

The Hydration of Carbon Dioxide-Catalysis by Transition Metal Hydroxo Complex Ions

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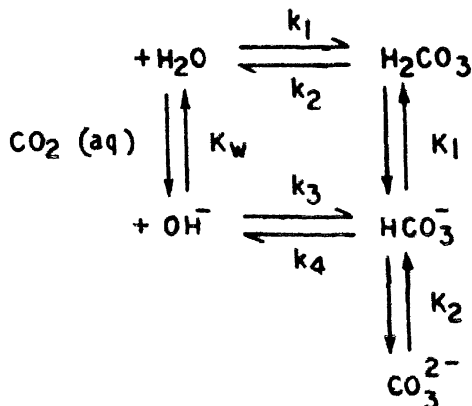
and

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The equilibration rate between dissolved carbon dioxide and ionic carbonate in aqueous systems is far from instantaneous in the absence of effective catalysts. In natural plant and animal systems, the catalysis is provided by the enzyme carbonic anhydrase. In this, the active site is known to be the $ZnN_3(OH)$ moiety, where the N's represent histidyl nitrogen ligands from units within the polypeptide chain of the enzyme. Some simple transition metal hydroxo complex ions also serve to convert CO_2 to ionic carbonate, though none so far reported shows activity anything like as great as that of the metalloenzyme. With cobalt(III) complexes, the product is always a rather stable carbonate complex. We have now completed studies of kinetics of such "carbon dioxide uptake" reactions for a series of complexes, comprising the types $Co(N_3)(OH)^{2+}$, $Co(N_4)(OH_1)(OH)^{2+}$ and $Co(N_4)(OH)_2^+$, where N_4 and N_3 represent amine ligand grouping of various kinds. The data obtained are discussed with respect to their mechanistic significance and some general conclusions are drawn concerning the nucleophilicity of hydroxo metal complexes toward carbon dioxide in aqueous systems.

THE equilibrium constants and rates of various reactions involved in aqueous carbonate solutions have long been of vital interest to chemists and biochemists. Several reviews of the chemistry of the non-catalyzed system have appeared^{1,2}. Much additional information has become available in recent years as a result of the growing interest in seawater carbonate chemistry^{3,4}. The major reactions of interest are as follows⁵:



In such a scheme, only the reaction rates identified by k_1 , k_2 , k_3 , and k_4 need be considered, since the other processes are acid/base proton transfers, the diffusion-controlled rates of which are instantaneous by comparison. The four specified rate constants have all been studied independently, and have the rate parameters quoted in Table 1².

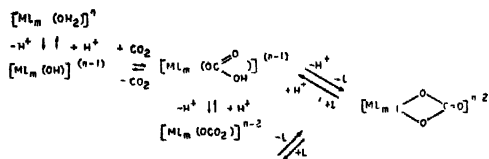
TABLE I—RATE PARAMETERS FOR AQUEOUS CO_2 REACTIONS

Reaction	(1)	(2)	(3)	(4)
k_a	0.035	20	8500 ^b	1.9×10^4
ΔH^\ddagger (Kcal/mole)	19	15	13.3	24.7
ΔS^\ddagger (cal/deg/mole)	-2	-3	3.8	6.9

^asec⁻¹ at 25°, low ionic strength
^bM⁻¹sec⁻¹

It is obvious from the above data that equilibrium will not become established among the various species in the aqueous carbonate system unless an appreciable time has elapsed or the slow reactions are catalyzed. Animals and plants are dependent for their lives on effective carbonate interconversions, and for them nature has provided the enzymatic catalyst carbonic anhydrase. The chemistry of this substance has been the subject of much study⁶. In recent years, the enzyme has become of considerable interest to co-ordination chemists, since the reactive site is now known to involve Zn^{2+} ion ligated to three nitrogens from the protein chain and to one water molecule. Interest has thus developed in the possibility of synthesizing a simplified aquo amine zinc(II) complex ion which would serve as a model of the enzyme action⁷. The basic hypothesis concerning this action relates to the fact that water co-ordinated to a metal ion becomes quite acidic, such that the pK of a typical aquo metal complex ion is close to 7, as compared to a value of about 16 for solvent water molecules. In near neutral solutions, it is thus possible to have an appreciable concentration of the M-OH moiety, so that the expected very slow $CO_2 + H_2O$ reaction effectively becomes, (in the presence of an appropriate metal complex ion) similar to the much more rapid $CO_2 + OH^-$ reaction, thereby greatly increasing the rate of CO_2 hydration.

