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The Heterogeneous Catalytic Hydrogenation of Bicarbonate to Formate in Aqueous Solutions

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The kinetics of the hydrogenation of aqueous solutions of HCO_3^- to HCO_2^- over Pd on C catalysts was studied. It was shown that the rate rose with increasing H_2 pressure in accordance with a Langmuir isotherm law. With increasing HCO_3^- concentration the rate passed through a maximum. Measurements of the equilibrium at 35°C indicated a Gibbs free energy change of about −2.2 kcal/mole. The highest concentration of HCO_2^- obtainable at 6 atm H_2 was limited by the common ion effect to 5.8 *M*.

INTRODUCTION

The reduction of bicarbonate to formate is one of the few links connecting inorganic with organic chemistry. From published thermodynamic data (*1*) the change of standard Gibbs free energy in the transformation

$$HCO_3^- + H_2 = HCO_2^- + H_2O \qquad \text{(i)}$$

at 25°C is +3.62 kcal/mole and that of the enthalpy −1.14 kcal/mole. It is, therefore, not surprising that the use of high hydrogen pressure has been advocated to obtain reasonable yields. In one of the earliest quantitative works on this subject (*2*) a 74.7% yield was obtained after 23 h at 70°C and 60 atm hydrogen pressure. More recently (*3*, *4*) up to 50% conversion was obtained with hydrogen at substantially atmospheric pressure.

In our laboratory formate salts have been used as hydrogen donors in various catalytic transfer hydrogenations (*5*). We have also proposed the use of formate as a chemical hydrogen carrier (*6*). Thus we were interested in working out a cycle in which on one hand hydrogen could be used to reduce bicarbonate to formate and on the other formate be made to release hydrogen and to revert back to bicarbonate. This work deals with aspects of the first step, the hydrogenation of bicarbonate to formate, and in particular with the practical limits to obtaining high conversions and rates of reaction.

EXPERIMENTAL

A Parr hydrogenation apparatus (rocking autoclave) was charged with 100 ml of sodium or potassium bicarbonate solution and varying amounts of Pd on C catalyst. The catalysts were purchased from "Engelhard" and contained 50% water and 5 or 10% Pd. Hydrogen was introduced and released three times. Hydrogen was then charged to the desired pressure, the rocking mechanism was activated, and the pressure change with time was monitored. The amount of formate produced was checked occasionally by an enzymatic method (*7*).

KINETICS

Initial Rates

In order to avoid complications due to back-reactions, we applied the method of initial rates to the determination of the kinetics of reaction (i). The initial rates were

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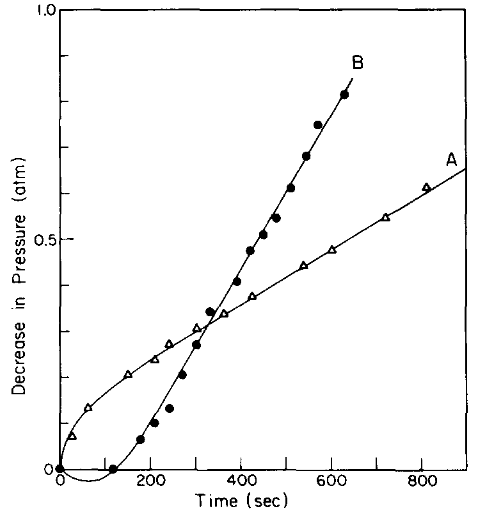

FIG. 1. Decrease in hydrogen pressure with time (10% Pd on C). (A), $KHCO_3$ (0.5 *M*), 4 atm initial pressure, 22°C, 3 g catalyst. (B) $KHCO_3$ (3 *M*), 3.7 atm initial pressure, 25°C, 3 g catalyst.

