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# The Catalysis of the Reaction between Carbon Dioxide and Water

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By A. E. Dennard and R. J. P. Williams

The rate of the reaction between carbon dioxide and water has been studied over a wide range of pH in the presence of different buffers by a manometric method. The catalysis of the reaction by a range of anions has also been examined. No correlation between the dissociation constant of the conjugate acid of the anion and its catalytic constant was observed. Possible explanations are offered in terms of the geometric and electronic structures of the bases.

THE rate of reaction between carbon dioxide and water has been studied many times. The observations have been reviewed by Kern<sup>1</sup> and by Davies,<sup>2</sup> the latter stressing the catalysis by the enzyme carbonic anhydrase. We are concerned with the effect of simple anions,  $B^-$ , upon the rate of the reaction. Previous work by Sharma and Danckwerts<sup>3</sup> suggested that a linear relationship might exist between the acid dissociation constant of the acid, HB, and the catalytic constant of the base for a related series of bases. We have not observed such a relationship and it appears that the individual geometry and electronic structure of the bases are of over-riding importance.

Method .- The reaction rate was followed manometrically at  $0^{\circ}$  by using a method not unlike that of Roughton and Booth.<sup>4</sup> The reaction was followed to equilibrium, so the rate equations

$$CO_2 + H_2O \xrightarrow[k_{-1}]{k_1} H_2CO_3 \tag{1}$$

$$\mathrm{CO}_2 + \mathrm{OH}^{-} \underbrace{\overset{k_3}{\longleftarrow}}_{k_{-3}} \mathrm{HCO}_3^{-} \tag{2}$$

can be analysed as follows.

By Henry's law the concentration of carbon dioxide in solution is  $[CO_2] = \alpha \beta$  where  $\beta$  is the partial pressure of carbon dioxide. The amount of carbon dioxide in the solution is then  $m = \alpha p v$  where v is the volume of absorbing liquid. The amount of carbon dioxide in the gas phase is  $n = \frac{\phi V}{RT}$  where V is the volume of the gas phase so that the total carbon dioxide in the system is  $(n + m) = p[(V/RT) + \alpha v]$ . Now in the solution carbon dioxide reacts to give H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub>-, and  $CO_3^{2-}$ , all three of which are in rapid equilibrium. The total concentration of these species at time t is  $T_t = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$ 

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$$T_t = [H_2 CO_3] \left\{ 1 + \frac{K'}{[H^+]} + \frac{K'K''}{[H^+]^2} \right\}$$
 (3)

where K' and K'' are the first and second dissociation constants of carbonic acid. The rate of formation of products,  $T_t$ , in solution, it being assumed that rapid

D. M. Kern, J. Chem. Educ., 1960, 37, 14.
 R. P. Davies, in "The Enzymes" eds. P. D. Boyer, H. Lardy K. Myrbäck, Academic Press, New York, 1961, vol. V, p. 545.
 M. M. Sharma and P. V. Danckwerts, Trans. Faraday Soc.,

1963, **59**, 386.

4 F. J. W. Roughton and V. H. Booth, Biochem. J., 1938, 32, 2049.

equilibration between the gas and the liquid phases (see Experimental section) occurs that only equation (1) operates, is

$$\frac{\mathrm{d}T_t}{\mathrm{d}t} = k_1 [\mathrm{CO}_2] - k_{-1} [\mathrm{H}_2 \mathrm{CO}_3]$$

But at time t,  $vT_t = (p_0 - p_l) \left\{ \frac{V}{RT} + \alpha v \right\}$ 

Therefore, 
$$[CO_2]_{\iota} = \alpha p_0 - \frac{\alpha v T_{\iota}}{(V/\mathbf{R}T + \alpha v)}$$
$$\frac{\mathrm{d}T_{\iota}}{\mathrm{d}t} = \alpha p_0 k_1 - \frac{\alpha v T_{\iota} k_1}{(V/\mathbf{R}T + \alpha v)} - \frac{T_{\iota} k_{-1}}{1 + \frac{K'}{[\mathrm{H}^+]} + \frac{K''K'}{[\mathrm{H}^+]^2}}$$
$$\mathrm{d}T_{\iota}/\mathrm{d}t = \alpha p_0 k_1 - CT_{\iota} \tag{5}$$

where C is a constant for any one experiment at constant hydrogen ion concentration.

