Triethyloxonium Tetrafluoroborate as an Ethylating Agent in Aqueous Solution

Sir:

Alkyloxonium salts have been used extensively as alkylating agents in inorganic chemistry.[1] With few exceptions, the alkylations have been conducted in organic solvents that do not effect the solvolysis of the alkyloxonium ion, most commonly dichloromethane.[2] This restriction often leads to the use of a solvent inappropriate to the particular reaction.[3] Here we report on the general use of triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$) as an ethylating agent in *aqueous solution.*

The generality of the procedure is exemplified by two paradigms important in inorganic chemistry: (i) the alkylation of a coordinated metal ion and (ii) the alkylation of a coordinated ligand. In addition, the simple aqueous esterification of a carboxylic acid is reported.

Ethyl cobalamin, ((ethyl 2-aminoethyl thioether)-*N*,*S*)bis(ethylenediamine)cobalt(III) perchlorate, and ethyl benzoate were synthesized in essentially quantitative yield from their unethylated parent compounds and triethyloxonium ion in aqueous solution.

Ethyl cobalamin was synthesized, following the reduction of cyanocobalamin (6.1 mM) with sodium borohydride (66.1 mM) to vitamin B_{12s}, by the addition of $Et_3O^+BF_4^-$ (27.63 mM) to the oxygen-free reaction solution. After 78 min at 25 °C, the product was identified as ethyl cobalamin by ultraviolet and ^1H NMR spectroscopy.[4,5]

((Ethyl 2-aminoethyl thioether)-*N*,*S*)bis(ethylenediamine)cobalt(III) perchlorate was synthesized from (2-aminoethanethiolato-*N*,*S*)bis(ethylenediamine)cobalt(III) perchlorate[6] (3.0 mM) and $Et_3O^+BF_4^-$ (74.25 mM) by mixing these reagents in water at 4 °C and immediately placing the reaction at −15 °C. The ethylation is essentially complete in 3 h, and after 16 h the product was identified as ((ethyl 2-aminoethyl thioether)-*N*,*S*)bis(ethylenediamine)cobalt(III) perchlorate by visible, ultraviolet, and ^1H NMR spectroscopy.[7]

Ethyl benzoate was synthesized by the reaction of the benzoate ion (57.3 mM) with $Et_3O^+BF_4^-$ (1.58 M) in saturated $NaHCO_3$ at 25 °C; the pH was maintained in the range 6.4–8.4 by the addition of 5 N NaOH. After 82 min, the product was dissolved by the addition of ethanol and identified as ethyl benzoate by ultraviolet spectroscopy[8] and by its complete alkaline hydrolysis.

The hydrolysis of $Et_3O^+BF_4^-$ is virtually pH-independent from pH 4 to pH 9, where the half-life is 7.4 min at 25 °C and 1.95 min at 38 °C. Further, the reaction of $Et_3O^+BF_4^-$ with Cl^-, Br^-, and I^- confirms that the reaction is at least largely an S_N1 ionization of Et_3O^+:

$$Et_3O^+ \rightarrow Et^+ + Et\text{–}O\text{–}Et \xrightarrow{\text{nucleophile}} \text{ethylated nucleophile}$$

A comparable reaction is that of the *N*,*N*-dimethyl-2-phenylaziridinium ion with nucleophiles.[9]

Because Et_3O^+ is so reactive toward nucleophiles, its side reaction with the aqueous solvent can be accommodated by a suitable choice of concentration. The syntheses presented here establish the triethyloxonium ion as an ethylating agent of great utility in inorganic chemistry carried out in aqueous solution and will serve as a basis for our studies of its reactivity toward metal ions and their ligands, particularly those commonly found in proteins.

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Transition-Metal Hydride Bond Energies: First and Second Row

Sir:

While thermochemistry for transition-metal systems is needed to understand and predict the reactivity and kinetics of metal systems, enumeration of this thermochemistry is a herculean task. Of equal value would be "typical" metal–ligand bond dissociation energies (BDEs) and a means of predicting how these BDEs vary with metal and metal environment. In this paper, we report new values for diatomic transition metal–hydride ion BDEs and analyze the periodic trends to identify such a typical BDE.

The thermochemistry reported here is measured by examining reaction 1 as a function of translational energy. The threshold

$$M^+ + H_2 \rightarrow MH^+ + H \qquad (1)$$

energy for these endothermic processes is determined and related to the metal hydride bond energy, $D(M^+\text{–}H)$. Detailed descriptions of our experimental apparatus[1] and methods of interpretation[2,3] have been published. The metal–hydride BDEs measured here, listed in Table I, typically fall below previously measured values.[4] Part of the difference results from correcting our values for excited electronic states in the reactant metal ion beam.[2,3] For several first-row metals (Cr, Mn, Fe, Co, Ni, and Cu), this is done explicitly by measuring the relative reactivity of these states. Details of these results will be published in subsequent papers.[5]

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