While progress toward the synthesis of inorganic species which approach anywhere near the catalytic activity of carbonic anhydrase has not yet been substantial, a considerable number of aquometal complex ions have now been found to be quite reactive to CO_2 . Most of these systems convert the CO_2 to co-ordinated carbonate in the form of stable carbonato complex ions, a very well-known class of transition metal compounds⁹. The resulting monodentate carbonato species may under suitable conditions subsequently form chelates by elimination of an adjacent less firmly bound ligand on the metal ion. One may generalize the series of possible reactions under consideration by means of the scheme (M = metal ion, L_{op} = other ligands necessary to complete the normal co-ordination shell of M) :



It is seen that a system of this type effectively hydrates CO_2 , but not catalytically, since the carbonato products are quite stable species except in strongly acidic solution. However, the process parallels that of catalytic CO_2 hydration to the extent that it involves a nucleophilic attack by the hydroxometal complex ion on dissolved CO_2 . For this reason, we have considered it desirable to investigate the " CO_2 uptake" reaction of a considerable number of M^{III} complex ions with a view to identifying the nature of the factors which determine their reactivities. To this end, the first studies in our laboratories involved complex ions^{9,10} of the type $[M(\text{NH}_3)_6\text{OH}_2]^{3+}$. In these, the process stops with the formation of the monodentate carbonato complex of type $[M(\text{NH}_3)_5(\text{OCO}_2)]^+$, since chelation by elimination of NH_3 cannot occur. Also, it has been possible to examine the three species where $M = \text{Co}^{III}$, Rh^{III} , or Ir^{III} , thereby providing some evidence concerning the role of the central metal ion. A further study with the pentammine species has been aimed at determining the effects of modifying the stereochemistry of the amine ligand environment around the Co^{III} metal ion, utilizing the complex ion¹¹ $\alpha\beta\text{S-}[\text{Co}(\text{tren})(\text{OH}_2)]^{3+}$ ($\text{tren} \equiv$ tetraethylenepentammine). Another series of investigations has embraced various diaquotetramine cobalt (III) complexes, which not only take up CO_2 but can under certain circumstances undergo the subsequent chelation reaction to form the bidentate carbonato congener. The species so far involved in this part of the work^{1,2,13,14} are $\text{Co}(\text{tren})(\text{H}_2\text{O})_2^{2+}$ ($\text{tren} \equiv \beta, \beta', \beta''$ -tri-aminotriethylamine), *cis* and *trans* $\text{Co}(\text{cyclam})(\text{H}_2\text{O})_2^{2+}$ ($\text{cyclam} \equiv 1, 4, 8, 11$ -tetraazacyclotetradecane), and *cis* and *trans* $\text{Co}(\text{en})_2(\text{H}_2\text{O})_2^{2+}$ ($\text{en} \equiv$ ethylenediamine). The data obtained in all these studies are presented in the following sections of this paper, together with a discussion of their significance. Finally, general conclusions are drawn concerning the reactivity of aquometal complex ions toward CO_2 itself and toward

related compounds containing the $\text{RC}=\text{O}$ grouping.