Now certain other equalities can be derived by using the equilibrium condition,  $\alpha T_{eq}/dt = 0$ , and therefore

$$\alpha p_0 k_1 = C T_{\rm eq} \tag{6}$$

(4)

Combination of (5) and (6) gives

or

$$dT_t/dt = C(T_{eq} - T)_t$$
$$d \ln (T_t - T_{eq})/dt = C$$

From equation (4) it follows that

$$-\ln(T_{eq} - T_l) = \ln(p_{eq} - p_l) + \ln\left(\frac{V}{vRT} + \alpha\right)$$

and

$$d \ln(T_t - T_{eq})/dt = d \ln(p_{eq} - p_t)/dt = C \quad (7)$$

Thus, following the changes of pressure in the manometer with time allow C to be determined by first-order kinetics, where

$$C = \frac{\alpha R T v k_1}{V + \alpha R T v} + \frac{k_{-1}}{1 + \frac{K'}{[H^+]} + \frac{K' K''}{[H^+]^2}}$$
(8)

Consideration of the second mechanism (2) merely adds a second term to the rate constant so that C is replaced by

$$C(\mathbf{1} + C_{\mathrm{OH}}\text{-}[\mathrm{OH}^{-}]) \tag{9}$$

where  $C_{\text{OH}^-}$  is the ratio of the "catalysis" constant for the reaction of OH<sup>-</sup> with carbon dioxide to that for water with carbon dioxide. The dependence on [H<sup>+</sup>] of (8) and (9) is such that the different rate constants  $k_1$ ,  $k_{-1}$ , and  $k/C_{\text{OH}^-}$  can be determined if suitable inert buffers can be found.

Catalysis by other anions or neutral molecules is observed by a change of rate constant,  $\ln(p_e - p_t)/t$ , which will be called  $k_{obs}$ , to

$$C(1 + C_{\text{OH}} - [\text{OH}^-] + C_{\text{HB}}[\text{HB}] + C_{\text{B}} - [\text{B}^-])$$
 (10)

Throughout this work the values for the acid dissociation constants, at 25° and zero ionic strength,  $K' = 4.5 \times 10^{-7}$  and  $K'' = 5.6 \times 10^{-11}$  have been used.

Buffers.—A very considerable series of buffer anions and neutral bases has been used including (a) phosphate, (b) carbonate, (c) acetylacetonate, (d) substituted pyridines (e) phenolate (f) imidazole in an attempt to find conditions where neither HB nor  $B^-$  is catalytic. In Figure 1 all the observed rate constants are plotted



FIGURE 1 Observed rate constants, k<sub>obs</sub>, in different buffer systems of total concentration 0.8M but of varying ratio of the two components. → Potassium dihydrogen phosphate plus potassium hydroxide. ○ α-Picoline plus perchloric acid. □ 2,6-Lutidine plus perchloric acid. △ Imidazole plus sulphuric acid. × Acetylacetone plus potassium hydroxide.
♦ Sodium bicarbonate plus sodium hydroxide. ● Phenol plus sodium hydroxide

against pH as determined in the buffers at 0°. The full line is a theoretical curve based on the literature values of  $k_1 = 2.0 \times 10^{-3}$  sec.<sup>-1</sup>,  $k_{-1} = 2.0$  sec.<sup>-1</sup>, and  $k_2 = 1.1 \times 10^3$  l. mole<sup>-1</sup> sec.<sup>-1</sup>.