measured by following the decrease in total pressure on starting the rocking mechanism. Without rocking the pressure did not change, indicating that effective mass transfer was important. It took up to 4 min for the establishment of a constant rate. In experiments with low bicarbonate concentration and at low temperatures the pressure dropped during these initial minutes more rapidly than it did later, after steady-state conditions had been reached. This indicated that during this period hydrogen dissolved in the solution and adsorbed onto the catalyst until saturation or a steady state was reached, possibly activating the catalyst as well. In experiments with high bicarbonate concentration and high temperatures the pressure rose initially before settling down to a constant steady-state rate. This indicated that the gas phase equilibrated with carbon dioxide in the solution. The data points pressure/time beyond the initial disregarded ones lay on a straight line, the slope of which was calculated by linear regression and taken as the initial rate (Fig. 1). With low bicarbonate concentration or pressure, a slight curvature of the plot was encountered; in this case fewer data points were used for calculating the slope (initial rate) by linear regression, sacrificing some accuracy. The cation did not enter the stoichiometric equation of the reaction and apparently exerted little influence, the rate with potassium bicarbonate being similar to that with sodium bicarbonate.

RESULTS AND DISCUSSION

Influence of Hydrogen Pressure

It was seen early in our experiments that at constant bicarbonate concentration the rate increased with pressure until a plateau was reached (Fig. 2). Unfortunately the equipment did not allow us to pursue the course of the rate at still higher hydrogen pressure. The existence of a plateau meant that in this region the order with respect to hydrogen was about zero and limitations imposed by mass transfer of hydrogen could not be of importance.

The existence of the plateau could be rationalized by either of two mechanisms:

(A) Deactivation of the catalyst through reduction by hydrogen to an inactive (perhaps lower valence) state followed by slow reoxidation with the bicarbonate to the catalytic active state. This would be similar to what happens to a vanadium oxide contact catalyst when the O_2/SO_2 ratio is lowered.

(B) Saturation of the catalyst surface

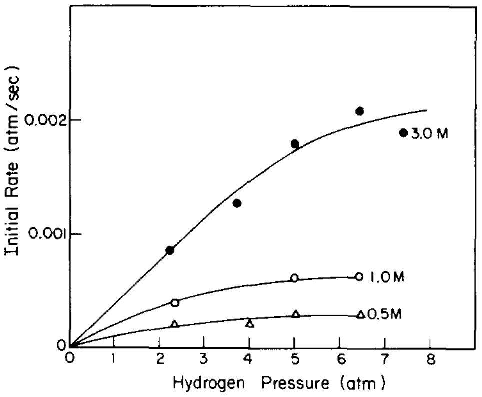

FIG. 2. Rate at different bicarbonate concentrations as a function of the hydrogen pressure. Temperature 35°C, 1 g catalyst (5% Pd).

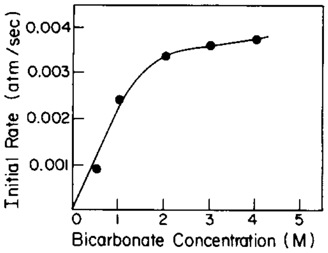

FIG. 3. Rate as a function of $KHCO_3$ concentration at 35°C, 6.44 atm with 3 g catalyst (5% Pd).

with hydrogen by a Langmuir-type adsorption isotherm.

Influence of Bicarbonate Concentration

In Fig. 3 the results for a series of runs with varying potassium bicarbonate concentration are shown. The rate rose linearly with an increasing concentration of bicarbonate and leveled off above a concentration of 1.2 *M*. It is suggested that the failure of the rate to increase linearly at higher bicarbonate concentration is due to the lowering of the solubility of hydrogen in the more concentrated solutions and/or to saturation of the catalyst.

On the basis of these postulates and applying steady-state Langmuir kinetics we should expect the rate at constant temperature to follow the law

$$r = k's(b)hb/(1 + zs(b)h + yb), \quad (1)$$

where r is the rate (atm/s), b is the concentration of bicarbonate (M), h is the hydrogen pressure (atm), $s(b)$ is the solubility of hydrogen in a solution of concentration b, and k', y, and z are constants.

