The Chemistry of Oxouranium(v)-A Novel Free Radical Forming Reaction

By J. SELBIN,* D. G. DURRETT, H. J. SHERRILL, G. R. NEWKOME, and J. H. WHARTON
(*Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana* 70803)

Summary During a study of the formation and properties of the monoxouranium(v) complexes, a novel reaction leading to the unexpected formation of stable crystalline salts of cationic free radicals of certain heterocyclic nitrogen compounds was discovered.

THE preparation of R_2UOX_5 compounds from RUX_6 (R = organic cation, X = F, Cl, or Br) was reported by Ryan[1] in 1971. We have verified preparative procedures used by him and also found[2] a convenient alternative method to produce the oxohalogeno species starting from UCl_5.TCAC (TCAC = trichloroacryloychloride). We prepared the first adducts of $UOCl_5^{2-}$ with such nitrogen bases as phthalazine, *o*-phenanthroline, and αα′-bipyridyl, but when we carried out the reaction of $UOCl_5^{2-}$ with phenazine, an entirely unexpected reaction occurred and the appearance of the product was very different.

Phenazine was dissolved to approximate saturation in spectroquality nitromethane and filtered. When solid blue $(Et_4N)_2UOCl_5$ was then added to the solution in approximate 1:1 mol ratio, a bright green solution resulted. After a few minutes, the solution turned dark and then slowly began to deposit very dark green (nearly black) well-formed crystals.† Subsequent studies proved this product to be the chloride salt of the dihydrophenazine semiquinone cation free radical (I). By evaporation of the reaction solution, the uranium was isolated as the very stable, well-known uranyl complex, $(Et_4N)_2UO_2Cl_4$.†

Evidence that we have indeed obtained the stable cation free radical comes from its e.s.r. spectrum, which was obtained for the polycrystalline powder ($\langle g \rangle = 2{\cdot}006$, Signal width = 1 G) and for the compound dissolved in either dry, degassed methanol or dimethyl sulphoxide. The solution signals, consisting of 7 main groups of lines each further split under high resolution into 11 to 13 lines, have been observed several times[3-8] for this radical cation in various solutions. Although the phenazine radical cation has apparently been produced many times in solution, by re-

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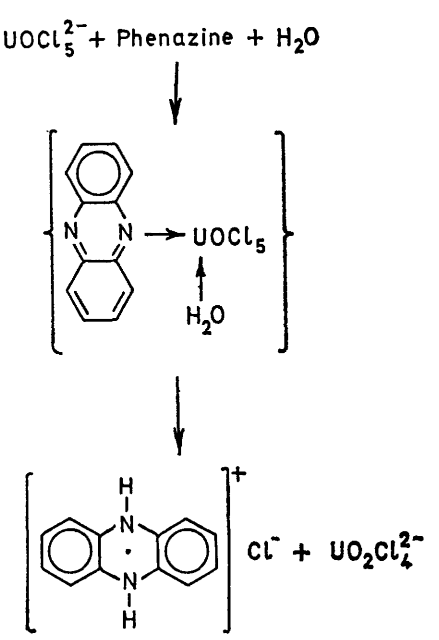
† All compounds reported gave satisfactory analyses.

ducing phenazine chemically,[6–9] photochemically,[10–11] and electrochemically[8,12] and by electrolytic oxidation of dihydrophenazine,[3] we believe this is the first example of the solid chloride salt having been isolated in stable pure crystalline form and characterized.

Other properties of compound (I) which confirm its structure, will be discussed elsewhere in a full article. They include its solubilities, mass spec., m.p., d.t.a., t.g.a., magnetic susceptibility, i.r. spectrum, and 25,000—3,000 Å electronic spectrum both at room temperature and at 77 K.

Alteration of: (a) the solvent from $MeNO_2$ to $PhNO_2$, as well as (b) the cation attached to the $UOCl_5^{2-}$ from Et_4N^+ to Ph_4As^+, did not retard the reaction. However, the reaction did not proceed under meticulously anhydrous conditions, (*e.g.*, dry box), but after the reactant mixture was subjected to atmospheric moisture, the reaction again proceeded normally indicating that H_2O is necessary for the reaction between $UOCl_5^{2-}$ and phenazine. We suggest the simple mechanism shown in reaction (1).



(I)

(1)

A large number of other phenazine and phenazine-like compounds are now being studied, using both UOX_5^{2-} and $MoOX_5^{2-}$ species as electron donors.

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