There is sufficiently good agreement for us to state that acetylacetonate and its acid, carbonate and its acids, and  $\alpha$ -picoline and its acid are not catalytic. Imidazole but not its acid, phenolate but probably not phenol, and phosphate, both as  $H_2PO_4^-$  and  $HPO_4^{2^-}$ , are weak catalysts. The evidence disposes of any suggestion <sup>5</sup> that carbonate or bicarbonate are catalysts, in agreement with Roughton and Booth. Before catalyst constants were calculated for other anions we established that salt concentration had only a random effect on the reaction rate (Table 1). Before going on to

## TABLE 1

Effect of ionic strength at different pH values; rate constants, C (sec.<sup>-1</sup>), at  $0^{\circ}$ 

KCl(M)	(i)	(ii)	(iii)	(iv)	(v)
0.0	2.18	0.78	0.72	0.57	3.1
0.5	2.24	0.76	0.70	0.54	2.8
$1 \cdot 0$	2.30	0.82	0.80	0.59	$2 \cdot 9$

(i)  $0.8M\text{-}\alpha\text{-}\text{Picoline}$  with 0.4M-perchloric acid. (ii) 0.8M-2,6-Butidine with 0.4M-perchloric acid. (iii) 0.8M-Imidazole with 0.2M-sulphuric acid. (iv) 0.8M-Acetylacetone with 0.4M-sodium hydroxide. (v) 0.8M-Phenol with 0.2M-sodium hydroxide.

consider catalysis, our main concern, we stress that excellent agreement between our values for constants  $k_1$  and  $k_{-1}$  and those of other workers is not to be expected as we have worked deliberately at very high

<sup>5</sup> D. Himmelblau, D.Phil. Thesis, University of Washington, 1957.

buffer strengths. This permits us to use high catalyst concentrations and hence to study weak catalysts. In those cases where it has been possible to extrapolate our results to infinite dilution of the buffer the agreement between our values of  $k_1$  and  $k_{-1}$  and those of other workers is good, see Figure 1.

Catalysts.—As the catalysts studied are mostly weak acid anions they have been examined over a range of



FIGURE 2 Variation of observed rate constant,  $k_{obs}$ , with catalyst (arsenite) concentration in (×) 0.8M-phenol plus 0.2M-potassium hydroxide, (•) 0.8M-acetylacetone plus 0.4M-potassium hydroxide, and ( $\Box$ ) 0.8M-imidazole plus 0.4M-perchloric acid



FIGURE 3 Variation of observed rate constant,  $k_{obs}$ , with pH for catalysis by arsenite in ( $\bigcirc$ ) imidazole, ( $\square$ ) acetylacetone, and ( $\bigtriangledown$ ) phenol buffers

pH by studying them in different buffers. At the highest and lowest pH used the dependence of catalysis on catalyst concentration has also been examined so as to detect activity due to polymerised forms of buffer anions. Where possible the effect of different buffer systems has also been examined to eliminate the possibility that ion-pairs of any kind were catalytic. A typical study, that of catalysis by arsenite, is given first and thereafter general results are presented.

Arsenite.—The linear dependence of the observed catalyst constant,  $C_{\text{Total}}$ , on the concentration of arsenite in different buffers is shown in Figure 2. The

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dependence of the catalysis constant on pH for the three buffer systems is shown in Figure 3. On Figure 3 we plot a curve assuming that arsenious acid,  $H_3AsO_3$  (or  $HAsO_2$ ), is not a catalyst, that the catalyst constant for  $H_2AsO_3^-$  (or  $AsO_2^-$ ) is  $1.9 \times 10^3$ , that there is no polymerisation or ion-pair formation of the acid, and that the  $pK_a$  of the acid as determined at the appropriate ionic strength of ~0.5 is 9.2. The fit between the experimental points and the theoretical curve is good. The catalyst constant obtained agrees reasonably well with the results of earlier workers, difference in experimental conditions being considered.

