems, with respect to those from the methane samples.

The relatively high yields of labeled C_6H_5R recovered in the decay samples demonstrate the distinct affinity of phenylium ion even toward pure σ electrons, although this appears appreciably lower than that for n-electrons, as shown by the competition data in the CH_4/CH_3OH systems. In fact, with the reasonable assumption that the first step of sequence 2 is the rate-limiting step, the apparent rate constant ratio for the formation of toluene and anisole in the CH_4/CH_3OH systems is calculated to range around 8.6 ± 0.9.

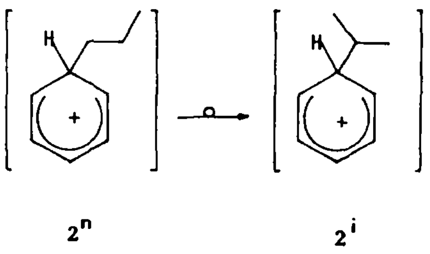
The high reactivity of phenylium ion toward the σ bonds of the selected hydrocarbons is accompanied by a significant site selectivity. Formation of ethylbenzene in the C_2H_6 systems, while toluene and isomeric xylenes are completely absent, indicates that the phenylating reactant 1 attacks exclusively the σ_{C-H} bonds of the substrate, while ignoring the σ_{C-C} bond (eq. 5).



(5)

A similar picture is obtained in the C_3H_8 systems, where the distinct preference of the ionic electrophile for the σ_{C-H} bonds of the hydrocarbon is demonstrated by the relatively high yields of isomeric propylbenzenes (19.2%) over that of ethylbenzene (2.4%), whose formation may in part be attributable to the direct insertion of 1 into a C-C bond of C_3H_8.

The significant site selectivity of phenylium ion 1 might be extensible to the primary and secondary C-H bonds of propane, in case formation of isomeric propylbenzenes occurs in proportions largely different from that expected on a statistical basis i.e. i-propylbenzene: n-propylbenzene = 0.33. As a matter of fact, formation of i-propylbenzene appears to exceed that of the n-propyl isomer, by a factor increasing at low pressures (1.4 at 100 torr, 4.0 at 1.0 torr). This trend lends support to an unimolecular isomerization of the side-chain of intermediate 2^n (n-propyl → i-propyl), whose extent increases with the lifetime of the excited arenium ion (eq. 6). The same energetically



(6)

favoured isomerization process has been observed in excited methylpropylphenyloxonium ions, when formed in the dilute gas state from the condensation of phenylium ion 1 with the appropriate methylpropylether.[2d]

In conclusion, the present investigation of the gas-phase reaction of phenylium ion with the simple hydrocarbons RH (R = CH_3, C_2H_5, and C_3H_7) has not only extended our knowledge of the nature and the reactivity of the ionic reactant toward pure σ-type substrates, but has also allowed direct evaluation of the fragmentation and the isomerization pathways opened to the ensuing excited addition intermediates in the dilute gas state.

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(7) Sequence $1 \rightarrow 2 \rightarrow 3$ is computed to involve an overall enthalpy change of ca. -36 kcal mol^{-1}.

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(11) Sequence $1 \rightarrow 2 \rightarrow 4$ is computed to involve an overall enthalpy change ranging around -38 kcal mol^{-1}.