Photocatalytic Reduction of Carbonate Ions: Use of Safranine-O

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Abstract: *Photochemical reduction of sodium carbonate was investigated in presence of safranine-O. The progress of the reaction was observed spectrophotometrically at $d_{max} = 410$ m. The effect of pH variation on the formation of formaldehyde and formic acid was investigated. Where two maxima were observed i.e. pH = 6.0 and 10.0. Effect of various other parameter like concentration of carbonate intensity of light etc. The rate of photocatalytic reduction was also studied. One of the most important and vital requirement of the society is energy since the ancient period. Here solar energy and photoreduction of carbonate ions entered the scene. Photocatalysis was number of application like solar energy conversion, synthesis of energy rich products etc. Recently in this field, Ortelli et al. Synthesized methanol and observed the reaction pathway for conversion CO and CO_2 over a CuZr based catalyst while Nerlov et al. studied the influence of CO on the methanol synthesis from CO_2 and H_2 on Cu (100) catalyst. Shen et al.[3] reported the impact of palladium precursors on the catalystic behaviour of Pd/CeO_2 catalysts for the production of methanol from the hydrogenation of CO. Furuya and Hoide et al.[4] studied the electrochemical reduction of CO_2 using different metal electrode. Arakawa et al.[5] used a RuS_2/SiO_2 photocatalyst. Calzaferri et al.[6] also used volites as a porous carrier material Tryk et al.[7] noted complete water splitting into H_2 and O_2 by using microheterogeneous semiconductor system in solar irradiation Kim et al.[8] produced hydrogen from the decomposition of methane by domestic activated carbons. Liguras et al.[9] reported that the production of hydrogen is possible during the partial oxidation of ethanol using R_4 as a catalyst.*

Keywords: Photochemical reduction, Carbonate, Safranine-O, Formaldehyde, Formic acid

1. Experimental

0.105 g of sodium carbonate was dissolved in 250 mL of doubly distilled water, so that the concentration of carbonate solution was 1.0×10^{-2} M. It was diluted to give 1.0×10^{-4} M solution. Four parts of this solution were placed under following conditions -
1) The first beaker containing only carbonate solution was kept in dark.
2) The second beaker containing Na_2CO_3 solution only was kept in sunlight.
3) One mL of safranine-O dye solution (5.0×10^{-6} M) was added to third beaker containing carbonate solution and it was kept in dark.
4) One mL of safranine-O dye solution (5.0×10^{-6} M) was added to fourth beaker containing carbonate solution and it was kept in sunlight.

Aliquots were drawn at different time intervals and then the amount of formaldehyde and formic acid were measured. It was observed that solutions of first three beakers had the same optical density (after treatment with Nash reagent) while the solution of fourth beaker showed an increase in its initial value of optical density. The above experiment confirms that the reaction between carbonate and dye solution is neither chemical nor photochemical but it follows the photcatalytic pathway.

2. Results and Discussion

Photogeneration of Formaldehyde And Formic Acid
The photochemical production of the formaldehyde and formic acid from sodium carbonate solution was investigated spectrophotometrically using Nash reagent ($\lambda_{max} = 410$ nm). For this purpose, safranine-O solution was used as a photocatalyst. A change in the yield of the photoproducts was observed with time of irradiation.

