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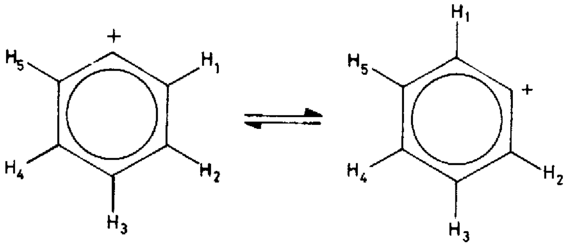
FIRST EVIDENCE FOR AUTOMERIZATION OF GASEOUS PHENYLIUM ION.

Maurizio Speranza
Laboratorio di Chimica Nucleare, CNR, Area della Ricerca di Roma, C.P. 10
00016 Monterotondo Stazione, Rome, Italy.

Tritium atom distribution in the anisole formed from the attack of a nucleogenic tritiated phenylium ion on gaseous methanol provides the first experimental evidence for a gas-phase automerization of phenylium ion.

Notwithstanding the high levels of sophistication attained by the current solvolytic methods for generating carbocations and investigating their chemical behaviour, any attempt to detect degenerate rearrangements in simple cations, such as (**1**), has to date met with no success.[1] High energy barriers for any isomerization in phenylium ion (**1**) or its exceedingly short lifetime even under conventional stable ion conditions may account for such failures.[2]

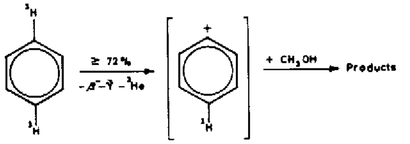


(**1**) (**1'**)

(1)

Recent development of kinetic methods based on nuclear decay in multitritiated molecules has opened up the way of generating carbocations of well-defined structure and energy even *in the gas-phase*,[3] wherein potential ion isomerizations have the best chance to occur and to be observed. This paper describes the first experimental evidence for a gas-phase degenerate rearrangement in phenylium ion (**1**) (eq.1), observed during the course of a systematic investigation of its gas- and condensed-phase reactivity toward a variety of substrates.

High yields ($\geq 72\%$) of free phenylium ions can be readily produced by beta-decay of tritiated benzene.[4] Thus, 1-mCi samples of *para*-$^3H_2$-benzene[5] were diluted with liquid or gaseous methanol, as the substrate, containing small amounts of oxygen, as thermal radical scavenger, and stored for 3.5 months in the dark, at room temperature. The absolute yields and the distribution of the recovered radioactive products are reported in the Table. Measurements of the

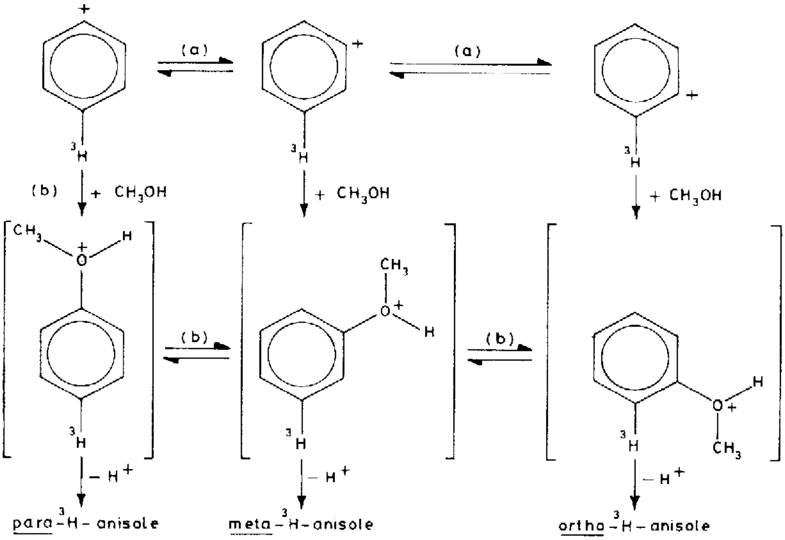


(1)

(2)

residual radioactivity in the tritiated anisole after partial or exhaustive ring chlorination,[6] gave the tritium distribution reported in the Figure.