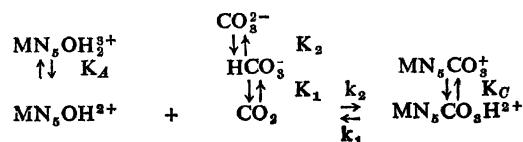
Experimental

The details of the preparation and identification of the various compounds studied is reported in the papers just mentioned.⁹⁻¹⁴ The rate measurements were made by means of a Durrum Model D-110 Stopped Flow Kinetics Spectrophotometer assembly. The procedures used were of three types - the "equilibration" and the "acidification" techniques already published^{9, 13}, or the "*pH* jump" technique.¹³ The latter was devised to follow the rates of CO_2 uptake by *cis*- $\text{Co}(\text{cyclam})(\text{H}_2\text{O})_2^{2+}$ and *cis* or *trans*- $\text{Co}(\text{en})_2(\text{H}_2\text{O})_2^{2+}$ in such a way as to avoid the *cis/trans* isomerization problem. In this, one reservoir syringe of the stopped flow device is filled with an appropriate buffer solution and the second syringe with a solution of diaquo complex and CO_2 at a *pH* of approximately 3. The second solution is prepared by dissolving weighed amounts of sodium bicarbonate and sodium perchlorate in water, adjusting to *pH* 3 with perchloric acid, and adding the requisite amount of stock solution of diaquo complex also at *pH* 3. The spectra of such solutions correspond to that of the original diaquo complex and exhibit no change on standing for a period of several hours. This shows that there is no CO_2 uptake by the acidified diaquo complex, and also that the *cis/trans* interconversions are very slow under these conditions. In the stopped-flow runs, the *pH* is "jumped" to a higher value ($7 < \text{pH} < 9$) as determined by the buffer solution placed in the first syringe. The CO_2 uptake rate is about 100 times the rate of *cis/trans* isomerization of the diaquo reactant even in the $7 < \text{pH} < 9$ range, so no overlap occurs between these processes. The subsequent ring closure of the hydroxobicarbonato intermediate to form the chelated carbonato final product is enough slower than CO_2 uptake to enable separate determination of the rates of each process. The rates of the various CO_2 uptake reactions were followed at wavelengths where maximum absorbance differences between reactants and products occur.¹⁵ Experimental pseudo-first-order rate constants were evaluated graphically in the conventional manner from semi-logarithmic plots of $(A_\infty - A_t)$ versus time, where A is the relative absorbance at infinite time and time t , respectively. The A values were obtained from photographs or contact copies of the oscilloscope trace of each successful run.

Results

When the "equilibration" technique is used, as in the studies of CO_2 uptake by $(\text{MN}_3\text{OH})^{2+}$ ($M =$ trivalent metal ion, $\text{N}_3 \equiv (\text{NH}_3)_3$ or (tren)) in the range $15^\circ < t < 25^\circ$ and $7 < \text{pH} < 9$, the data may be interpreted by the mechanism shown in Scheme I.

Scheme I



In this scheme, k_2 and k_1 are the rate constants for the rate-determining carboxylation and decarboxylation processes, respectively, and the K 's are the acid dissociation constants of the species identified. The corresponding rate law is of the form ($h=[H^+]$, $b=[CO_2]+[HCO_3^-]+[CO_3^{2-}]$)

$$k_{obs} = k_1 h / (h + K_C) + k_2 b K_A h^2 / (h + K_A) (h^2 + K_1 h + K_1 K_2)$$

Since the values for k_1 and the various K 's are known from earlier work, a linear plot can be made of $(k_{obs} - k_1 h / (h + K_C))$ vs $b K_A h^2 / (h + K_A) (h^2 + K_1 h + K_1 K_2)$, and a least squares analysis of the data in this form yields the best-fit values of k_2 . In using the "acidification" technique, the CO_2 concentration is relatively high so that the rate of the decarboxylation reaction is negligible relative to the carboxylation rate. Also, the

CO_2 uptake. The experimental data for the CoN_4 complexes can best be accommodated by a mechanism of the form shown in Scheme II.