In this equation $r \rightarrow k'b/z$ as $h \rightarrow$ infinity. If we define H as that hydrogen pressure which will cause the rate to be one-half the rate at infinite hydrogen pressure then

$$1/2 = zs(b)H/(1 + zs(b)H + yb),$$

$$1 + yb = zs(b)H; \quad (2)$$

inserting (2) into (1) yields

$$r = khb/(H + h), \quad (3)$$

where $k = k'/z$.

Using Eq. (3) allowed us to check our assumptions irrespective of whatever form the dependence of the solubility on the bicarbonate concentration took. By adjusting H for each set of experiments at constant b until the sum of squares of (ratio of calculated to actual rate -1) was a minimum (method of variance), a provisional estimate of k and H could be obtained. For this purpose additional sets of experiments were carried out, all with potassium bicarbonate and 3 g of catalyst (10% Pd). In Fig. 4 the drawn out curves were plotted by using these estimates of H and k in Eq. (3). The form of the curves fitted the data within the experimental error.

It is customary (*8*) to assume that the solubility of a permanent gas like hydrogen in a salt solution of concentration $[S]$ is given by

$$s(b) = s(0)\exp(-q[S]) \quad (4)$$

and indeed from the solubility data of hydrogen in potassium carbonate (*9*) (we have not found data for bicarbonate) at 15°C we have calculated $s(b) = 0.0184$

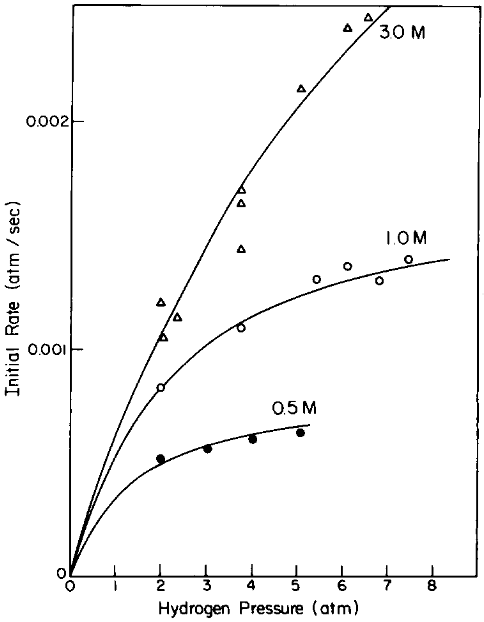

FIG. 4. Rate as a function of hydrogen pressure at room temperature. Drawn out curves from Eq. (3).

TABLE 1

Initial Rate at Room Temperature with 3 g Catalyst (10% Pd)

Hydrogen pressure (atm)	Bicarbonate concentration (*M*)	Rate (actual) (atm/s)10^3	Rate (calculated) (atm/s)10^3
2.02	0.5	0.514	0.487
3.04	0.5	0.558	0.568
4.06	0.5	0.605	0.619
5.08	0.5	0.631	0.655
2.02	1	0.768	0.839
2.02	1	1.09	0.839
3.72	1	1.027	1.090
5.42	1	1.236	1.227
6.10	1	1.285	1.266
6.78	1	1.219	1.299
7.46	1	1.312	1.327
2.02	2	1.033	1.149
3.72	2	1.569	1.646
3.72	2	1.555	1.646
4.06	2	1.760	1.720
6.10	2	1.848	2.059
6.78	2	2.006	2.143
7.46	2	1.918	2.217
7.46	2	2.457	2.217
2.02	3	1.115	1.076
3.72	3	1.704	1.682
3.72	3	1.365	1.682
6.10	3	2.602	2.275
6.10	3	2.502	2.275
7.46	3	1.861	2.530
7.46	3	2.852	2.530

