Catalysis by Brönsted bases of the reaction between CO_2 and water

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The catalysis of the reaction $CO_2+H_2O \rightarrow HCO_3^-+H^+$ by a number of anions has been studied at 0°C. Anions which have a negatively-charged oxygen atom and at least one hydroxyl group attached to the same central atom, and in which the negative charge is not delocalized by resonance effects, form a single group which obeys the Brönsted relationship. Anions of other types are in general weaker catalysts for a given pK.

The removal of CO_2 from mixtures of gases by liquid absorbents is an important industrial process in several contexts. For economic reasons the solution must (*a*) have a large capacity for CO_2, (*b*) be capable of regeneration by driving off the CO_2 (usually by heating or stripping with steam and/or air), and (*c*) have a high specific absorption rate. Solutions of potassium carbonate (which is more soluble than sodium carbonate) are satisfactory in respect of (*a*) and (*b*), and are in common use. However, the dissolved CO_2 must react with the solution before the absorptive capacity of the latter can be realized, and this reaction is relatively slow. Normally the dissolved CO_2 reacts with the OH^- in the solution:

$$CO_2+OH^- \rightarrow HCO_3^-. \tag{1}$$

The second order rate-constant is about 6000 l./mole sec at 20°C; thus, in an equimolal mixture of carbonate and bicarbonate, with a pH of about 10, the CO_2 will undergo a pseudo-first order reaction with a rate constant of about 0·6 sec^{-1}. The CO_2 will also react with water:

$$CO_2+H_2O \rightarrow HCO_3^-+H^+, \tag{2}$$
$$H^++OH^- \rightarrow H_2O.$$

The rate-determining step, reaction (2), has a rate constant of about 0·02 sec^{-1} at 20°C, and thus plays a minor part in the absorption process. However, reaction (2) can be catalyzed by a variety of agents: arsenite ion is used as a catalyst in one industrial process,[1] thus speeding up the absorption and desorption of CO_2. Roberts and Danckwerts[2] have shown that the catalytic constant for arsenite ions (defined below) is about 160 l./mole sec at 25°C.

Roughton and Booth [3,4] and Kiese and Hastings [5] have studied the catalysis of reaction (2) and its reverse extensively because of the physiological importance of the latter. It was found that a number of anions of weak acids, such as selenite, arsenite, tellurate, hypochlorite, hypobromite, etc., possess a high catalytic power, but no general correlation between ionization constant, structure and catalytic power has been put forward. A critical examination of the data suggested to us that the various anions might be grouped according to the distribution of the negative charge, and that the Brönsted relationship might be obeyed within each group.

The work reported here was undertaken to throw more light on the catalytic effect of various types of anions, and at the same time as a search for catalysts of possible industrial value. The catalysts tried include the anions of (A) telluric, germanic, arsenious and silicic acids, chloral hydrate, chloral alcoholate, and the hydrates of butyl chloral, glyoxal, formaldehyde, acetaldehyde, and diacetyl: (B) trichloroethanol and trifluoroethanol; hydrogen peroxide; (C) some sugars; and (D) sulphurous, selenous, tellurous, phosphoric and phenyl arsonic acids and phenol.

EXPERIMENTAL

The rate of reaction was measured by a manometric method, similar to that employed by Roughton and Booth.[6] The reaction flask, compensating flask and CO_2 flask were all kept in a water-bath maintained at the desired temperature. The solution in the reaction flask (10 ml) was vigorously agitated by a magnetic stirrer operated through the bottom of the water-bath, which was made of a sheet of Perspex. All the experiments were carried out at a total pressure of 152 mm Hg (0·2 atm) and a maximum partial pressure of CO_2 of about 25 mm Hg. The constants of the apparatus were evaluated by the method given by Dixon.[7]

The value of the reaction-rate constant calculated from the observations is based on the assumption that the solubility of CO_2 in the buffers employed was substantially the same as in water. The solubility of a gas in a solution with which it reacts cannot be determined by equilibrium measurements. The available data on the solubility of CO_2 in a number of electrolytes akin to the constituents of the buffers employed, as also the general thermodynamic considerations pertaining to the solubility of electrolytes,[8] indicate that this assumption is unlikely to lead to an error greater than 5%.