The diaquo form is inactive to CO_2 addition and, in any case, is in negligible concentration in the pH range of the experiments. Also, k_3 and k_4 are much smaller than $k_2[CO_2]$ or $k_4'K_2[CO_2]$, so the rate law for CO_2 uptake takes the form

$$k_{obs} = \left(\frac{k_2' h + k_2'' K_2}{h + K_2} \right) [CO_2]$$

Thus, one can obtain a straight line by plotting $k_{obs} (h + K_2) / [CO_2]$ vs h , and linear regression analysis enables evaluation of k_2' and k_2'' .

The rate parameters for CO_2 uptake obtained in the various studies mentioned above are listed in Table 2.

TABLE 2—RATE PARAMETERS FOR CO_2 UPTAKE
(Temp. = 25°C, I = 0.5M)

Complex Ion	λ (nm) ^a	k (M ⁻¹ S ⁻¹)	ΔH^\ddagger (k cal/mole) ^b	ΔS^\ddagger (cal/deg/mole) ^b	pK ^c
(1) $Co(NH_3)_4(OH)^{2+}$	510	220	15.3 ± 0.9	3.6 ± 3.0	6.6
(2) α -BS-Co(tetren)(OH) ²⁺	490	170	15.4 ± 1.2	3.3 ± 4.1	6.3
(3) $Rh(NH_3)_4(OH)^{2+}$	340	490	17 ± 1	12 ± 3	6.8
(4) $Ir(NH_3)_4(OH)^{2+}$	260	590	—	—	6.7
(5) $Co(tren)(OH)_2(OH)^{2+}$	503	44	14.7 ± 0.1	-1.9 ± 0.2	5.3
(6) $Co(tren)(OH)_2^+$	503	170	32 ± 6	53 ± 22	7.9
(7) <i>cis</i> -Co(cyclam)(OH) ₂ (OH) ²⁺	330	57	14.8 ± 1.0	0.8 ± 3.5	4.9
(8) <i>cis</i> -Co(cyclam)(OH) ₂ ⁺	330	200	15.2 ± 0.5	3.0 ± 1.9	8.0
(9) <i>trans</i> -Co(cyclam)(OH) ₂ (OH) ²⁺	370	37	29.0 ± 0.6	46.2 ± 0.4	2.9
(10) <i>trans</i> -Co(cyclam)(OH) ₂ ⁺	370	70	28.3 ± 0.6	44.6 ± 1.9	7.2
(11) <i>cis</i> -Co(en) ₂ (OH) ₂ (OH) ²⁺	370	300	15.3 ± 0.9	3.4 ± 3.2	6.1

- ^a Wavelength at which reaction was monitored.
- ^b Error limits are standard deviations.
- ^c K is acid dissociation constant of parent aquo complex.

$CO_2/HCO_3^-/CO_3^{2-}$ equilibration does not occur within the time of reaction¹⁶, so we have :

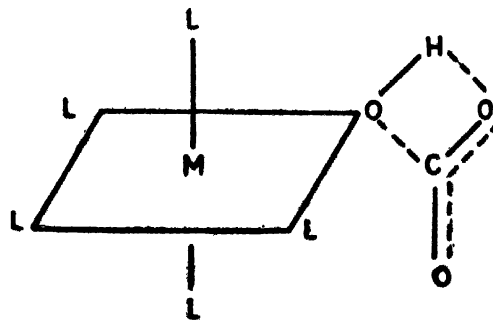
$$k_{obs} = k_2 b K_A / (h + K_A)$$

with $b = [CO_2]$.

In the case of the cobalt(III) diaquo complexes $CoN_4(OH)_2^{2+}$ where $N_4 = (en)_2$, (tren), or (cyclam), the studies were performed in the range $15^\circ < t < 25^\circ$ and $5.9 < pH < 9$. Under these conditions the reactant complex consists of a pH-dependent mixture of $CoN_4(OH)_2(OH)^{2+}$ and $CoN_4(OH)_2^+$ and each of these ions undergoes CO_2 uptake independently. In species of the N_4 -type, *cis/trans* isomerization is possible, though when $N_4 = (tren)$, the structure of the tetradentate amine ligand limits the complex to the *cis* configuration only. With $N_4 = (en)_2$ or (cyclam) *cis* and *trans* isomers exist, but, as already mentioned, the rate of *cis* \rightleftharpoons *trans* isomerization is too slow to interfere with the study of