A calibration curve drawn earlier between optical density and corresponding known concentrations of formaldehyde was used to determine the concentration of the formaldehyde in test solution. The formic acid was also estimated in the similar manner. The formic acid produced during the photoreduction of sodium carbonate solution was reduced to formaldehyde with magnesium powder and hydrochloric acid. Then the amount of formaldehyde (corresponding to formic acid) was estimated spectrophotochemically. Here, it has been assumed that formic acid is completely reduced to formaldehyde under these conditions. Again the amount of formaldehyde was determined in this solution using Nash reagent. The difference of the two observations corresponding to the amount of formic acid present in the test solution. The results are reported in Table 1 and graphically represented in Figure i
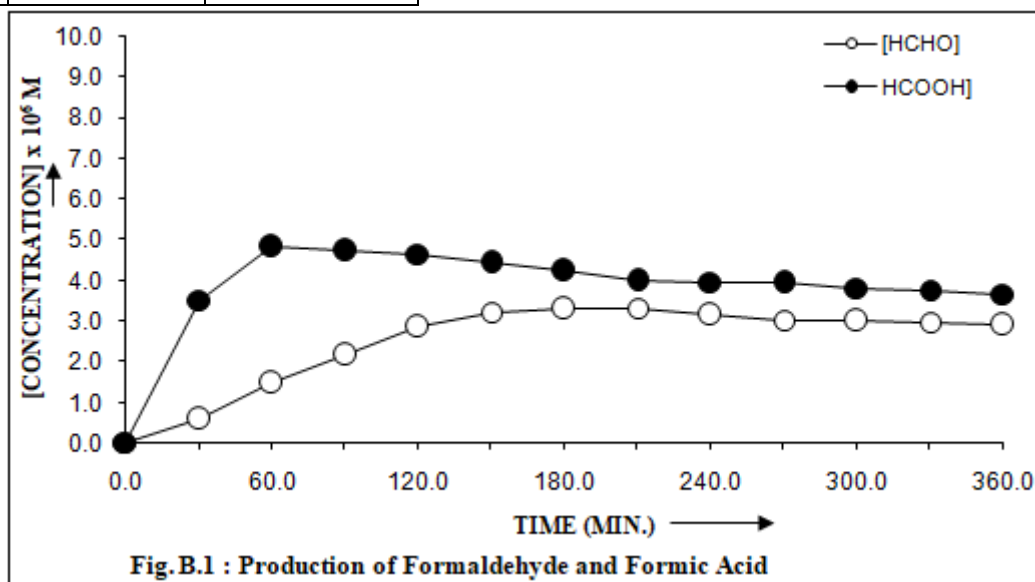
Table 1: Photogeneration of Formaldehyde and Formic Acid

[Safranine-O] = 5.0×10^{-6} M Temperature = 303 K
[Na_2CO_3] = 1.0×10^{-4} M Intensity = 21.0 mW cm^{-2}

Time (Min.)	[HCHO] x 10^6 M pH = 6.0	[HCOOH] x 10^6 M pH = 10.0
0.0	0.00	0.00
30.0	0.58	3.50
60.0	1.47	4.80
90.0	2.15	4.72
120.0	2.85	4.63
150.0	3.20	4.40
180.0	3.28	4.20
210.0	3.30	3.98

240.0	3.12	3.95
270.0	3.00	3.92
300.0	2.98	3.80

330.0	2.95	3.75
360.0	2.88	3.65

Fig.B.1 : Production of Formaldehyde and Formic Acid

Effect of pH

The pH is likely to affect the photocatalytic reduction of carbonate and, therefore, the effect of pH on the photoproduction of formaldehyde and formic acid was investigated in pH range (4.0 to 11.0). The results are reported in Table 2 and are graphically represented in Figure 2

Table 2: Effect of pH

[Safranine-O] = 5.0×10^{-6} M Temperature = 303 K

[Na_2CO_3] = 1.0×10^{-4} M Intensity = 21.0 mW cm^{-2}

pH	[HCHO] x 10^6 M	[HCOOH] x 10^6 M
4.0	2.80	3.90
5.0	3.00	4.12
6.0	3.30	4.75
7.0	2.90	4.43
8.0	2.80	4.40
9.0	2.95	4.45
10.0	3.10	4.80
11.0	2.80	4.41

It has been observed that the production of formic acid was optimum at pH = 10.0 and of formaldehyde at pH = 6.0 in sodium carbonate solution. It was observed that the amount of formaldehyde and formic acid initially increased upto pH 6.0 and then decreases. On further increase in pH, another maxima was observed at pH = 10.0. It is concluded from these observations that the photoreduction of carbonates not only depends on pH of the medium but also on some other parameters.

It may be also explained on the basis of that in the photoreduction of carbonate ions into formic acid and then into formaldehyde is attributed by different species. These may be free electrons in conduction band or hydrated electron in one case and superoxide anion radical in the other. In case of carbonate, the reduction in acidic medium proceeds in the two stages and in the first step, carbonate is reduced into formic acid. It involves carbon dioxide anion radical as an intermediate, which will react with water to give formic acid, hence this is one electron reduction

process. On the other hand, in alkaline medium, OH radicals generated by reaction between hydroxyl ions and holes will be responsible for formation of carbon monoxide and O_2. In a subsequent step, carbon monoxide will react with OH$^-$ ions to form formate ions. Hence, two maxima at pH = 6.0 (in acidic range) and pH = 10.0 (in alkaline range) were obtained.