The manometer readings were recorded every 15 sec, the first reading being taken after 30 sec. Normally, readings were continued for 5-10 min. The first 15 to 60 sec, depending upon the pH and the catalyst employed, represented the period during which physical saturation was taking place. At least 5 or 6 points beyond this time were used to obtain the reaction rate. All the experiments were carried out in triplicate or quadruplicate, the maximum variation in the rate-constants being about ±5%. A series of experiments with phosphate and veronal buffers gave results comparable with those obtained by Roughton and co-workers.[9, 10] Spot checks were made at frequent intervals with these buffers. The catalytic activity of the desired material was obtained by carrying out experiments with 2 or 3 different concentrations of the catalyst in a given buffer. The pH values of the buffers employed were measured with a pH meter (Radiometer, Copenhagen). Four buffer solutions were employed, namely, phosphate pH 7·52 (0°C) (M = 0·132, [ion]/[acid] = 5·2, μ = 0·35), veronal pH 8·75 (0°C) (M = 0·12, [ion]/[acid] = 3, μ = 0·09), carbonate buffer—I pH 9·5 (0°C) (M = 0·2, $[HCO_3^-]/[CO_3^{2-}] = 4$, μ = 0·28), and carbonate buffer-II pH 10·1 (0°C) (M = 0·14, $[HCO_3^-]/[CO_3^{2-}] = 1$, μ = 0·28).

MATERIALS

All the materials employed were either A.R. or technical grade. The acetaldehyde and formaldehyde solutions were analyzed by the hydroxylamine hydrochloride method. The aldehydes tend to undergo reactions in alkaline solution so all the solutions were prepared and stored at 0°C. All experiments with aldehydes were carried out on the day on which the solutions were prepared. Consistent results were obtained, indicating that degradation of the materials employed was insignificant during the period of storage.

RESULTS AND DISCUSSION

In general, the rate constant of the reaction in any particular buffer was found to be a linear function of the concentration of the total catalyst added (ionized + unionized forms), in conformity with the expressions

$$R = (k_u + k_B[B^-])[CO_2], \qquad (3)$$

$$[B^-] = ([B^-] + [HB])/(1 + [H^+]/K_A), \qquad (4)$$

where R = rate of reaction of CO_2, moles/l. sec, $[CO_2]$ = concentration of CO_2 mole/l., $[B^-]$ = concentration of anion, moles/l., [HB] = concentration of conjugate acid, moles/l., k_u = rate constant for hydration of CO_2 in absence of catalyst, sec^{-1}, k_B = catalytic rate constant corresponding to base B^-, l./mole sec, K_A = stoichiometric dissociation constant of HB, g ion/l.

The velocity constant k_B can be calculated from the slope of the plot of reaction-rate constant against catalyst concentration (ionized+unionized), together with the pH of the buffer solution and the pK of the acid conjugate to the catalytic anion. The effect of ionic strength on the dissociation of the acid should be known, but such data are not always available and an assumption had to be made in some cases. On the basis of the thermodynamic considerations and the data available on a number of substances of the type under consideration, a correction factor of −0·2 was applied to the value of pK at infinite dilution to get its value at an ionic strength of 0·28.

Experimental results are presented in table 1. Values of the quantity k, defined by

$$R = (k_u + k\{[B^-]+[HB]\})[CO_2], \tag{5}$$

are also reported, so that k_B can be recalculated if necessary in the light of further information about pK values.

All the aldehydes investigated exist in the solution in the hydrated form. For acetaldehyde and diacetyl hydration is incomplete and it is therefore necessary to consider the hydration equilibria when calculating the catalytic power of the hydrate anion. The relevant references are given in table 1.