Other catalysts. Table 2 lists constants obtained for

Table	<b>2</b>
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Catalyst constants (l. mole<sup>-1</sup> sec.<sup>-1</sup>) at 0°

		Rate constant
Catalyst	$pK_a$	С
[B(OH)]	9.2	1
H <sub>3</sub> SiO <sub>4</sub> -	9.5	$(\sim 10^3)$
$H_3GeO_4^-$	9.0	$(\sim 2 imes 10^3)$
HPO4 <sup>2-</sup>	$7 \cdot 2$	10
H <sub>2</sub> PO <sub>4</sub>	$2 \cdot 1$	2
HAsO <sub>4</sub> <sup>2-</sup>	$7 \cdot 0$	5
AsO <sub>2</sub> -	$9 \cdot 2$	$2 imes10^{3}$
SO3 <sup>2~</sup>	$7 \cdot 2$	$1 imes 10^{3}$
SeO <sub>3</sub> <sup>2-</sup>	$8 \cdot 1$	$6 imes 10^{3}$
TeO(OH)5 <sup>-</sup>	8.0	$7 imes10^{2}$
Te(OH <sub>4</sub> O <sub>2</sub> <sup>2-</sup>	11.0	$4 imes 10^{3}$
HTeO <sub>3</sub> <sup>-</sup>	7.7?	$(\sim 10?)$
C1O	7.5	$5 imes 10^4$
BrO	8.5	$> 10^{4}$
Phenolate	10.0	10

The following anions showed no catalytic activity:  $CO_3^{2-}$ ,  $HCO_3^{-}$ , various organic acid anions,  $NO_4^{-}$ ,  $NO_3^{-}$ ,  $HS^{-}$ ,  $S^{2-}$ ,  $SO_4^{2-}$ ,  $H_2PO_3^{-}$ ,  $H_2PO_3^{-}$ , pyrophosphate, benzenesulphonate and benzenesulphinate. The  $pK_a$  values are those considered to be the best and most appropriate for this study from Stability Constants, Special Publication No. 17, Chemical Society, London, 1964 ed. L. G. Sillén and A. E. Martell. The values of rate constants in parentheses are from ref. 3.

other anions together with some comments. Where there is a possible comparison with earlier work agreement is not always good. We can only account for this by noting that earlier workers have not studied catalysts over a wide pH range, and it may well be that their constants do not refer to catalysis by single species HB or  $B^-$ .

### DISCUSSION

Our primary consideration is base catalysis of the hydration of carbon dioxide. Table 2 shows that there is no relationship between  $pK_a$ , proton affinity of a base, and its catalytic constant. However no strong acid anion is catalytic and hence a good proton-acceptor centre is required. That this is not sufficient for catalysis is shown by the absence of catalysis with the anions acetylacetonate, carbonate, cyanide, and hydrosulphide. Clearly too the "polarisability" of an anion is not important for HS<sup>-</sup> and CN<sup>-</sup> are extremely polarisable but inert. In order to be a good catalyst the base must be in one of two classes.

Class I.—If the oxyanion is of the highest oxidation state of a non-metal there must be no equivalent oxygen atom in the anion to that from which the proton has been removed, e.g., [OTe(OH)<sub>5</sub>]<sup>-</sup>, [OGe(OH)<sub>3</sub>]<sup>-</sup>, and  $[OSi(OH)_3]^-$  are good catalysts.  $HCO_3^-$  and  $ClO_2^-$  are not catalysts and HPO42-, HAsO42-, and O2I(OH)4- are only weak catalysts though the last three anions are of basicity equal to the three good catalysts just mentioned. In the Paper of Sharma and Danckwerts<sup>3</sup> the anions of the aldehydes RCH(OH)O<sup>-</sup> are included with the first group of catalysts and it is suggested that these anions give rise to a good Brønsted plot,  $pK_a$  against log (rate constant). Inspection of their data (Table 1 of ref. 3) shows however that much turns on the accuracy of their estimated  $pK_a$  values and the rather poorly evaluated catalyst constants. (The catalyst constant often had to be determined at very low anion concentration and the estimated  $pK_a$  was then used to find the true catalyst constant.) We cannot accept that the Brønsted relationship has been established.