For the label rearrangement to be observed in the ^{3}H-anisole formed in the gaseous samples, *i.e.* at relatively long ion lifetimes, only two different pathways can be envisioned. Thus, an automerization process in the nucleogenic phenylium ion *before* condensation with methanol (eq.3a), or a mechanism involving ^{3}H isomerization in the intermediates arising from the phenylium-ion attack on methanol (eq.3b), can both provide a plausible explanation for the obtained results. In order to verify the significance of the latter pathway, *para*-dimethoxy-benzene has been exposed to protonation by radiolytically formed H_3^+ ions,



(3)

under conditions resembling, as much as possible, the decay experiments. The failure to detect any protonation-induced methoxy-group shift within the substrate, in spite of the marked exothermicity ($-\Delta H^{\circ} = 85 \div 90$ kcal mol^{-1}) of the protonation process, spells against any significant contribution of

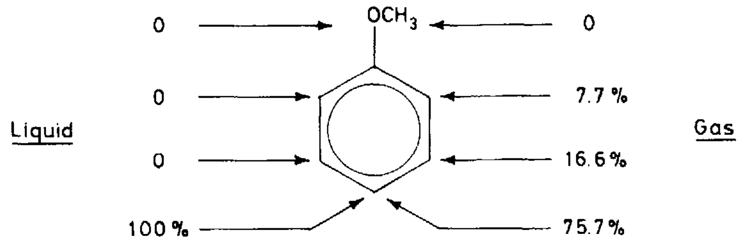
Table. Radioactive Product Distribution from Phenylium-Ion Condensation with Methanol (T = 25°C).[a)]

System Composition[b)]	Absolute Yields of Radioactive Products (%)		
	Anisole	Others[c)]	Total[d)]
Liquid CH_3OH saturated with O_2	64.7	26.8	91.5
Gaseous CH_3OH(18 torr) + O_2 (4 torr).	44.9	23.9	68.8

a) Product analyses carried out by radiogaschromatography and liquid scintillation counting. Standard deviation of data ca. 10%. b) The liquid samples were stored in the absence of vapours, the gaseous ones in sealed vials.

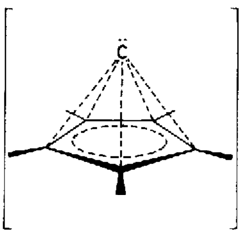
c) Aromatic condensation products. d) Low boiling fragmentation products account for the residual activity.

Figure: Tritium Distribution in the Radioactive Anisole Recovered from the Liquid and Gaseous Para-$^3H_2$-Benzene/Methanol/Oxygen Samples.



path (3b) to the isomeric tritiated anisoles. As a consequence, the obtained results provide the first experimental evidence in favour of a gas-phase phenylium-ion automerization process and allow to draw the following conclusions:

i - Even though the present results do not permit to ascertain whether the observed automerization is due to H or CH-group migration they nevertheless exclude any significant intermediacy of the nonclassical carbene structure (2), since involving uniform probability of ^3H rearrangement on all the positions of the phenylium ion.



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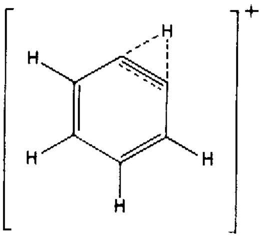

(3)

ii - Retention of the original tritium position in the ring of the ^{3}H-anisole from the liquid samples, *i.e.* at relatively short ion lifetimes, indicates that automerization of phenylium ion is a rather slow process requiring passage over substantial energy barriers. These findings are fully consistent with theoretical calculations[7] which assign to the most likely transition state (3) of the observed automerization, energy levels lying much above (from 44 to 77 kcal mol^{-1}) that computed for the ground-state phenylium ion (1).

iii - Finally, isolation of high yields of anisole in the liquid and gaseous systems further confirms retention of the cyclic structure by $C_6H_5^+$ ions from the beta-decay of the tritiated benzene precursor.

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