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P A R T I

SYNTHESIS OF LACTIC ACID FROM ACETALDEHYDE,

CARBON MONOXIDE AND WATER

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Among the old materials that have found new and exciting uses as a result of the development of high pressure technology is carbon monoxide<sup>1,2</sup>. Its reactivity is generally attributed to the existence of free electrons in its molecule. Pauling<sup>3</sup> postulates the structure of carbon monoxide to be represented by resonance between



with structures (a), (b) and (c) contributing about equally to the normal state of the molecule.

The potential availability of carbon monoxide as a cheap raw material for chemical synthesis is indeed enormous<sup>1</sup>. For industrial purposes, coal, coke, and naturally occurring hydrocarbons like petroleum and natural gas are the primary sources of carbon monoxide. Perhaps the largest source of carbon monoxide is to be found in the gases made from coal and coke by blue water gas generators, producers, blast furnaces, and coke ovens. Blue water gas contains the highest percentage of carbon monoxide and is most frequently employed as a source of pure carbon monoxide. Even higher proportions of carbon monoxide may be obtained by blowing a water gas set with carbon dioxide,

instead of steam, over hot coke. In areas producing natural gas and petroleum, carbon monoxide may be produced by reacting the hydrocarbon gases with oxygen, air, steam, or carbon dioxide. Various by-product gases also contain carbon monoxide in sufficient concentration for use on a limited scale. There is no doubt that the production of fuel gases containing carbon monoxide must be in very large quantities. With such vast resources for carbon monoxide, its use as a chemical raw material is certainly one of great economic interest.

High pressure reactions involving carbon monoxide lead to the synthesis of various technically important organic compounds. These may be grouped as follows :

I. Reactions of carbon monoxide and hydrogen: These may be

summarised as follows :

Process	Catalysts	Promoters	Temperature	Pressure	Products
Fischer-Tropsch Synthesis	Fe, Co, Ni	ThO <sub>2</sub> , MgO Al <sub>2</sub> O <sub>3</sub> , K <sub>2</sub> O	150-350°C.	1-30 atm.	Paraffinic and olefinic hydrocarbons varying from methane to waxes; small to large quantities of oxygenated compounds.
	Ru		150-250°C.	100-1000 atm.	
Methanol Synthesis	ZnO, Cu, MnO Cr <sub>2</sub> O <sub>3</sub>		200-400°C.	100-1000 atm.	Methanol
Higher Alcohol Synthesis	ZnO, Cu, MnO Cr <sub>2</sub> O <sub>3</sub>	alkali	300-450°C.	100-400 atm.	Methanol and higher alcohols
Iso Synthesis	ThO <sub>2</sub> , ZrO Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	400-500°C.	100-1000 atm.	Saturated branched hydrocarbons

II. Reactions of carbon monoxide, acetylene and water or other compounds containing active hydrogen atoms, -- the so-called carboxylation of acetylene which leads to the synthesis of acrylic acid and its derivatives. The development of this type of reactions was marked by the use of carbonyls of cobalt, nickel and iron as catalysts. These new reactions and new catalysts are of great interest and potential value. They permit the production of numerous derivatives of acrylic acid, such as esters, amides, acid anhydrides, thioesters, etc. The process may also be employed for any substituted acetylenes.

III. Reactions of carbon monoxide, olefins or olefinic compounds, and water or compounds containing active hydrogen atoms: These reactions lead to the synthesis of saturated carboxylic acids and their derivatives, lactones and alcohols. The type of catalysts used is the same as that used for acetylene and acetylenic compounds. A part of this thesis comprises of the reaction between carbon monoxide, ethylene and water to synthesise propionic acid.