The anions of group A have a negative charge localized on a single oxygen atom, and there is no possibility of this being spread over the molecule by resonance. The atom to which the ionized oxygen atom is attached also carries at least one unionized hydroxyl group, except with chloral alcoholate. The large catalytic activity of ions of this type may be due to the ability of the unionized hydroxyl group to attach itself to and orient favourably one of the reacting molecules. A similar role for the hydroxyl group in the alkaline hydrolysis of α- hydroxy cyclopentyl acetate has been suggested by Bruice and Fife.[34a]

The effect of pH on the catalytic power of the anions of group A is not great except with germanite. It is known that variations of pH change the nature of the species present in germanite solutions[14,15]. The plot of log k_B against pK_a for this group is shown in fig. 1, which indicates that the results can be fitted reasonably well to a straight line of slope 0·56, although the catalytic activities of acetaldehyde hydrate and diacetyl hydrate are rather low. The Brönsted relation thus holds among members of the group. It is interesting that the catalytic activity of choral alcoholate appears to be nearly the same as that of chloral hydrate, although its anion carries an $-OC_2H_5$ rather than an −OH group. It is likely that this substance was hydrolyzed to chloral hydrate.

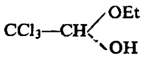
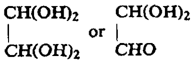
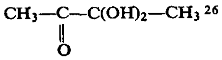
Trichloroethanol, trifluoroethanol (group B) and the sugars (group C) display much lower apparent catalytic powers than substances in group A having comparable pK values. Indeed, it seems probable that the observed rates of reaction of CO_2 did not correspond to catalysis of reaction (2), but could be accounted for by the formation of mono-alkyl carbonates:

$$RO^- + CO_2 \rightarrow RCO_3^-. \tag{6}$$

Reactions of this type have been investigated extensively by Faurholt and co-workers [33,34] and their data on the kinetics indicate that with sucrose, lactose and glucose the whole of the observed rate of reaction in our experiments can be accounted for in this way. In our experiments on substances in this group, the quantity of

TABLE 1.—CATALYTIC POWER OF VARIOUS SUBSTANCES, TEMP. 0°C.

k, rate constant in terms of total concentration of catalyst, l./mole sec; k_B, rate constant for Brönsted base, l./mole sec.

no.	catalyst	pK$_1$ $\mu = 0$	pK$_1$ $\mu = 0{\cdot}28$	maximum concentration of catalyst (ion + acid) M	phosphate buffer pH 7·52 (0° C)		veronal buffer pH 8·75 (0° C)		carbonate buffer, I pH 9·5 (0° C)		carbonate buffer, II pH 10·1 0° C)		remarks
					k	k_B	*k*	k_B	*k*	k_B	*k*	k_B	
	GROUP A Anions of:												
1	telluric acid, $Te(OH)_6$ [11-13a]	8·1	7·76						4·6	4·7	4·75	4·75	
2	germanic acid, $Ge(OH)_4$[14, 15]	9·0	8·85	0·005	0·572	12·8	8·8	21·2	25·5	31·2			
3	arsenious acid, $As(OH)_3$ [14, 16-18]	9·45	9·35	0·01	0·345	23·7	5·2	25·9	19·0	32·4	26	30	
4	silicic acid $Si(OH)_4$ [19]	10·1	11·5 *	0·005					0·9	91	3·1	81·5	
5	chloral hydrate, $CCl_3CH(OH)_2$ [20-22]	10·4	10·2 *	0·0005					30	180	130	294	
5*a*	chloral alcoholate,  $CCl_3{-}CH(OEt)(OH)$		10·2 *	0·0005					32	192			
6	butyl chloral hydrate, $CH_3{-}CH(Cl){-}C(Cl_2){-}CH(OH)_2$	11·4 *	11·2 *	0·001					12·2	620	35	735	
7	glyoxal hydrate,  $CH(OH)_2{-}CH(OH)_2$ or $CH(OH)_2{-}CHO$	13·2 *	13·0 *	0·0075					1·28	4050	5·1	4050	
8	formaldehyde hydrate: (methylene glycol) $CH_2(OH)_2$ [21, 23-25]	13·9	13·7 *	0·02					0·52	8250	2	7980	
9	acetaldehyde hydrate $CH_3{-}CH(OH)_2$ [21, 24-26]	14·0	13·8 *	0·03					0·1235	2470	0·615	3070	hydration equilibria considered
10	diacetyl hydrate,  $CH_3{-}C({=}O){-}C(OH)_2{-}CH_3$ [26]	14·3 *	14·1*	0·025							0·515	5150	hydration equilibria considered

