Photochemical Generation of CO_3^- Radicals in Neutral Aqueous Solution

By Virgil W. Cope and Morton Z. Hoffman*
(*Department of Chemistry, Boston University, Boston, Massachusetts* 02215)

Summary Flash photolysis of $Co(NH_3)_4CO_3^+$ in neutral aqueous solution generates the CO_3^- radical.

The CO_3^- radical can be generated pulse-radiolytically[1] by attack of OH radicals on CO_3^{2-}. However, the solution must be strongly alkaline in order to maintain the carbonate in the CO_3^{2-} form; HCO_3^- reacts very much more slowly with OH than does CO_3^{2-}. This factor does not permit CO_3^- to be generated conveniently in neutral solution, ruling out any study of the reactivity of the radical with substrates, such as enzymes, at biologically meaningful pH values. The CO_3^- radical would be expected to act as an oxidizing agent reacting *via* electron or H atom transfer and as such could have implications for the mechanism of enzymatic inactivation in radiation-damaged biological systems.[2] The CO_3^- radical can also be generated photochemically in the flash photolysis[3] of HCO_3^- and CO_3^{2-}. However, these ions absorb only at very short wavelengths (*ca.* 200 nm) which severely restricts their utility as a source of CO_3^-.

The 254 nm continuous photolysis of $Co(NH_3)_4CO_3^+$ (as the ClO_4^- salt) in neutral solution (phosphate buffer) produces Co^{2+} (ϕ 0·064), NH_3, and $Co(NH_3)_4(OH_2)_2^{3+}$ (ϕ < 0·1). The flash photolysis of the complex (5—9 × 10^{-5} M; pH 6·44) yields two transients, one of which shows a tail absorption at $\lambda < 350$ nm, decays slowly *via* first-order kinetics, and is identified as $Co(NH_3)_4(OH_2)CO_3^+$. The other transient species shows λ_{max} 600 nm and decays *via* second-order kinetics and is identified as CO_3^-. Taking $\epsilon_{600} = 1830$ M^{-1} cm^{-1},[1] a value of $2k = 1{\cdot}1 \times 10^8$ M^{-1} s^{-1} is obtained; the dependence of $2k$ on ionic strength is in the same sense as has been described before.[1] The CO_3^- radical clearly arises from intramolecular electron transfer resulting from irradiation of the ligand-to-metal charge-transfer band of the complex and its quantum yield of formation can be identified with that of Co^{2+}.

The presence of O_2 in the system has no effect on either the intensity or the rate of decay of the absorption. The introduction of oxidizable non-absorbing scavengers into the system converts the normal second-order decay of the radical into pseudo first-order with the observed rate constant varying linearly with the concentration of the scavenger. The Table shows $k(CO_3^- + S)$ for a number of scavengers. In comparison, the values of k for $(-SCH_2{\cdot}CH_2{\cdot}CO_2H)_2$ and cysteine as scavengers are greater than 10^7 M^{-1} s^{-1} indicating the increased reactivity of the radical for molecules containing the disulphide linkage, presumably owing to a change in the site and mechanism of attack.

TABLE

Scavenger	$k(CO_3^- + S)$, M^{-1} s^{-1} [a]
MeOH	$2{\cdot}6 \times 10^3$
Pr^{i}OH	$4{\cdot}0 \times 10^4$
Bu^{t}OH	$1{\cdot}6 \times 10^2$
Formate	$6{\cdot}6 \times 10^4$

[a] At pH 6·44

The advantages of $Co(NH_3)_4CO_3^+$ as a photochemical source of CO_3^- radicals in neutral solution are as follows: (i) the complex is easy to synthesize,[4] (ii) it absorbs strongly ($\epsilon > 10^3$ M^{-1} cm^{-1}) at $\lambda < 280$ nm and weakly ($\epsilon < 10^2$ M^{-1} cm^{-1}) at higher λ, and (iii) the generation of Co^{2+} serves as an internal actinometer. However, the following drawbacks must also be noted: (i) the complex undergoes acid-catalysed thermal decarboxylation[5] to give $Co(NH_3)_4(OH_2)_2^{3+}$ with pH 4 being the practical lower pH limit for this work; base hydrolysis in alkaline solution is very slow,[5] (ii) flash photolysis also generates the aquo-carbonato-intermediate, (iii) $\phi(CO_3^-)$ has only a moderate value. In balance, however, the generation of CO_3^- in neutral solution by this technique has obvious advantages over existing methods and provides a means of studying the reactivity of the radical with a wide range of scavengers.

We thank the National Science Foundation for financial support.

(*Received*, 8*th November* 1971; *Com.* 1931.)

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