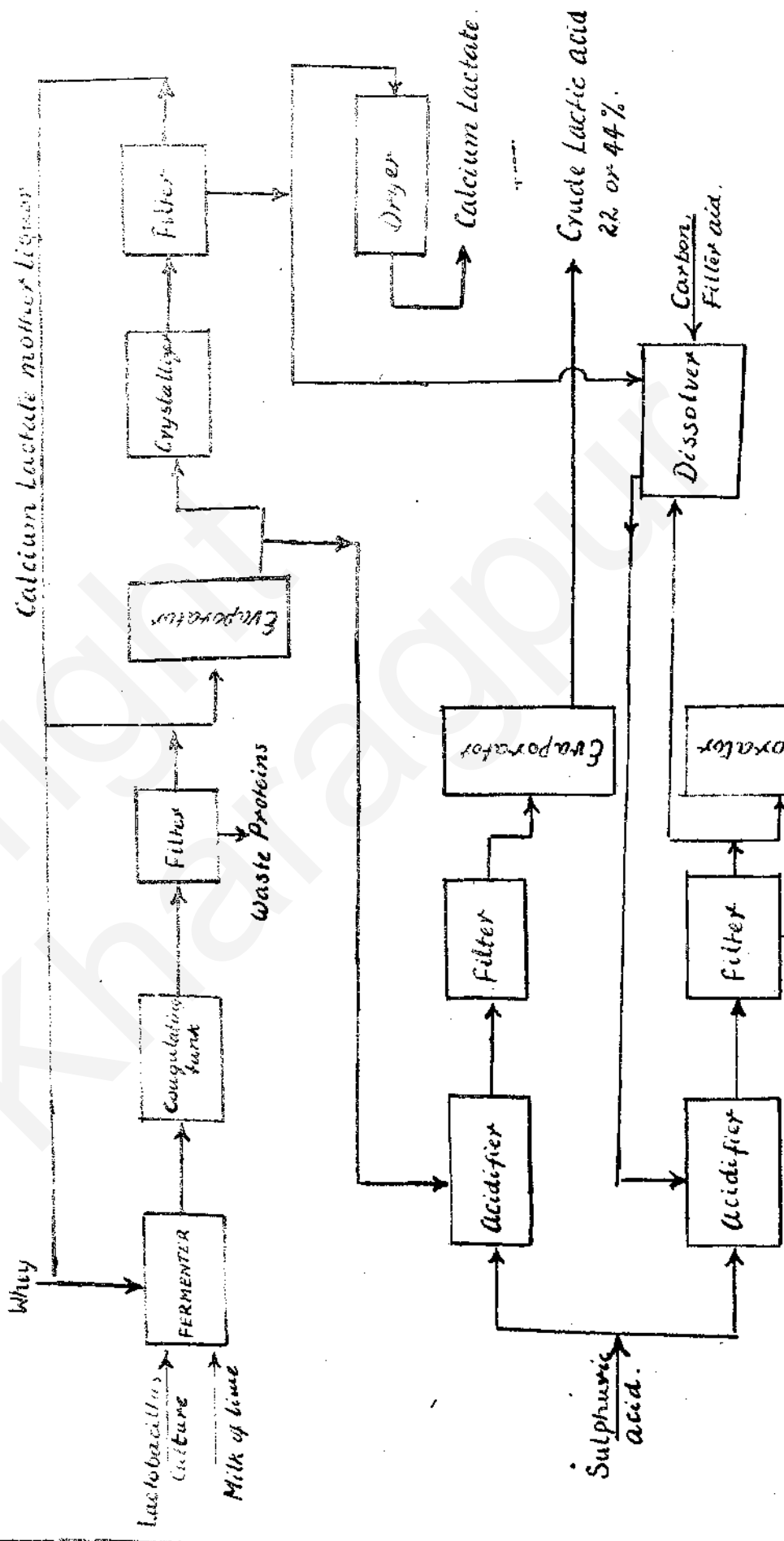
IV. Reactions of carbon monoxide with water, alcohols, aldehydes, etc., to give saturated carboxylic acids: In this type of reaction, which has been utilised for the work presented in this thesis, carbon monoxide reacts with water and/or an organic compound to produce saturated carboxylic acids and esters<sup>4-12</sup>. As examples may be cited the syntheses of formic acid from water<sup>13-28</sup>, acetic acid from methanol<sup>29-40</sup>, propionic acid from ethanol<sup>41-43</sup>, adipic acid from tetrahydrofuran<sup>44</sup>, glycollic acid from formaldehyde and water<sup>45-53</sup>, lactic acid from acetaldehyde and

water<sup>54,55</sup>, benzoic acid from chlorobenzene and water<sup>56</sup>, iso-butyric acid from n- or iso-propanol and water<sup>57</sup>, chloroacetic acid from formaldehyde and hydrochloric acid<sup>58</sup>, etc. In a number of similar reactions, substitution of water by alcohols produces corresponding esters of carboxylic acids<sup>59,60</sup>.