Effect of Sodium Carbonate Concentration

The effect of concentration of sodium carbonate on the production of formaldehyde and formic acid was observed using safranine-O as a photocatalyst. With increasing concentration of carbonate the yield of formaldehyde and formic acid also increases. The results are represented in Table 3. and graphically represented in Figure 3

Table 3: Effect of Sodium Carbonate Concentration

[Safranine-O] = 5.0×10^{-6} M Temperature = 303 K

Intensity = 21.0 mW cm^{-2}

[Na_2CO_3] x 10^4 M	[HCHO] x 10^6 M pH = 6.0	[HCOOH] x 10^6 M pH = 10.0
0.5	3.10	4.78
1.0	3.30	4.80
2.0	3.17	4.82
3.0	3.19	4.85
4.0	3.20	4.88
5.0	3.25	4.90
6.0	4.68	4.92
7.0	3.28	4.95
8.0	3.30	5.00
9.0	3.52	5.02
10.0	3.53	5.03

It is clear from the observed data that photocatalytic reduction of carbonate increases on increasing its concentration. This may be explained on the basis that on increasing the concentration of carbonate, more carbonate ions are available for photoreduction and hence the yield of products also increases. This rise in concentration is large for lower concentrations but the effect is suppressed in the higher concentration range. It may be due to the hindrance in

the movement of carbonate ions to reach excited dye molecules in the desired time limit.

Effect of Safranine-O- Concentration

The effect of variation of safranine-O concentration on the yield of formaldehyde and formic acid was also studied. It was found that the yield of photoproducts was optimum at a particular concentration of the dye i.e. [Safranine-O] = 5.0 x 10^{-6} M. These variations are summarised in Table 4 and graphically presented in Figure 4

Table 4: Variation of Safranine-O Concentration
$[Na_2CO_3]$ = 1.0 x 10^{-4} M Temperature = 303 K
Intensity = 21.0 mW cm^{-2}

[Safranine-O] x 10^6 M	[HCHO] x 10^6 M pH = 6.0	[HCOOH] x 10^6 M pH = 10.0
2.0	2.20	3.95
3.3	2.80	4.25
5.0	3.30	4.80
7.0	2.85	4.42
8.5	2.80	4.39
10.0	2.76	4.36
12.0	2.70	4.33
14.0	2.64	4.27
16.0	2.62	4.24
18.0	2.61	4.21
20.0	2.60	4.18

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7.0	2.85	4.42
8.5	2.80	4.39
10.0	2.76	4.36
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It was observed that the concentration of safranine-O necessary for efficient conversion of carbonate into energy rich products like formic acid and formaldehyde is ∼ 5.0 x 10^{-6} M. The lower concentration of safranine-O gives a poor yield of photoproducts because of the limited number of dye molecules available in the system for excitation and consecutive donation of the electrons to the carbonates, whereas the larger concentrations of dye again resulted into the lower yield of products because of the lowering of intensity of light reacting the interior reaching species as the major part of light was observed by the dye molecules presents in the path.

Effect of Light Intensity

To observe the effect of light intensity on the photogeneration of products. The distance between light source and exposed surface of solution in reaction vessel was changed. The results are given in following Table 5 and represented graphically in Figure 5

Table 5: Effect of Light Intensity
[Safranine-O] = 5.0 x 10^{-6} M Temperature = 303 K
$[Na_2CO_3]$ = 1.0 x 10^{-4} M

Intensity [I] (mWCm^{-2})	$\log_{10}$ I	[HCHO] x 10^6 M pH = 6.0	[HCOOH] x 10^6 M pH = 10.0
5.0	0.6989	2.80	4.31
7.0	0.8450	2.85	4.38
9.5	0.9778	2.90	4.45
11.5	1.0606	2.95	4.52
13.9	1.1430	3.00	4.58
16.0	1.2041	3.15	4.65
18.0	1.2552	3.18	4.75
21.0	1.3222	3.30	4.80

The results obtained above indicates that the yield of the products does not show a linear increase with an increase in the light intensity, however, a linear behaviour was observed between $\log_{10}$. I and the yields of formaldehyde and formic acid. When light sources of higher intensities were used, then more amounts of formic acid and formaldehyde were obtained in a smaller time of illumination. A decrease in the yield of photoproducts was also observed with the light sources of poor intensities. An increase in the light intensity increases the number of photons per unit area striking the dye molecules and there is a corresponding increase in the photoreduction of carbonate to formaldehyde and formic acid. However, increase in light intensity will also raise the

temperature of the solution, so a water filter was used to cut off thermal radiations and the light intensity of medium order (21.0 mWcm^{-2}) was used for all variations.

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