$\exp(-0.634[S])$. Applying this type of function to Eq. (2) gives

$$H = (1 + yb)\exp(qb)/(zs(0)). \qquad (5)$$

Using again the method of variance on the provisional estimate for H obtained above, it was found that the data could best be described by setting $y = 0$. The physical meaning of this was that adsorption of bicarbonate on the catalyst, if it occurred at all, was far from its saturation value. The discrepancy from a first-order law with respect to bicarbonate concentration was solely due to the declining solubility of hydrogen with increasing bicarbonate concentration. Inserting Eq. (4) and setting $y = 0$ transform Eq. (1) to

$$r = k's(0)\exp(-qb)hb/(1 + zs(0)\exp(-qb)h). \qquad (6)$$

After combining the data for different bicarbonate concentrations, we were allowed by the method of variance to find best estimates for the two free parameters of Eq. (6) [$k's(0)$ and $zs(0)$], and for the solubility exponent q. The rates were found to fit the equation

$$r = 0.001574\, hb \exp(-0.648b)/[1 + 0.93h \exp(-0.648\, b)] \text{ atm/s}. \qquad (7)$$

It might surprise one that the exponent for the solubility of hydrogen in potassium carbonate solutions (−0.634) was practically identical with the exponent which gave the best fit for our results with bicarbonate. However, inspection of the published data for other salt solutions (9) showed that the exponents for sodium sulfate, potassium carbonate, and sodium carbonate were all within 1.5% of each other. The closeness of the value for potassium bicarbonate derived from our data lends credence to the general scheme proposed here. In Table 1 the results of our calculation are compared with the experimental data. Figures 5 and 6 show the family of curves calculated from Eq. (6) for rates at constant hydrogen pres-

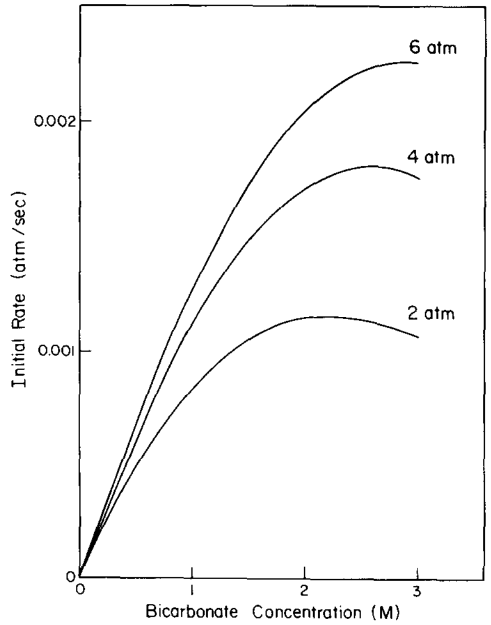

FIG. 5. Family of curves calculated from Eq. (7) describing rate as a function of $KHCO_3$ concentration for constant hydrogen pressure at room temperature (3 g 10% Pd).

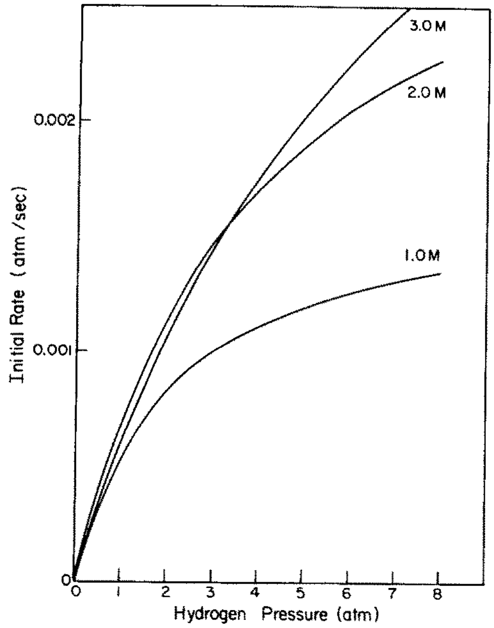

FIG. 6. Family of curves calculated from Eq. (7) describing rate as a function of hydrogen pressure for constant $KHCO_3$ concentration at room temperature (3 g 10% Pd).