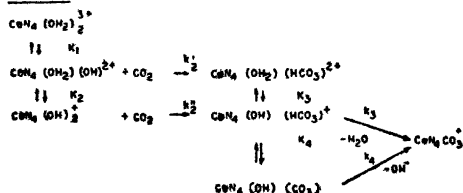
Discussion

The common feature of the intimate mechanisms of all the reactions may be visualized in terms of the transition state :



This is seen to involve nucleophilic attack by the ligand OH on the carbon of CO_2 , accompanied by a concerted transfer of the OH proton to one of the CO_2 oxygens. The possibility that hydrated CO_2 , bicarbonate ion, or carbonate ion displaces the OH ligand completely is ruled out by the speed of the reaction, which is several

Scheme II



orders of magnitude greater than any known ligand substitution for OH^- in any hydroxo complex ion of the type listed¹⁷. It is also known that the decarboxylation of $\text{Co}(\text{NH}_3)_5(\text{HCO}_3)^{2+}$ ion occurs with retention of the Co-O bond¹⁸, so that the principle of microscopic reversibility would dictate that retention of the same bond should occur in the reverse process of carboxylation. In this regard it is also significant that the CO_2 uptake rate constants (Table 2) are only moderately sensitive to the nature of the central metal ion or of the non-participating ligands. This suggests a minimum readjustment of the $\text{N}_2\text{M-O}$ or $\text{N}_4\text{OM-O}$ moieties during reaction with CO_2 .

Some interesting comparisons are possible on the basis of the data of Table 2. One notes that the naive statistical expectation of a factor of about 2 between the rate constants for mono- and dihydroxo complexes of similar type is fulfilled for the *trans* reactants (9) and (10), but not for the *cis* pairs (5) and (6) or (7) and (8). Apparently the *cis* geometry of the latter offers some additional assistance to CO_2 entry when in the dihydroxo form, perhaps related to the possibility of strengthened M-O-H-O bonding in the transition state. Furthermore, for the $\text{CoN}_2\text{OH}^{2+}$ complexes and all the $\text{CoN}_4(\text{OH})_2(\text{OH})^{2+}$ complexes except the

trans cyclam species, ΔH^\ddagger is constant at 15 kcal/mole and ΔS^\ddagger at approximately zero, attesting to the uniformity of mechanism throughout the series. The only deviants from this pattern are the aforementioned *trans*-Co (cyclam) $(\text{OH})_2(\text{OH})^{2+}$ and the two dihydroxo complexes *trans*-Co (cyclam) $(\text{OH})_2^+$ and Co (tren) $(\text{OH})_2^+$. With these ΔH^\ddagger is in the vicinity of 30 kcal/mole and ΔS^\ddagger is close to 50 cal/deg/mole. For the two *trans* species, an explanation can be given in terms of the impossibility of achieving strengthened hydrogen bonding to adjacent OH ligands in the transition state, as already suggested for the *cis* series of complexes. However, Co (tren) $(\text{OH})_2^+$, which is constrained by the amine ligand in the *cis* geometry, remains an exception to the general rule which is apparently applicable to the other *cis* complexes.

