

SOLVOLYSIS OF TRITYL DERIVATIVES: ETHANOLYSIS OF TRI-p-TOLYL METHYL

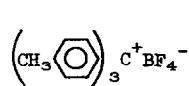
TETRAFLUOROBORATE AND BENZOATE

Stanley G. Smith

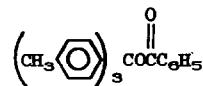
Department of Chemistry, University of Illinois, Urbana, Illinois 61801

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Studies of the properties of carbonium ion intermediates under conditions commonly employed in solvolysis reactions of typical alkyl halides and various esters are important to the elucidation of the mechanism of this class of reactions. Some trityl derivatives yield carbonium ions with reactivity levels such that their solvolyses can be conveniently measured.¹ In this communication the behavior of tri-p-tolylmethyl tetrafluoroborate (I) is compared with the reaction of the corresponding benzoate derivative (II) in methylene chloride/ethanol solvent.



I



II

The fluoroborate salt (I) in methylene chloride solution was rapidly mixed² with an equal portion of a 4:1 mixture of methylene chloride and ethanol at 25°. As summarized in Table I, the rate of disappearance of the carbonium ion, measured at 452 m μ ,³ increases as the concentration of salt increases. Apparently ion aggregation affects the rate of solvolysis. Extrapolation to zero concentration gives a rate constant of ca. 350 sec⁻¹. Addition of up to 0.1 M of the common anion salt tetra-n-butylammonium fluoroborate does not depress the observed rate (Table I).

In contrast to the fluoroborate, the covalent benzoate ester (II) solvolyzed relatively slowly under the same conditions,⁴ with the observed first-order rate constant being (2.5 ± 0.1) × 10⁻³ sec⁻¹. Addition of (CH₃)₄NOBz·HOBz results in common ion rate depression⁵ with a k_t^0/k_t^d of about 60.

The solvolysis of the carbonium fluoroborate salt in the presence of the benzoate salt $(\text{CH}_3)_4\text{NOBz}\cdot\text{HOBz}$ is of particular interest,⁸ since a solution of carbonium ion (5×10^{-3} M) in methylene chloride was found to react with 6×10^{-3} M benzoate salt in methylene chloride/ethanol

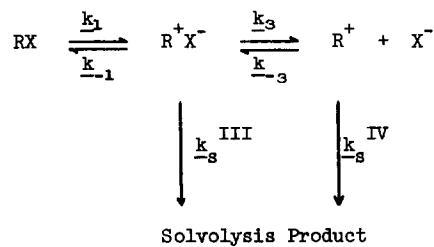
Table I. Summary of Rate Constants for the Solvolysis of Tri-*p*-tolylmethyl Fluoroborate in Methylene Chloride/Ethanol^a Solvent at 25.0°

$(\text{CH}_3\text{C}_6\text{H}_4)_3\text{CBF}_4$, 10^3 M	$(\text{n-Bu})_4\text{BF}_4$, 10^2 M	k^b_{obs} , sec ⁻¹
0.11	--	370
0.50	--	450
1.0	--	440
1.4	--	490
2.5	--	530
7.5	--	550
10.0	--	560
1.4	0.56	480
1.4	1.1	480
1.4	2.8	480
1.4	5.6	500
1.4	7.5	590
1.4	10.0	480

^a The solvent was prepared by mixing equal portions of methylene chloride with a 4:1 (Vol-Vol) mixture of methylene chloride and ethanol. Experimental reproducibility of a given determination is ca. $\pm 5\%$.

at a rate which is too fast to be observed under the conditions employed to study the solvolysis of the carbonium ion in the absence of added salt. In preparative experiments, the benzoate ester II was the only product detected from the reaction of the carbonium ion with benzoate salt. Apparently, anion exchange and collapse to covalent benzoate proceeds with a rate constant greatly in excess of the measured rate constant of 350 sec⁻¹ for the ethanolysis of the carbonium ion in these methylene chloride solutions. That is, in the reaction scheme in

equation 1, $\frac{k_1}{k_{-1}}$ is large compared to $\frac{k_1}{k_s}$ III, and $\frac{k_1}{k_s}$ IV.



The similar dominance of ion pair return over solvolysis in the reaction of propene with p-bromobenzenesulfonic acid has been noted recently by Shiner and Dowd.⁸

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