*estimated

TABLE 1.—CATALYTIC POWER OF VARIOUS SUBSTANCES, TEMP. 0°C.

k, rate constant in terms of total concentration of catalyst, 1./mole sec; k_B, rate constant for Brönsted base, 1./mole sec.

no.	catalyst	pK pK_1 $\mu = 0$	pK_1 $\mu = 0{\cdot}28$	maximum concentration of catalyst (ion +) acid M	phosphate buffer pH 7·52 (O°C)		veronal buffer pH 8·75 (O°C)		carbonate buffer, I pH 9·5 (O°C)		carbonate buffer, II pH 10·1 (O°C)		remarks
					k	k_B	k	k_B	k	k_B	k	k_B	
	GROUP B												
	Anions of:												
	trifluoroethanol CF_3CH_2OH [27]		12·8	0·02							0·26	130	
2	trichloroethanol CCl_3CH_2OH [28]		12·7	0·02							0·4	160	
3	acetophenoxime [29]		11·7	0·01							<0·25	<10	
4	H_2O_2		12·2	0·05	0·03				<0·03				
	GROUP C												
	Anions of: pK*	1											
1	glucose [33]	12·9		0·1							0·04	25	
2	fructose [24]	12·5		0·1							0·12	30	
3	sucrose [34]	13·36		0·05							0·39	710	
4	lactose [34]	12·75		0·05							0·36	160	
	GROUP D		pK_2										
1	sulphite, SO_3^{2-} [5]		7·0	0·005	1·0	1·3	0·64	0·65					
2	hydrogen phosphate, HPO_4^{2-}		7·1	0·15		0·016							
3	selenite† SeO_3^{2-} [5]		8·2	0·005 (5°C)	2·08 3·1	12·0 17·9	2·17	2·78					
4	tellurite, TeO_3^{2-} [30–31]		8·0	0·002	4·4	17·7	8·0	20·8	30·0	31·0			
5	phenylarsonate,[32] $C_6H_5AsO_3^{2-}$		8·7							<0·15			
6	phenolate $C_6H_5O^-$		10·2							<0·25			
7	carbonate, CO_3^{2-}	10·5	10·1							<0·1	<0·1		

†experiments with O·2M phosphate buffer, pH 6·83 (O°C) gave $k = 0{\cdot}51$ and $k_B = 12{\cdot}5$

" catalyst " present in the solution was always much larger than the amount of CO_2 absorbed. The carbonates, when formed, hydrolyze slowly. It is therefore not possible to assign true values of k_B to substances in this group. They are almost certainly much less than the apparent values reported in table 1.

