Gas-phase Reaction of Benzoyl Cation with Arenes. High Selectivity of a Gaseous, Charged Electrophile

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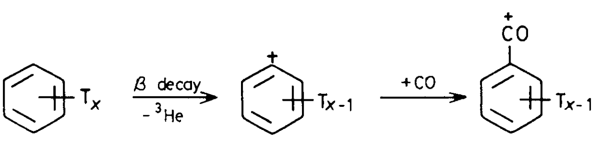
Gaseous benzoyl cations have been obtained from the reaction of CO with Ph^+ ions formed by the β-decay of multitritiated benzene; the benzoyl ions display high selectivity in their gas-phase reaction with ambident aromatic substrates, *e.g.* phenol and aniline, with a marked bias in favour of the n-type nucleophilic centres and do not react appreciably with the π-system, even if it is strongly activated as in the case of pentamethylbenzene.

A comprehensive investigation of the gas-phase acetylation of selected aromatic substrates was recently carried out using free, unsolvated $MeCO^+$ ions, generated in the dilute gas state by radiolytic[1] and nuclear decay[2] methods. In particular, the *intrinsic* reactivity, selectivity, and steric requirements of the ionic acylating electrophile were evaluated under conditions excluding interference from complicating factors (solvation, ion-pairing, catalysis, *etc.*) which affect conventional acylation reactions in condensed media.

Recently, we reported on the synthesis of gaseous benzoyl cations from the reaction of carbon monoxide with phenylium ions, formed by β-decay in multitritiated benzene [reaction (1)].[3] Gaseous benzoyl cations, while entirely unreactive toward pure π-type nucleophiles, *e.g.* benzene, displayed a considerable affinity for a simple n-type base, *i.e.* ethanol.

The study has now been extended to the reactivity of the gaseous benzoyl cation with other aromatic substrates such as pentamethylbenzene, phenol, and aniline. The choice of these representative aromatics was suggested by the fact that pentamethylbenzene is a strongly activated, pure π-type substrate, considerably more reactive than benzene towards acylating agents in solution.[4] Phenol and aniline offer the possibility of evaluating in the dilute gas state the intrinsic intramolecular selectivity of the benzoyl cation in its attack on the nucleophilic centres of an ambident substrate, *i.e.* the heteroatom and the aromatic ring.

Multitritiated benzene (1.0—1.4 mCi) (100 mCi $mmol^{-1}$)[5] was allowed to decay at 100 °C in a large excess of CO (630 Torr), in the presence of trace amounts (4—5 Torr) of the aromatic substrate. The analysis of the labelled products was carried out by radio-g.l.c. and radio-h.p.l.c., the identity of the products being established by comparison of the retention volumes of their elution peaks from various g.l.c. and h.p.l.c. columns with those of authentic reference compounds.



(1)

The yields of the acylated products are given in Table 1, together with the experimental conditions adopted. The results can be itemized as follows: (i) pentamethylbenzene appears quite unreactive toward gaseous benzoyl cations, in spite of the considerable activation of the aromatic ring by five methyl groups. (ii) The n-centres of phenol and aniline do react efficiently with gaseous benzoyl ions, giving high yields of the corresponding n-benzoylated derivatives, *i.e.* phenyl benzoate (59.4%) and benzanilide (41.4%).

The gaseous benzoyl cation is characterized by the present

Table 1. Gas-phase reactions of decay-formed tritiated benzoyl cations with activated arenes.

System composition	Products (absolute yield, %)[a]
$C_6H_xT_{x-6}$ (1.17 mCi) CO (630 Torr) C_6Me_5H (5 Torr)	C_6Me_5COPh (< 0.5)
$C_6H_xT_{x-6}$ (1.03 mCi) CO (630 Torr) PhOH (5 Torr)	PhOCOPh (59.4) HOC_6H_4COPh (<0.5) [b] (8.5)
$C_6H_xT_{x-6}$ (1.40 mCi) CO (630 Torr) $PhNH_2$ (4 Torr)	PhNHCOPh (41.4) $H_2NC_6H_4COPh$ (< 0.5) [b] (12.4)

[a] Absolute yields, *i.e.*, the ratio of the activity of the tritiated product to the maximum activity theoretically incorporable in the products. The remaining activity is mostly accounted for by low-boiling fragmentation products. Standard deviation of data, *ca.* 10%. [b] Ring and heteroatom phenylation products.

results as a very mild electrophile, as demonstrated by its inertness toward pentamethylbenzene. It is worth noting that the acetylium ion, regarded as a mild gaseous electrophile, reacts efficiently with polymethylbenzenes, such as mesitylene and prehnitene, *less activated* than pentamethylbenzene.[1a]

The lack of reactivity of the gaseous benzoyl cation towards π-type nucleophilic centres, even when activated by powerful electron-releasing substituents, is confirmed by the observation that phenol and aniline undergo benzoylation exclusively at the heteroatom. The unusual degree of positional and substrate selectivity of the benzoyl cation, unusual among gaseous charged electrophiles, emerges clearly from a comparison with other cations that are regarded as 'mild' reagents, such as $MeCO^+$ [1b,c] and t-Bu^+,[6] whose discrimination is substantially lower.[7]

The sharp selectivity of the free benzoyl cation for n-type nucleophilic centres demonstrated in the gas phase can be contrasted with the highly diversified behaviour of conventional benzoylating reagents in solution. As an example, the isomeric composition of the products from the Friedel–Crafts benzoylation of phenol is subject to large variations; the ratio of *O*-acylated to ring acylated derivatives depends on the solvent, the catalyst, the reaction conditions, *etc.*[8] By virtue of the absence of such environmental factors, the gas-phase results from this study allow a more direct and unequivocal estimate of the intrinsic reactivity and selectivity of the free benzoyl cation, now recognized as one of the mildest charged electrophiles in the dilute gas state.

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