Class II.—The best catalysts of all are the oxyanions of lower oxidation states of non-metals and which have at least one lone-pair of electrons, e.g.,  $SO_3^{2-}$ ,  $SeO_3^{2-}$ ,  $AsO_2^{-}$ ,  $ClO^-$ ,  $BrO^-$ . The ions  $HPO_3^{2-}$  and  $H_2PO_2^{2-}$ , on the other hand, have no lone pair of electrons and are not catalysts although they are anions of weak acids.

The reason for the low catalysis by oxyanions with more than one equivalent oxygen (see Class I) has been given by Sharma and Danckwerts using an earlier suggestion based on work on hydration of aldehydes. Bell and Higginson<sup>6</sup> pointed out that spread of charge over (n + 1) oxygens on ionisation of an acid XO<sub>n</sub>(OH)<sub>m</sub> is likely to lead to a low effective charge on any oxygen essential for catalysis. In this way it is possible to explain the low catalytic activity of anions which are relatively good proton acceptors, e.g., HPO42-, HAsO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, and AsO<sub>3</sub><sup>-</sup>, as compared with  $[Te(OH)_{5}O]^{-}$ ,  $[Ge(OH)_{4}O_{2}]^{2-}$ ,  $[Ge(OH)_{3}O]^{-}$ . Again phenolate itself is a better catalyst than acetylacetonate in which more extensive charge redistribution occurs in the anion. This explanation still leaves two paths for catalysis of hydration: (a) direct attack of the anion on carbon dioxide:



and (b) attack of the anion on water adjacent to carbon dioxide:

Whereas mechanism (b) is expected to give rise to a Brønsted plot, the first mechanism may or may not do so depending upon the stability of the first intermediate, *i.e.*, whether XO<sup>-</sup> is a good leaving group or not. We return to this point below but note that in the absence

<sup>6</sup> R. P. Bell and W. C. E. Higginson, Proc. Roy. Soc., 1949, A, 197, 141.

of more extensive observations than have been provided so far the two mechanisms cannot be distinguished. The fact that the heavily hydrated anions,  $OH^-$  and  $HO_2^-$ , are relatively poor catalysts, though strong bases, suggests that the removal of water from the anion is essential, as in mechanism (*a*) but not in (*b*).

The second class of anion forms a clear example of what Pearson and Edwards 7 have called the "alphaeffect," *i.e.*, enhanced catalysis by nucleophiles with lone pairs of electrons on the atom adjacent to the donor atom. Moreover carbon dioxide does react more rapidly with nitrogen bases such as hydrazine and hydroxylamine than would be suggested by their base constants. However no marked catalysis by acetophenoximate and HO<sub>2</sub><sup>-</sup>, the original examples of the " alphaeffect " in nucleophilic substitution, is observed.3 Moreover comparison between our catalytic constants and the rate constants of nucleophilic attack on either the carbonyl carbon of p-nitrophenylacetate or on methylisoperoxyphosphoryl fluoride <sup>6</sup> shows that whereas some good nucleophiles in the latter reactions, e.g., hypochlorite, are also good catalysts of the carbon dioxide plus water reaction, others such as phenolate are not. It is clear that mechanism (b) cannot explain catalysis by class II anions for there is no correlation between catalysis and  $pK_a$  in this class. However mechanism (a), because it contains two steps (a catalyst must be a good nucleophile and a good leaving group) can explain the absence of a correlation with  $pK_a$  and the absence of a close parallel between substitution rates and catalysis of the hydration of carbon dioxide. In order to understand the catalysis, the properties of an anion which make it both a good nucleophil and a good leaving group must be understood. Some general comments about the properties of oxyanions are therefore pertinent.