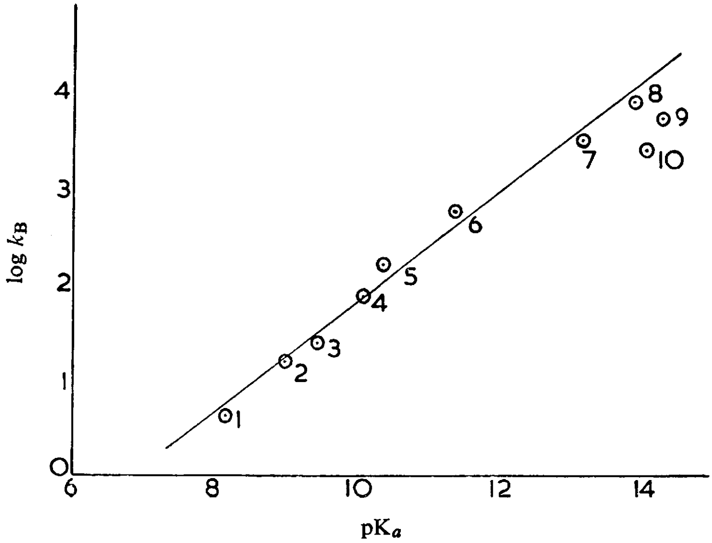


FIG. 1.—Brönsted plot for catalysts of group A at 0°C

The substances in group A do not, as far as is known, form stable carbonates, and in any case the amounts of catalyst were in some cases much less than the amounts of CO_2 absorbed. Hydrogen peroxide and acetophenoxime, which do not form carbonates, exhibit very low catalytic powers as compared to substances in group A with comparable pK values.

The data of Kiese and Hastings [5] (table 2B) indicate that ClO^- and BrO^- are powerful catalysts; the effect of pH on the catalytic power of ClO^- is not significant but with BrO^- it is very pronounced. The latter ion is rather unstable in alkaline solution and this might partly account for the observed behaviour.

TABLE 2A.—DATA OBTAINED BY ROUGHTON AND BOOTH [3] USING THE BUFFERS OF THE APPROPRIATE SPECIES; TEMP. = 0°C

no.	catalyst	pK		k_B, l./mole sec
1	phosphite	pK_2	6·7	0·013
2	arsenate	pK_2	6·8	0·013
3	cacodylate	pK_1	6·3	0·018
4	phosphate	pK_2	7·1	0·017
5	sulphite		7·0	1·89
6	selenite		8·0	3·57
7	borate	pK_1	9·5	0·315
8	tellurate	pK_1	7·8	1·26
	KIESE AND HASTINGS, 5°C [5]			
9	phosphate	pK_2	7·1	≈0·03
10	pyrophosphate	pK_3	6·7	
		pK_4	9·4	≈0·08-0·3
11	borate	pK_1	9·5	≈1·5

TABLE 2B.—DATA OBTAINED BY KIESE AND HASTINGS;[5] TEMP. 5°C. CALCULATIONS HAVE BEEN DONE ON THE BASIS OF $k_u = 0{\cdot}0036\ \text{sec}^{-1}$ AT 5°C

no.	catalyst	pK	phosphate buffer pH = 6·9		phosphate buffer 7·55		borate buffer 9·0		carbonate buffer 10·0	
			k	k_B	k	k_B	k	k_B	k	k_B
		pK_2	pH=7·0							
1	sulphite	7·0	1·09	2·18	1·8	2·3	2·57	2·57	0·41	0·41
2	selenite	8·2	0·68	11·5	2·78 *	15·1	2·25	2·63	0·515	0·52
		pK_1								
3	ClO^-	7·55	1·35	7·45	5·14	10·3	13·5	13·5	13·5	13·5
4	BrO^-	9·0	21·2	2680	72	2020	360	720	180	190

* agrees well with our data.

The data of Roughton and Booth and of Kiese and Hastings indicate that the catalytic power of borate is very low in view of the pK value of boric acid. This material apparently falls in group A and might be expected to give rise to $B(OH)_2O^-$ ions. However, it is known that in aqueous solutions boric acid gives rise to $B(OH)_4^-$[36] which can accept a proton only with simultaneous expulsion of a water molecule.

