Is Gaseous Phenylium Ion Unreactive towards Acetylene?

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At variance with previous ion cyclotron resonance (i.c.r.) evidence, gaseous phenylium ion, from the β-decay of tritiated benzene, has been found to react efficiently with acetylene at relatively high pressure (100 Torr), a result which is of interest to the chemistry of soot formation in fuel-rich acetylenic flames.

The high reactivity of gaseous ionic electrophiles toward alkynes is well documented,[1] but in contrast it has recently been reported, on the basis of measurements carried out under low-pressure ion cyclotron resonance (i.c.r.) conditions (10^{-5}—10^{-6} Torr), that the $C_6H_5^+$ ion, having the cyclic phenylium-ion structure, is unreactive towards acetylene, and, therefore, is unlikely to be responsible for soot formation in fuel-rich acetylenic flames.[2] The discrepancy between such a conclusion and the proven ability of gaseous phenylium ion (**1**) to react with relatively inert molecules, such as hydrogen, methane, and carbon monoxide,[3] prompted the present investigation using the decay technique.

Spontaneous β decay of a tritium atom in multitriated benzene C_6X_6 (X = H or T) (0.7—1.0 mCi; 83 mCi $mmol^{-1}$) gives phenylium ion (**1**),[4] which is allowed to react at room temperature with acetylene in the presence of methanol [reaction (1)], (total pressure: 100 Torr). The yields of the recovered products are given in Table 1, together with experimental conditions. Anisole arises from the well established highly selective attack of (**1**) at the oxygen atom of MeOH.[5] Formation of the accompanying products requires addition of tritiated phenylium ion to the acetylene triple bond yielding presumably the primary $C_8H_7^+$ adduct (**2**) [reaction (2)], which eventually isomerizes to the α-phenylvinylium structure (**3**) before reacting with MeOH [reaction (3)].[6] Direct interaction of MeOH with the positively charged α-carbon atom of (**3**) leads to the oxygen-protonated enol ether (**4**) [reaction (3a)], which eventually gives acetophenone and its acetal.[7] Alternatively, loss of an acidic β-proton from (**3**) to a cluster of methanol molecules can account for the formation of tritiated phenylacetylene [reaction (3b)].

$$C_6X_6 \xrightarrow{\beta\ \text{decay}} [C_6X_5{}^3He]^+ \xrightarrow[-{}^3He]{\text{fast}} \underset{(\mathbf{1})}{C_6X_5^+} \xrightarrow[+\ MeOH]{+\ C_2H_2} \text{Products} \qquad (1)$$

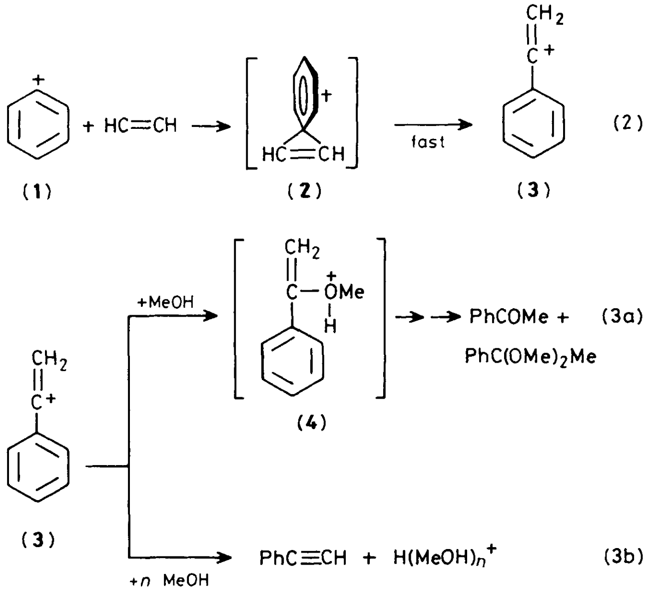
With regard to a quantitative estimate of the phenylium-ion reactivity towards acetylene, an apparent phenylium-ion reactivity ratio $[k(C_2H_2)/k(MeOH)]_{app.}$ of 0.36 can be deduced from the data of Table 1, which is consistent with the collisional rate ratio $[k(C_2H_2)/k(MeOH)]_{theor.}$ of 0.29, calculated from current ion–neutral interaction theories.[8]

It follows that addition of phenylium ion (**1**) to gaseous acetylene is at least as fast as its addition to methanol, whose

Table 1. Tritiated products from phenylium ion attack on acetylene.

System composition,[a] *P*/Torr		Relative yields of products,[b] (%)			
C_2H_2	MeOH	PhOMe	PhCOMe	PhC≡CH	$PhC(OMe)_2Me$
70	25	50	41	6	3
30	68	86	9	3	2

[a] 5 Torr of O_2 present in all systems. [b] Absolute yields range between 60 and 90%. They represent the ratio of the activity of the tritiated products to the maximum activity that can be incorporated theoretically in the products, range 60—90%.



efficiency is estimated to approach unity.[5] Such a conclusion contrasts with previous i.c.r. evidence of the complete non-reactivity of the $C_6H_5^+$ ion, having the phenylium structure, towards acetylene.[2] One rationalization of this discrepancy is based on the different experimental conditions (10^{-6} *vs.* 100 Torr) under which the reaction was investigated. At the high pressures involved in the decay and radiolytic experiments, survival of the addition product (**3**), from the phenylium-ion attack on C_2H_2, is allowed by collisional quenching, which rapidly removes the excess of energy from the highly exothermic reaction (2) ($-\Delta H^\circ$ 226—360 kJ mol^{-1}). At the much lower pressures (10^{-5}—10^{-6} Torr) prevailing in i.c.r. experiments, apart from radiative emission, unimolecular fragmentation represents the only channel for dissipating the excess energy of an excited adduct. Given the structure of the adduct from reaction (2), it is most likely that its energy-dissipation mechanism involves back-dissociation into the reactants, which amounts to an apparent inefficiency of the process.

These experiments provide an additional demonstration of the decisive role of environmental factors in determining the efficiency of gas-phase ion–molecule reactions and spells a word of caution against generalization of low-pressure mass spectrometric data as representative of ionic processes normally occurring at atmospheric pressures, such as those involved in flames.[2]

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