Acid–Base Properties of the CO_3^- Radical in Aqueous Solution

By Schoen-nan Chen and Morton Z. Hoffman*

(*Department of Chemistry, Boston University, Boston Massachusetts* 02215)

Summary The p*K* for the reaction $CO_3H \rightleftharpoons CO_3^- + H^+$ is 9·5 ± 0·3.

The possibility that the CO_3^- radical can exhibit acid–base properties in aqueous solution was recently[1] ruled out on the following grounds: (*a*) the recombination rate constant of the CO_3^- radical is pH independent[2] and (*b*) the spectrum of the radical is invariant between pH 8 and 13.[1] It must be pointed out, however, that the recombination rate data of Weeks and Rabani,[2] obtained by pulse radiolysis from the reaction of $OH + CO_3^{2-}$, only cover a range from pH 10·5—13·5 in which there is a linear relationship between log (radical recombination rate constant) and a function of (ionic strength)$^{\frac{1}{2}}$. It is this linear relationship that leads to the knowledge of the charge of the CO_3^- radical; a point at pH 8·4 lies conspicuously below the line. Furthermore, it must be noted that it is not a requirement that the acid–base forms of a radical have different spectra. While in many cases this is true, the CO_2H/CO_2^- [3] and $C_2O_4H/C_2O_4^-$ [4] pairs provide examples of the near identity of the spectra.

Table

pH		7·0	7·7	8·0	8·5	9·0	9·7	10·0	10·5	11·0	11·5	12·0	13·0
$k\ (CO_3^- + IPA) \times 10^{-8}\ (M^{-1}\ s^{-1})^a$	..	4·2	4·2	4·6	4·8	5·5	5·6	5·6	6·0	6·5	6·7	6·6	6·9

[a] Rate constants known to ±10%.

We have generated the CO_3^- radical in neutral and alkaline solution by the flash photolysis of $Co(NH_3)_4CO_3^+$.[5] The recombination rate constant of the radical at pH 7 is only slightly dependent on ionic strength (varied using $NaClO_4$). Unfortunately, at pH > 10, the flash photolysis of the complex generates an additional species which rapidly scavenges the radical. In order to compete with this adventitious scavenging, we added to the system indole-3-propionic acid (IPA) which reacts rapidly with the radical and exists in neutral and alkaline solution as its −1 charged conjugate base. By monitoring the pseudo first-order decay of the radical at its absorption maximum of 600 nm, we were able to determine $k(CO_3^- + IPA)$ as a function of ionic strength and pH. At pH 7, k is only weakly dependent upon ionic strength; at pH 11–12, a plot of log k *vs* $\mu^{\frac{1}{2}}/(1 + 0{\cdot}8\,\mu^{\frac{1}{2}})$ is linear with a slope of unity showing that the radical is neutral at pH 7 and has a -1 charge in alkaline solution. The Table shows the dependence of $k(CO_3^- + IPA)$ on pH at a constant ionic strength of 0·1 M with $[Co(NH_3)_4CO_3^+] = 5{\cdot}0 \times 10^{-5}$ M and $[IPA] = 1{\cdot}1 \times 10^{-5}$M.

Although the change in the value of k over the pH range is less than a factor of two, it is well outside the experimental error. A plot of the data in the table provides the kinetic evidence that the pK of the reaction $CO_3H \rightleftharpoons CO_3^- + H^+$ is $9{\cdot}5 \pm 0{\cdot}3$.

That the pK_a of CO_3H (9·5) is lower than that of CO_3H^- (10·36) is not unexpected from a consideration of charge. A similar situation in thich the radical anion is more acidic than its more highly charged parent has been reported[6] for radicals derived from phosphate anions. The fact that the reaction rate of the CO_3^- radical with -1 charged IPA is somewhat greater than that of the neutral CO_3H radical at 0·1 M ionic strength does not necessarily imply that it is so at zero ionic strength. In fact, our data indicate that the rate at zero ionic strength remains more or less constant throughout the measured pH range with the increase in rate reported here arising primarily from the ionic strength effect.

We thank the National Science Foundation for financial support.

(*Received, 3rd July* 1972; *Com.* 1156.)

[1] D. Behar, G. Czapski, and I. Duchovny, *J. Phys. Chem.*, 1970, **74**, 2206.
[2] J. L. Weeks and J. Rabani, *J. Phys. Chem.*, 1966, **70**, 2100.
[3] P. Neta, M. Simic, and E. Hayon, *J. Phys. Chem.*, 1969, **73**, 4207.
[4] N. Getoff, F. Schwörer, V. M. Markovic, K. Sehested, and S. O. Nielsen, *J. Phys. Chem.*, 1971, **75**, 749.
[5] V. W. Cope and M. Z. Hoffman, *Chem. Comm.*, 1972, 227.
[6] E. D. Black and E. Hayon, *J. Phys. Chem.*, 1970, **74**, 3199.