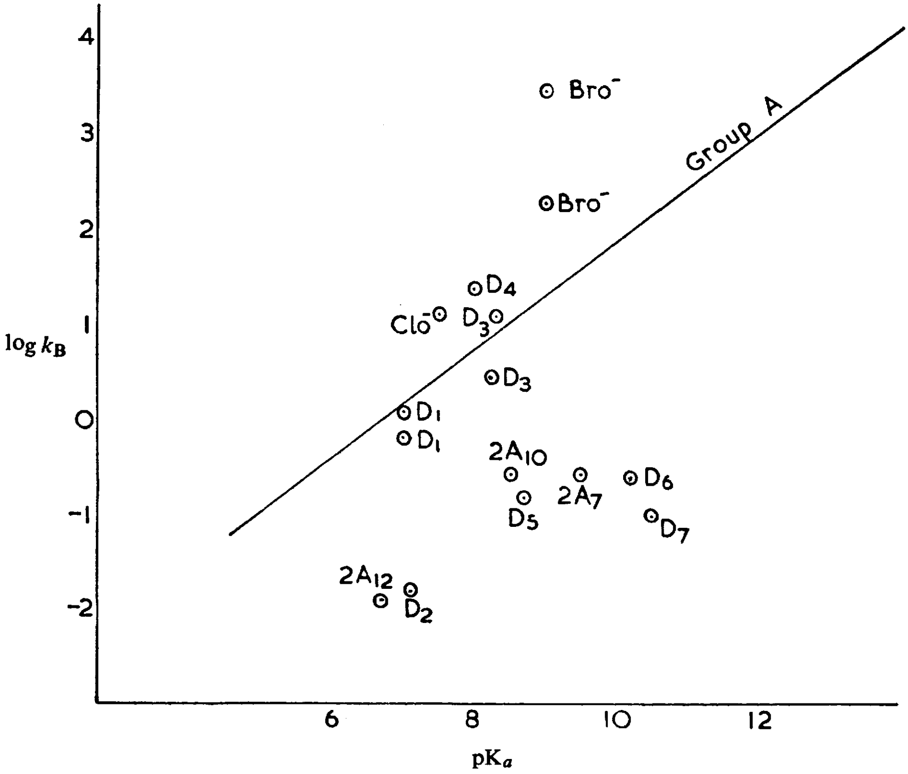


FIG 2.—Catalytic constants of various species at or about 0°C.

In fig. 2 are plotted the results for anions of group D together with some other ions for which the catalytic constants have been evaluated at or close to 0°C. These anions are all apparently of the types in which the residual negative charge is spread over the ion by resonance rather than localized on the oxygen atom from which the hydrogen ion has been removed. All these materials except sulphite, selenite and tellurite, which are discussed below, exhibit much lower catalytic powers than substances in group A with comparable pK values. Bell and Higginson [29] in their extensive experiments on the acid-base catalysis of the hydration of acetaldehyde have observed that charge distribution in the anion plays a very significant role in base catalysis.

Sulphite, $O = S(O^-)_2$, selenite, $O = Se(O^-)_2$, and tellurite, $O = Te(O^-)_2$ have apparently delocalized charges and yet possess catalytic powers comparable to the materials in group A. It appears that there may be a number of special circumstances involved. Both our measurements and those of Kiese and Hastings [5] showed that pH had a pronounced effect on the catalytic activity of sulphite, selenite and tellurite. It has been reported [35] that sulphite has a tendency to acquire a structure of the type $S^+(O^-)_3$ which might account for its comparatively high catalytic power. It is conceivable that selenite ions exist in solution in the hydrated form $(HO)_2Se(O^-)_2$ which would have localized charges. [30a] The extent of hydration may well vary with pH. There is a considerable controversy [30-31,30a] regarding the nature of tellurous acid and it has been suggested that it may well have the structure $Te(OH)_4$ which would give rise to $(HO)_3TeO^-$ and $(HO)_2Te(O^-)_2$.