sure and at constant bicarbonate concentration, respectively. It should be noted that the curves at constant hydrogen pressure pass through a maximum with increasing bicarbonate concentration. By partial differentiation of the rate equation (6) with respect to b it can be shown that the maximum occurs (see Table 2) when

$$zh \exp(-qb) = qb - 1. \quad (8)$$

Influence of Temperature

Experiments carried out with 1 M sodium bicarbonate, 3 g catalyst (5%), and 6.44 atm between 15 and 50°C gave a value of 4100 for the Arrhenius exponent. Raising the temperature decreased the solubility of hydrogen in the solution and increased the rate constant of the chemical reaction. However, the absorption coefficient for hydrogen (reduced to STP) in water decreased only from 0.0183 at 15°C to 0.0146 at 50°C (*10*), which corresponded to an exponent of −600. Bracketing out the solubility effect the exponent of 4700 would lead to an apparent activation energy of 9.4 kcal/mole. Furthermore, since these experiments were carried out at the plateau for hydrogen, it was the adsorption equilibrium rather than the adsorption kinetics of hydrogen which was involved; adsorption equilibria decline with rising temperature so that the true activation energy relating to the bicarbonate would be higher than the value given above. The relatively low apparent activation energy was, therefore, not necessarily due to diffusion control.

TABLE 2

Bicarbonate Concentration (M) at Which Maximum Rate Is Attained for Varying Hydrogen Pressure (atm)

Hydrogen pressure (atm)	Bicarbonate concentration (M)
1	1.95
2	2.22
3	2.43
4	2.60
6	2.88
8	3.09
10	3.27

Influence of Amount of Catalyst

Different amounts of catalyst were added to 100 ml of 1 M bicarbonate solution in two sets of experiments. Results are given in Table 3. The rate rose linearly with the amount of catalyst up to 3 g catalyst/charge. Above this value the rate increase started to level off. The assumption that hydrogen in the gas phase was in equilibrium with dissolved hydrogen, which gave reasonable results for up to 3 g catalyst, would have to break down when dissolved hydrogen was depleted below the equilibrium value by increasingly fast uptake and chemical reaction. Instead, mass transfer then became rate determining.

Influence of Carbon Dioxide Pressure

It might be thought that the bicarbonate in reaction (i) served as a precursor for carbon dioxide and the latter species reacted

TABLE 3

Influence of the Amount of Catalyst on the Rate

Condition	Amount of catalyst (g)	Temperature (°C)	Initial rate (atm/s)10^3
A	1	17	0.395
	2	22	0.699
	3	17	1.013
	5	22	1.590
B	3	35	2.423
	5	35	3.401
	7.5	35	4.027
	10	35	4.535
	15	35	5.066

Note. A, 1 *M* $NaHCO_3$ at 6.78 atm with 5% Pd; B, 1 *M* $KHCO_3$ at 6.44 atm with 10% Pd.

with hydrogen to give formate. To gauge the effect of added carbon dioxide on the initial rate of reaction, two experiments were carried out at 35°C with 3 *M* potassium bicarbonate and 3 g catalyst. In both runs the initial hydrogen pressure was 3.72 atm, but in the first run 3.72 atm of carbon dioxide was admixed. In this first run carbon dioxide was rapidly absorbed by the solution during the first 150 s during which its pH dropped; thereafter the rate of decrease in pressure drop (assumed due to hydrogenation) was constant at 0.00219 atm/s, while in the experiment without admixed carbon dioxide the measured rate was 0.00207 atm/s. These two virtually equal rates showed that small amounts of carbon dioxide and small changes of pH had no effect on the rate. It could, therefore, safely be argued that bicarbonate rather than carbon dioxide was the active species.