Among the catalysts that have been used for such syntheses are: mineral acids like hydrochloric acid and sulphuric acid; acid salts like potassium acid sulphate and sodium acid phosphate; phosphoric acid, phosphates, phospho-molybdates; boron trifluoride, fluoboric acid and other complexes of boric acid with hydrofluoric acid; halogen gases, especially chlorine; activated carbon; heavy metal salts such as zinc and cuprous chlorides; oxides and silicates of chromium, molybdenum, tungsten, etc.; oxides of thorium, zirconium, titanium, aluminium, magnesium, vanadium, boron and alkali and alkaline earth metals; aliphatic carboxylic acids like formic, acetic acids, etc.; ammonium halides; metal carbonyls with small quantities of halides; metallic halides and hydriodic acid; cobalt, iron, nickel in the reduced state, etc.

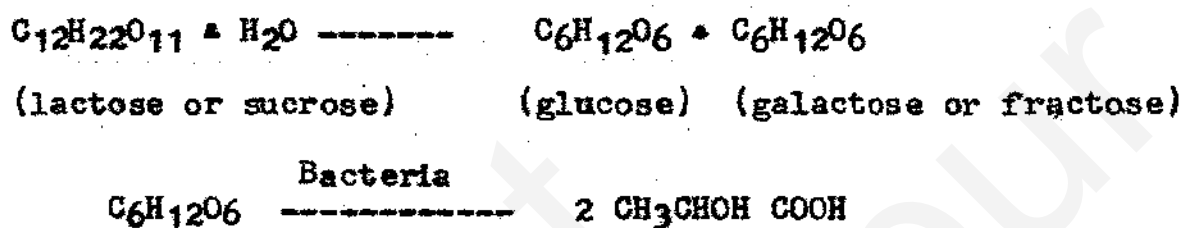
There are no published papers on the synthesis of lactic acid from acetaldehyde, carbon monoxide and water. Hardly there are one or two patents. A patent by Loder<sup>55</sup>, discloses a process which involves the reactions, in the presence of a solvent and in the liquid phase, of carbon monoxide and a compound of the general formula  $RCH_2CHO$  in which R represents H or an alkyl, aralkyl, cyclic or alicyclic radical, under super atmospheric pressure and at temperatures of 50-350°C; e.g.

Calcium Lactate mother liquor



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lactic acid is prepared from carbon monoxide, acetaldehyde in the presence of  $H_2SO_4$  as a catalyst at 130-200°C under 900 atms. pressure. Lactic acid is prepared from whey by fermentation<sup>65</sup>. Flow sheet of process is given in Figure 5. The reaction which occurs may be given by the following equations :



The commercial acid is the inactive or racemic form, consisting of mixture of dextro and levo forms and is sold as a solution containing about 22 or 44 or 85 percent acid and some organic impurities.

A considerable portion of the acid (more than 80 percent) is used for delimiting in tannery operations and for acid dyeing of wool. A much more recent use is as a plasticiser and catalyst in the casting of phenol-aldehyde resins. Some enters the medical field in the form of a very pure calcium lactate for calcium metabolism derangements. Increasing amounts are used in food and beverage products because of its pleasing taste and marked preservative action. If the price of lactic acid could be reduced markedly, there is no doubt that its use as a chemical intermediate would also be expanded.

The method of manufacture of lactic acid industrially depends largely on the raw material sources of the producer. A strong raw material position determines to a considerable extent whether or not a



given manufacturer can enter the field economically.

As the cost of the agricultural commodities is increasing now days, and as stated earlier, the potential availability of carbon monoxide as a cheap raw material for chemical synthesis is plenty, it may be conjectured that in future, the synthesis of lactic acid from acetaldehyde, carbon monoxide and water would be more economical than the fermentation process.

A number of catalysts, especially of an acidic character as stated earlier, have been employed for the synthesis of the carboxylic acids from carbon monoxide. As is well known, nickel<sup>61,62</sup> and other elements of the I transition group and their salts have in recent years been increasingly employed in organic synthesis. The use of halide catalysts, particularly of nickel, has been reported for carboxylic acid synthesis by Reppe and Kutepow<sup>12</sup>, Carpenter<sup>15</sup>, and Woodhouse<sup>11</sup>. These catalysts have been the subject of an intensive investigation by Bhattacharyya and his coworkers and have been employed by them for the syntheses of acetic<sup>31-34</sup>, propionic<sup>41,42</sup>, formic<sup>14</sup>, adipic<sup>44</sup>, glycolic acids<sup>45-47</sup>, and ethyl propionate<sup>63,64</sup>.

In the present work, halides of nickel, cobalt and iron, particularly the iodides, have been systematically studied for the synthesis of lactic acid from acetaldehyde, carbon monoxide and water.