One of the criteria which can be utilized to correlate nucleophilicity of a reactant in aqueous solution is its proton basicity. This has recently been discussed in detail by R. B. Martin¹⁹, who has applied the concept to the rates of hydration of CO_2 by various hydroxo metal complex ions. An expanded version of this $\log k$ vs pK_a correlation including all the data of Table 1, together with some additional results from the literature, is presented in Figure 1²⁰. While the correlation is

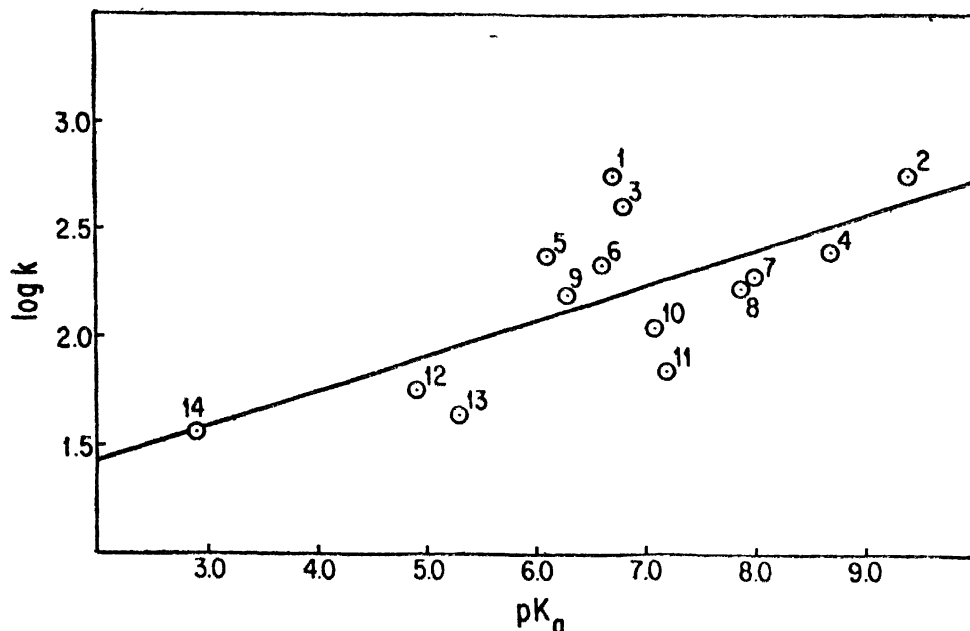
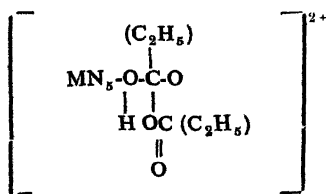


Fig. 1. Plot of log of rate constant for CO_2 reaction with various hydroxo metal complexes vs pK_a of parent aquo form of complex. (Data from Table 2 except those referenced).

- (1) $[\text{Ir}(\text{NH}_3)_5\text{OH}]^{2+}$, (2) $[\text{Cu}(\text{glycylglycinate})(\text{OH})]$ (ref. 21), (3) $[\text{Rh}(\text{NH}_3)_5\text{OH}]^{2+}$, (4) $[\text{Zn}(\text{CR})\text{OH}]^+$ (ref. 7, 22), (5) *cis*- $[\text{Co}(\text{en})_2(\text{OH})_2(\text{OH})]^{2+}$, (6) $[\text{Co}(\text{NH}_3)_5\text{OH}]^{2+}$, (7) *cis*- $[\text{Co}(\text{cyclam})(\text{OH})_2]^+$, (8) $[\text{Co}(\text{tren})(\text{OH})_2]^+$, (9) $\alpha\beta\text{S}-[\text{Co}(\text{tetren})(\text{OH})]^{2+}$, (10) *cis*- $[\text{Co}(\text{Cr}(\text{C}_2\text{O}_2)_2(\text{OH})_2(\text{OH}))]^{2-}$ (ref. 23), (11) *trans*- $[\text{Co}(\text{cyclam})(\text{OH})_2(\text{OH})]^{2+}$, (12) *cis*- $[\text{Co}(\text{cyclam})(\text{OH})_2(\text{OH})]^{2+}$, (13) $[\text{Co}(\text{tren})(\text{OH})_2(\text{OH})]^{2+}$, (14) *trans*- $[\text{Co}'(\text{cyclam})(\text{OH})_2(\text{OH})]^{2+}$.

