Cerium(IV) Ammonium Nitrate-promoted Aromatic Substitution with Peroxydicarbonates

By MICHAEL E. KURZ,* EDWARD S. STEELE, and ROBERT L. VECCHIO
(*Chemistry Department, Illinois State University, Normal, Illinois* 61761)

Summary The reaction of a mole of dialkyl peroxydicarbonates with an excess of toluene in the presence of a two-fold molar excess of cerium(IV) ammonium nitrate produces two moles of tolyl alkyl carbonates.

THE decomposition of peroxydicarbonates and diacyl peroxides in the presence of toluene can be modified by the inclusion of suitable redox agents (*e.g.*, $CuCl_2$,[1] $FeCl_3$,[2] I_2,[3] or O_2[4]) which oxidize oxy-radical–aromatic adducts to form aryl esters. The resulting lower valence inorganic species then reduce the peroxide leading to a chain process.[1–3]

We report on an analogous system in which tolyl alkyl carbonates were produced by treating peroxydicarbonates, toluene, and cerium(IV) ammonium nitrate (CAN) at 60° for 24 h in acetonitrile. By this method the yields of tolyl isopropyl carbonates and tolyl s-butyl carbonates were 161 and 181%, respectively, based on the corresponding dialkyl peroxydicarbonate. Unlike the previously reported copper halide system, where the copper(I) ion reduced the peroxide limiting the aryl ester yield to one mol per mol of peroxide, the CAN involvement was stoicheiometric as both halves of the peroxide were made to substitute onto the aromatic. Utilization of less than 2 mol of CAN per mol of peroxide led to diminished yields. Quantitative analysis of the inorganic products was consistent with the following overall stoicheiometry:

$$2\,\mathrm{PhMe} + (\mathrm{ROCO_2})_2 + 2\,\mathrm{Ce(NH_4)_2(NO_3)_6} \xrightarrow[60^\circ]{\mathrm{MeCN}}$$

$$2\,\mathrm{ROCO_2C_6H_4Me} + 4\,\mathrm{NH_4NO_3} + 2\,\mathrm{Ce(NO_3)_3} + 2\,\mathrm{HNO_3}$$

No peroxide–cerium(III) ion interaction seemed to occur; indeed kinetic studies indicated that the peroxide decomposition rate was actually retarded relative to that in the absence of metal salts and all of the cerium was recovered as cerium(III) nitrate. Isomer distributions ($o/m/p \approx$ 58/11/31) and relative rates ($k_{\text{toluene}}/k_{\text{benzene}} = 6{\cdot}35$) for the aromatic products revealed that the substituting entity had more selectivity than a non-complexed alkyl carbonate radical. No polymer production was noted in reactions performed with acrylonitrile in the system suggesting low concentrations of free oxy-radicals. These observations were all consistent with the formation of some sort of peroxide–hexanitratocerate(IV) complex which dissociates to a metal-complexed oxy-radical. Attack by this species (which would possess greater selectivity) onto the aromatic is followed by efficient oxidation by the cerium(IV) species to the aryl ester. An alternative mechanistic possibility would be an immediate electron transfer from oxy-radicals to cerium(IV) ion followed by normal electrophilic substitution of toluene by the oxy-cations resulting. Although such electron transfer oxidations are well known for alkyl radicals with iron(III)[5] or copper(II) ions,[6] the analogous process with oxy-radicals is unprecedented and would be expected to be energetically unfavourable.[6] The importance of the hexanitratocerate(IV) complex as an oxidant in the overall substitution process was established by studying a variety of other cerium(IV) and cerium(III) salts in this reaction. Whereas cerium(IV) potassium nitrate was about as efficient as CAN, cerium(IV) hydroxide and nitrate were totally ineffective in bringing about aromatic substitution by the peroxide. CAN has been reported to oxidize aryl alcohols[7] and to promote azide addition to alkenes[8] but its involvement here appears to be substantially different.

Under the usual reaction conditions only small amounts ($< 5\%$) of aromatic side products (benzyl alcohol, benzaldehyde, nitrotoluenes) were found. The direct high yield production of aryl esters which can be readily separated and hydrolysed suggests possible synthetic utility for this method in making phenolic compounds.

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