TABLE 3.—EFFECT OF TEMPERATURE ON CATALYTIC POWER OF ANIONS OF ARSENIOUS AND GERMANIC ACID

pH range 8·5-8·8 ; veronal buffer

no.	temp. °C	$k_{As(OH)_2O^-}$	$k_{Ge(OH)_3O^-}$
1	0	25·9	21·2
2	5	41·4	41·7
3	10	71·5	67·8
4	15	95·5	102

The effect of temperature on the catalytic power of arsenious and germanic acid is recorded in table 3. The data have been correlated by the method of least squares and the following results obtained.

$$As(OH)_2O^-: \log k_B = 9{\cdot}837 + \log T - 2967/T, \ (T \text{ in } {}^\circ K)$$

$$\Delta H^{+} = 13{,}570 \text{ cal/mole}; \ \Delta S^{+} = -2{\cdot}2 \text{ cal/deg. mole.}$$

$$Ge(OH)_3O^-: \log k_B = 11{\cdot}617 + \log T - 3470/T,$$

$$\Delta H^{+} = 15{,}880 \text{ cal/mole}; \ \Delta S^{+} = +6{\cdot}0 \text{ cal/deg. mole.}$$

The relevant data for the hydration and hydroxylation reactions of CO_2 are as follows:

	ΔH^{+}	ΔS^{+}
(*a*) hydration	14,600	−16·8
(*b*) hydroxylation	12,620	+ 1·76.

It appears, therefore, that the essential effect of the catalyst is to change the entropy of activation favourably. A number of base-catalysed reactions are reported to exhibit this characteristic feature. The above figures also suggest that the hydroxylation reaction may itself be regarded as an example of catalysis of reaction (2) by an anion. The pK of water is normally taken as 16·69 (i.e., 14·94+log 55·5) at 0°C. On the basis of fig. 1 it would appear that if it is regarded as a member of group A the pK_a value corresponding to its catalytic power would be about 12. Bell [37] has pointed out that invariably the catalytic effect of OH^- falls well below that corresponding to the apparent pK value of water and the " true " value appears to be in the range 12-13.

From a practical point of view it seems likely that the most powerful catalysts are to be sought among anions of the type of those in group A which do not form stable carbonates. There are not many inorganic substances which belong to group A and which have reasonable solubilities. The hypobromite ion possesses a particularly high catalytic power but suffers from the serious drawback of instability under industrial conditions in addition to being extremely corrosive. The pH values of the carbonate +bicarbonate solutions encountered in industrial practice range from 8·5 to 10 and therefore materials having their pK values in the range 8-11 would be the most attractive, as they would yield sufficient quantities of ions. Arsenite occupies a key position in this group by virtue of its high catalytic power, favourable ionization constant, stability, reasonably high solubility in both acid and salt form, availability and low cost. Inorganic substances like germanate and tellurite have comparable catalytic power and ionization constant but are relatively unstable and have low solubility. Tellurite, like sulphite and selenite, is highly susceptible to oxidation. Technical and economic considerations rule out most of the materials which we have investigated. It is unlikely that there is an alternative inorganic substance which is as effective a catalyst as arsenite and yet possesses its other attractive features. Most of the organic substances are ruled out because of their instability. However, the use of formaldehyde merits further consideration. In spite of its relatively high volatility and tendency to undergo reaction in alkaline solutions it might in certain circumstances find industrial applications. In an equimolal carbonate+bicarbonate solution at 20°C 1 % by weight of formaldehyde would be expected to increase the total rate of reaction of CO_2 eight-fold, an effect comparable to that obtainable with about 0·5 % by weight of As_2O_3, The effect of formaldehyde on the rate of absorption of carbon dioxide in alkaline solutions has already been noted by Riou and co-workers,[38] Killeffer [39] and Fujikawa.[40] In future work, attention will be directed towards higher specific reaction rates.