rather scattered in detail, the overall pattern is satisfactory in that the long extrapolation to the pK_a value of H_2O (15.7) predicts a reasonable value for the rate constant of the CO_2/OH^- reaction ($\log k_{cat} = 3.7 \pm 0.4$, $\log k_{obs} = 3.9$). However, the naturally occurring metalloenzyme, carbonic anhydrase, does not fit into this pattern at all well. The site of CO_2 hydrolysis in this enzyme is believed to be the $Zn^{II}\text{-OH}$ grouping²⁴, which has a pK_a of between 7 and 8, so that the predicted k from Figure 1 should be around $300 M^{-1}sec^{-1}$. The observed value of this rate constant⁹ for bovine carbonic anhydrase is in fact about $4 \times 10^{-8} M^{-1}sec^{-1}$. This major discrepancy attests to highly specific catalytic properties of enzymes, and may in this case be attributed to the known strong binding of CO_2 at the active site, possibly facilitated by the conical cavity²⁵ in the enzyme at that location. Certainly, factors well beyond the mere existence of the hydroxo-zinc (II) grouping in the enzyme must come into play, as attested by the fact that the model complex^{7,22} $Zn(CR)(OH)^+$ hydrolyses CO_2 with a rate constant of $250 M^{-1}sec^{-1}$ at 25° , very close to the prediction of Figure 1.

Evidence for the reactivity of co-ordinated hydroxide has been obtained in connection with some entirely different types of reactions from the ones just reviewed. Thus, Buckingham and Engelhardt have recently shown²⁶ that the hydrolysis of propionic anhydride is catalyzed in a similar manner by metal complex ions of the type $M(NH_3)_5OH^{2+}$ where $M = Cr^{III}, Co^{III}, Ru^{III}, Rh^{III},$ and Ir^{III} . The reaction is visualized as involving the formation of the intermediate :



with subsequent splitting off of propionic acid to leave $[MN_5-O-C(C_2H_5)]^{2+}$ as one of the products. A similar

mechanism has been proposed by T. C. Bruice and co-workers,²⁷ who show that the hydrolysis of the ester side-chain of the compound 2-(2'-hydroxyphenyl)-4(5)-methyl-5(4)-(2'',2''-dimethylacetate)-imidazole is greatly facilitated by the presence of $Co(H_2O)_6^{2+}$ and $Ni(H_2O)_6^{2+}$ ions in the pH range where an appreciable fraction of the aquo ions are dissociated into the hydroxo-aquo form.

In conclusion, mention should be made of some entirely different types of " CO_2 uptake" which have been observed in studies of a variety of organometallic compounds. In some instances, metal-carbon bonds are formed as in the studies of the triphenylphosphine and carbonyl transition metal complexes reported by Vol'pin and his school,²⁸ and similar findings have

been reported elsewhere.^{29,30} Some recent studies³¹ illustrate a new type of CO_2 insertion reaction, involving carbon-nitrogen bond formation, which converts tungsten alkylamido complexes into carbamate species. None of these reactions can be classed as " CO_2 hydrolysis", but are further examples of the burgeoning possibilities of CO_2 uptake reactions in transition metal co-ordination chemistry.

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15. The CO_2 uptake reactions were monitored at the wavelength indicated in Table 2.
16. In the "equilibration" method, carbonic anhydrase is added to the reactant system to ensure that the $CO_2/HCO_3^-/CO_3^{2-}$ species are in constant equilibrium. However, in using the "acidification" procedure no carbonic anhydrase is present, so direct CO_2 hydrolysis by reaction with water is slight during the CO_2 uptake process (see Table 1).
17. For example, the rate of exchange of ^{18}O -labelled water with the ion $cis-Co(en)_2(H_2O)(OH)^{2+}$ is about $10^{-8} sec^{-1}$ and with $cis-Co(en)_2(OH)^+$, about $3 \times 10^{-6} sec^{-1}$ (W. KRUSE and H. TAUBE, *J. Amer. Chem. Soc.*, 1961, 83, 1280).
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20. A fuller discussion of this correlation is presented in ref. 13.

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