EQUILIBRIUM

We have attempted to determine the equilibrium value for reaction (i) by allowing the reaction to proceed from either side until no further change of pressure could be observed. A 4 *M* solution of potassium formate at 25°C gave a rise in pressure of 5.51 atm which corresponded to 0.814 *M* bicarbonate (vapor space, 360 ml). Since the water concentration of a 4 *M* formate solution is 47 *M* the estimate of the equilibrium constant could be calculated to be 33 *M*/atm. Approaching the equilibrium from the other side at 23°C and starting with 1 *M* potassium bicarbonate and 6.1 atm hydrogen gave a value of 45 *M*/atm. If these estimates were exact it would mean that there was some overshooting of the equilibrium value. However, both bicarbonate concentration and hydrogen pressure at the end of the latter experiment were too low to achieve an accurate value; we considered 38 *M*/atm to be a reasonable estimate for the equilibrium value from which we could calculate the standard free energy change to be −2.2 kcal/mole. The discrepancy of this value from that calculated from Rossini's tables (*1*) has been commented on before (*4*).

CONVERSION

The solubility of formate is high and allows one to make up aqueous solutions of 14 *M*; the solubility of the bicarbonates on the other hand is much lower, the limit at 35°C being 4.4 *M* for the potassium salt and 1.1 *M* for the sodium salt. Considering the use of formate as a hydrogen carrier, we were interested in testing the upper limit of formate concentration obtainable from a slurry of solid bicarbonate in a concentrated solution of the salt. Toward this aim we introduced into our reaction vessel at 35°C a mixture of 0.5 mole of sodium bicarbonate, 100 ml water, and 5 g of catalyst and applied a nearly constant hydrogen pressure of 6 atm. After 28 h, only 0.25 mole of hydrogen was consumed from which we deduced that the final solution was 2.5 *M* in formate. This meager conversion was to be expected since on hydrogenation and further dissolution of sodium bicarbonate the sodium ion concentration increased and thus the solubility of bicarbonate decreased (common ion effect). This caused a decrease in the formate concentration in equilibrium with the bicarbonate concentration at constant hydrogen

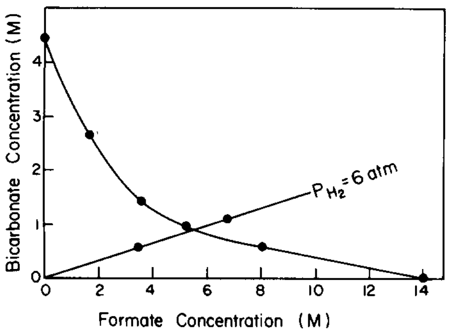

FIG. 7. Solubility of $KHCO_3$ in aqueous solutions containing $KHCO_2$ at 35°C. The straight line shows the calculated equilibrium ratio $KHCO_3/KHCO_2$ for 6 atm hydrogen.

pressure. Repeat experiments with potassium bicarbonate gave essentially similar results. In Fig. 7 the solubility of potassium bicarbonate [B] as a function of potassium formate concentration [F] is shown. On the same plot the equilibrium ratio of [B]/[F] at 6 atm hydrogen is presented. On hydrogenation of a saturated solution of potassium bicarbonate of 4.4 *M*, the concentration of the saturated solution decreases during the course of reaction until at the intersection at 5.8 *M* the chemical equilibrium is reached. This is the maximum attainable formate concentration under these conditions and the value we obtained experimentally.

CONCLUSIONS

It was shown that under mild conditions of temperature and pressure, alkali metal bicarbonates could be reduced over a Pd on carbon catalyst to their respective formate salts. The influence of hydrogen pressure on the rate paralleled a Langmuir isotherm and decreased with increasing pressure. Increasing bicarbonate concentration lowered the solubility of hydrogen so that there was no net increase in the rate above about 2 *M* (depending on the hydrogen pressure).

Conversions were limited by the equilibrium value for the reaction. As a result of the common ion effect the highest concentration of formate obtainable at 6 atm hydrogen at 35°C was found to be 2.5 *M* for sodium formate and 5.8 *M* for potassium formate. Although pressures above 10 atm hydrogen hardly increase the rate of reaction they have a considerable influence on the maximum conversion that can be obtained.

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