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[1] Reisenfeld and Mullowney, *Pet. Ref.*, 1959, **38,** no. 5, 161.
[2] Roberts and Danckwerts, *Chem. Eng. Sci.*, in press.
[3] Roughton and Booth, *Biochem. J.*, 1938, **32,** 2049.
[4] Roughton, *Harvey Lectures*, 1943, **39,** 96.
[5] Kiese and Hastings, *J. Biol. Chem.*, 1940, **132,** 267.
[6] Roughton and Booth, *Biochem. J.*, 1946, **40,** 309.
[7] Dixon, *Manmetric Methods* (Cambridge University Press, 1952).
[8] van Krevelen and Hoftyzer, *Chim. Ind., XXIeme Congrés Int. de Chim. Ind.*, 1948, p. 168
[9] Pinsent and Roughton, *Trans. Faraday Soc.*, 1951, **47,** 263.
[10] Pinsent, Pearson and Roughton, *Trans. Faraday Soc.*, 1956, **52,** 1512.
[11] Antikainen, *Suomen kemist. B*, 1955, **28,** 135.
[12] Antikainen, *Suomen kemist. B*, 1957, **30,** 201.
[13] Earley, *J. Amer. Chem. Soc.*, 1959, **81,** 1295.
[13a] Ellison *et al.*, *J. Amer. Chem. Soc.*, 1962, **84,** 1820.
[14] Lourijsen-Teysseore, *Bull. soc. Chim.*, 1955, 1118.
[15] Antikainen, *Suomen kemist. B*, 1957, **30,** 123.
[16] Jander and Hofmann, *Z. anorg. Chem.*, 1958, **296,** 134.
[17] Antikainen and Rossi, *Suomen kemist. B*, 1959, **32,** 185.
[18] Antikainen and Trevanen, *Suomen kemist. B*, 1961, **34,** 3.
[19] Greenberg, *J. Amer. Chem. Soc.*, 1958, **80,** 6509, and personal communication.
[20] Gustafsson and Johanson, *Acta. Chem. Scand.*, 1948, **2,** 42.

[21] Bell and Onwood, paper to be published (personal communication).
[22] Federlin, *Bull. Soc. Chim.*, 1953, no. 10, C-11.
[23] Walker, *Formaldehyde* (Reinhold Publ. Corpn., N.Y., 2nd ed., 1953).
[24] Rumpf, *Bull. Soc. Chim.*, 1946, 546.
[25] Bell and McTigue, *J. Chem. Soc.*, 1960, 2983.
[26] Bell and McDougall, *Trans. Faraday Soc.*, 1960, **56,** 1281.
[27] Henne and Kelly, *J. Amer. Chem. Soc.*, 1952, **74,** 1426.
[28] Ballinger and Long, *J. Amer. Chem. Soc.*, 1960, **82,** 795
[29] Bell and Higginson, *Proc. Roy. Soc. A*, 1949, **197,** 141.
[30] Issa and Awad, *J. Physic. Chem.*, 1954, **58,** 918.
[30a] Brintzinger and Ratanarat, *Z. anorg. Chem.*, 1935, **222,** 317.
[31] Ricketts and Tresselt, *J. Amer. Chem. Soc.*, 1959, **81,** 2305.
[32] Pressman and Brown, *J. Amer. Chem. Soc.*, 1943, **65,** 540.
[33] Thamsen, *Acta Chem. Scand.*, 1956, **10,** 1165.
[34] Smidt and Thamsen, *Acta Chem. Scand.*, 1956, **10,** 1172.
[34a] Bruice and Fife, *J. Amer. Chem. Soc.*, 1962, **84,** 1973.
[35] Sidgwick, *The Chemical Elements and their Compounds* (Oxford University Press, 1950).
[36] Ingri *et al.*, *Acta Chem. Scand.*, 1957, **11,** 1034.
[37] Bell, *Acid-Base Catalysis* (Oxford University Press, 1941); *The Proton in Chemistry* (Methuen, 1961).
[38] Riou *et al.*, *Compt. rend.*, 1927, **184,** 325; 1928, **186,** 1543, 1727.
[39] Killeffer, *Ind. Eng. Chem.*, 1937, **29,** 1293.
[40] Fujikawa, *J. Chem. Soc., Japan, Ind. Chem. Sect.*, 1949, **52,** 39