Gas-phase Acylation Reactions. Formation of Free Benzoyl Cations in the Gas Phase

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Free benzoyl cations, obtained in the gas-phase by the nuclear β-decay of [1,4-T_2]benzene in the presence of carbon monoxide, display a high substrate discrimination between an n-base (ethanol) and a π-base (benzene).

Benzoylation, under Friedel–Crafts conditions, has long received a great deal of attention from organic chemists owing to its importance as a synthetic route to aromatic ketones. Mechanistic studies have shown that the benzoyl cation is only one of the conceivable aroylating reactants active in these systems. Their reactivity is found to be strictly dependent upon the structure of their neutral precursors, the nature of the catalyst used, and the properties of the solvent.[1]

In this communication, a new procedure is proposed for generating known amounts of free, unsolvated aroyl cations in the dilute gas state, where those environmental factors (solvation, ion-pairing, catalysis, etc.) normally affecting the nature and the reactivity of the acylating reactant in solution, are completely eliminated.[1,2]

The nuclear-decay approach has been followed for generating a free benzoyl cation in the gas-phase.[3] The method, whose principles and features have been recently reviewed,[4] has been successfully applied to producing free acetyl cations from the decay of multitritiated methane in the presence of carbon monoxide.[5]
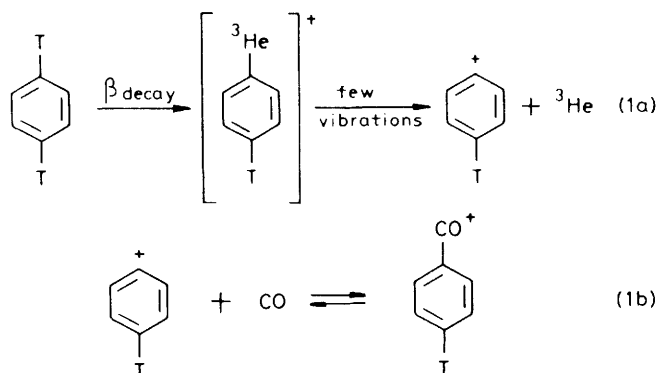
In the same way, [1,4-T_2]benzene was allowed to decay in the presence of a large excess of carbon monoxide, equation (1), and trace amounts of a nucleophilic substrate, such as benzene or ethanol. The relevant results are shown in Table 1 together with the experimental conditions used.

Table 1. Gas-phase reactions of decay-formed PhCO⁺ ions with EtOH and benzene.

System Composition	Products (Activity, %)[a]	
$C_6H_4T_2$ (1.73 mCi)	Phenyl ethyl ether	(4.9)
CO (760 Torr)	Ethyl benzoate	(95.1)
EtOH (7 Torr)		
$C_6H_4T_2$ (2.47 mCi)	(Benzophenone)[b]	
CO (760 Torr)	Biphenyl	(96.9)
C_6H_6 (10 Torr)	Benzoic acid	(3.1)

[a] Standard deviation of data ca. 10%. The total activity recovered in the products accounts for 35% of the theoretical yield in the case of EtOH and for 16% in the case of benzene. [b] Not detectable (<0.5%).

The absolute yields of the products (16—35%), reported in Table 1 are obtained by comparing their total 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% $C_6H_4T_2$ and 46% C_6H_5T),[6] the decay rate of the tritium, the abundance (72%) of the $C_6H_5^+$ structure retained after the nuclear transition,[7] and the absolute counting efficiency of the detector employed. Isolation of labelled ethyl benzoate in the presence of ethanol demonstrates the actual formation of the tritiated benzoyl cation via equation (1) and its subsequent reaction with ethanol, equation (2).

The formation of a benzoyl cation from phenylium ion attack on CO is further substantiated by the recovery of small yields of benzoic acid in the decay systems which contain benzene contaminated with traces of water.

However, the absence of benzophenone among the tritiated products would imply limited reactivity of the benzoyl cation toward pure π-type substrates, such as benzene.

The substrate discrimination of PhCO⁺ agrees well with the known,[5] considerable affinity of the acetyl cation for n-type substrates and with its unreactivity toward pure π-bases, such as benzene.

Gas-phase addition of a benzoyl cation to the selected substrates is a thermochemically allowed process ($-\Delta H° = 12$—15 kcal mol⁻¹).† Thus, the lack of reactivity of PhCO⁺ toward benzene would imply that the reaction has an appreciable activation energy. Furthermore, the ethyl benzoate vs. phenetole yield ratio (ca. 19.3:1) is much lower than the relative concentration of the CO vs. EtOH (ca. 109:1) in the corresponding gaseous mixtures, thus suggest-

† 1 kcal = 4.18 kJ.

(1)
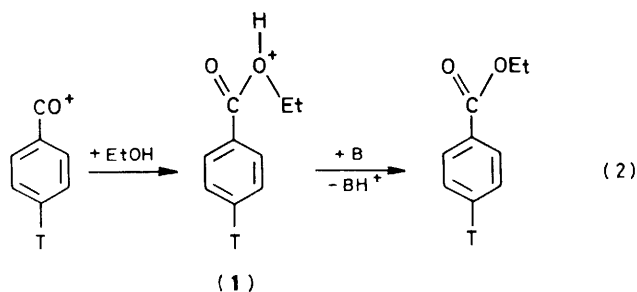
ing that the phenylium ion addition to a CO molecule may be reversible, equation (1b). This view is further supported by the predominance of biphenyl among the labelled products from the decay systems with benzene as the substrate.

The decrease in the molar radioactivity of the tritiated ethyl benzoate, when the residual tritium atom in the ring is replaced by inactive nitro-groups (HNO_3–H_2SO_4, 20 °C), shows that over 96% of the undecayed tritium atom maintains its original para position. This would imply that reaction of Ph⁺ with CO to form PhCO⁺ and its condensation with EtOH are occurring at rates higher than that of any conceivable intramolecular tritium migration within the corresponding ionic intermediates ($k = 10^7$ s⁻¹).[7b]

In conclusion, the present preliminary results show that the spontaneous decay of tritiated benzene in the presence of gaseous CO is a convenient route to the formation of thermal unsolvated benzoyl cations in the gas phase.

References

1 For a review see P. H. Gore, in 'Friedel-Crafts and Related Reactions,' Vol. III, ed. G. A. Olah, Interscience, N.Y., 1964.

2 G. A. Olah, J. Lukas, and E. Lucas, *J. Am. Chem. Soc.*, 1969, **91**, 5379.

3 F. Cacace, Proceedings of the Conference on the Methods of Preparing and Storing Marked Molecules, Euratom, Bruxelles, 1964.

4 For reviews see: (a) F. Cacace, in 'Interactions between Ions and Molecules,' ed. P. Ausloos, Plenum, N.Y., 1975; (b) F. Cacace, in 'Kinetics of Ion-Molecule Reactions,' ed. P. Ausloos, Plenum, N.Y., 1979.

5 P. Giacomello and M. Speranza, *J. Am. Chem. Soc.*, 1977, **99**, 7918.

6 G. Angelini, M. Speranza, A. L. Segre, and L. J. Altman, *J. Org. Chem.*, 1980, **45**, 3291.

7 (a) T. A. Carlson, *J. Chem. Phys.*, 1980, **32**, 1234; (b) G. Angelini, S. Fornarini, and M. Speranza, *J. Am. Chem. Soc.*, in the press.