The oxyacid-anions of the lower oxidation states of the non-metals concerned have in common (1) a lone pair of electrons, implying that the non-metal rather than oxygen could act as a donor. In fact sulphite does add to a carbonyl group by its sulphur rather than its oxygen atom. Thus in mechanism (a) the special feature of the catalysis by the lower oxidation states could be attack by X of XO<sup>-</sup> rather than by oxygen. However reactions of XO<sup>-</sup> with electrophilic centres generally proceed through  $XO^- \longrightarrow Z^+$  attack. The oxyanions also have (2) the ability to act as acceptors. The rate of exchange of oxygen in an anion  $XO_n$  is faster the lower the oxidation state of X (the fewer the number of oxygen atoms) and the higher the negative charge on the anion. In such reactions the mechanism is believed to involve prior formation of a bond between the entering group, H<sub>2</sub>O or OH<sup>-</sup>, and the anion as a first step (*i.e.*,  $XO_n$  acts as an acceptor). A similar path apparently holds for two-electron oxidation of the anions, e.g.,  $\text{ClO}_2^- + \text{SO}_3^{2-} \longrightarrow \text{ClO}^- + \text{SO}_4^{2-}$  goes through a bimolecular intermediate. This provides a 7 R. G. Pearson and J. O. Edwards, J. Amer. Chem. Soc., 1962, 84, 16.

further alternative for hydration of carbon dioxide (c) in which the function of X is to act as an electrophilic centre. Such a mechanism explains immediately why



 $HO_2^{-}$  is a poor catalyst compared with ClO<sup>-</sup> while both are good nucleophils and leaving groups. We conclude that at the present stage of the study of this reaction it is not possible to decide definitely in favour of a particular mechanism and it could be that different anions act in different ways.

Catalysis by uncharged bases and complexes. We have also investigated catalysis by the neutral species imidazole, pyridine, and 2-methyl-, 2,6-dimethyl-, and 2,4,6-trimethyl-pyridine. Only imidazole showed activity but this was very weak. Addition of metal ions to imidazole solutions causes some increase in catalysis comparable with that by the zinc(II) and copper(II) ammines and glycinate complexes. On the other hand zincethylenediaminetetra-acetate and tris-(2,2'-bipyridyl) zinc had no activity. Di(acetylacetonate) zinc is active, having a catalytic constant of  $\sim 10$ . The activity of metal chelates will be reported in detail later as they provide a possible model for the action of the enzyme, carbonic anhydrase.

## EXPERIMENTAL

All chemicals were of AnalaR grade. pH was measured on a Pye Cambridge pH meter reading to  $\pm 0.02$  unit. Reaction Rates.—The essential feature of the rate study was the elimination of diffusion control. This was achieved by working at 0° in an ice-water thermostat controlled to  $\pm 0.1^{\circ}$  and by using very rapid stirring. The reaction vessel was a conventional Warburg flask connected to a manometer. The contents of the flask could be stirred at a controlled rate by an external rotating magnet and an internal follower. The reaction could be followed at any desired total CO<sub>2</sub> pressure below atmospheric.

In a typical reaction-rate study 5 ml. of solution were put into the Warburg flask and the contents of the flask brought to the temperature of the thermostat. Carbon dioxide was then allowed into the apparatus displacing all air. The pressure in the apparatus was then adjusted to the required value by using a large evacuated flask as a reservoir. The reaction vessel and manometer were isolated and the magnetic stirrer switched on. The fall in pressure in the manometer was read off as CO2 was absorbed. The run continued until equilibrium was reached. It was essential to show that the rate of reaction was not diffusion-controlled. Two procedures were used. (1) Rate constants were compared with values in the literature (Figure 1). (2) The effect of increasing reaction rate at high and low pH (Figure 1) was examined. It was shown that reaction rates of greater than about  $k_{\rm obs} = 10^{-2} \text{ sec.}^{-1}$  became partially diffusion rate-limited.

Salt Effects.—Ionic strength has no effect on the rate of the reaction of carbon dioxide and water. This is shown in Table 1.

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WADHAM COLLEGE, OXFORD.

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