

622. The Synthesis of Aliphatic Acids by the Interaction of Olefins with Carbon Monoxide and Steam, and Related Reactions.

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It is shown that ethylene and carbon monoxide, in the presence of a suitable catalyst and at temperatures of 250° and upwards, can unite with neutral or basic molecules, such as water, ethanol, benzyl alcohol, ammonia, and aniline, to give acids, esters, and amines. The synthesis of propionic acid by this reaction has been studied at 150—400 atmospheres and 250—330°. The yield of acid in the products depends on the relative rates of its formation and thermal decomposition and also on the extent to which carbon monoxide undergoes decomposition to the dioxide.

It has long been known that, under suitable conditions of temperature and pressure, olefin will react with steam and with steam and carbon monoxide to give alcohols and acids, respectively. The former reaction is reversible and its equilibrium constants for ethylene, propylene, and butene have been measured over a wide range of temperatures (Stanley, Youell, and Dymock, *J. Soc. Chem. Ind.*, 1934, **53**, 205T). There are few quantitative results in the literature on the acid synthesis, although numerous patent specifications recommend specific catalysts and claim yields of 40—80% of acid based on the ethylene consumed.

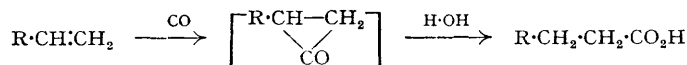
Hardy (*J.*, 1936, 364) describes experiments in which a mixture of ethylene, carbon monoxide, and steam was passed through phosphoric acid at 290—300° and 150 atmospheres. He found that, for every molecule of ethylene converted into acid, approximately three were hydrated and two were polymerised. Propylene gave a mixture of isobutyric acid and homologues, and but-2-ene produced pivalic, α -methylbutyric, and higher acids. No indication is given of the yield obtained in these cases but, since a hydration catalyst was employed and considerable quantities of alcohol were simultaneously formed, they were probably not high.

In a F.I.A.T. report (No. 273), Reppe describes work on the synthesis, in which a nickel catalyst was employed at 270° and 200 atmospheres. He states that conversions of 95% were obtained, but this figure may refer to the results of re-cycling.

Hardy considers the formation of acids must be due primarily to activation of the olefin molecule which is then able to unite with carbon monoxide, reaction being completed by addition of the elements of water :

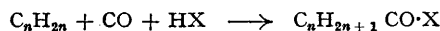


Reppe also considers that reaction occurs first between the olefin and oxide to give a *cyclo*-propanone ring which then undergoes hydrolytic fission :



He further states that, in the reaction, water may be replaced by alcohol, ammonia, or an amine.

The experiments described below were designed to obtain quantitative information about the conditions favourable to the syntheses of the pure acid and of its esters and amides. They indicate that there is a general reaction of the type :



where HX is a neutral or basic molecule; whilst pressure is found to favour this reaction, there may be an upper limit to the pressure which can usefully be employed owing to the simultaneous occurrence of the reaction $2\text{CO} \longrightarrow \text{CO}_2 + \text{C}$ which removes one of the reactants from the system.

Synthesis of Propionic Acid.—The reaction between ethylene, carbon monoxide, and water was carried out in a static system, with a stoichiometric mixture, in the presence of a reduced nickel catalyst. The influence of temperature, pressure, and time of contact on the yield of acid were determined.

(i) *The effect of time.* At 248 atmospheres and 300°, the reaction proceeds at a measurable rate giving gaseous and liquid products, the latter yielding mainly an aqueous fraction containing most of the acid and a small quantity of a lighter fraction containing polymerised hydrocarbon.

TABLE I.

Products from the reaction of a $\text{C}_2\text{H}_4 + \text{CO} + \text{H}_2\text{O}$ mixture at 248 atmospheres and 300°.

Duration of reaction, hrs.	Gaseous products, % by vol.					Yield of acid, %, based upon C_2H_4 in reactants.
	C_2H_4 .	CO.	CO_2 .	C_2H_6 .	H_2 .	
1	32.0	34.0	16.2	17.4	0.4	20.6
1.5	26.4	30.2	19.3	23.7	0.4	42.7
2	23.6	34.7	16.2	24.8	0.7	46.6
2.5	20.7	25.2	26.2	27.8	0.1	34.1
3	9.4	10.4	39.8	40.3	0.1	6.6
4	5.8	6.9	42.9	42.3	2.0	2.6
6	2.4	3.8	46.3	47.1	0.4	0.1

The variation in the products with time is shown in Table I. The considerable quantities of ethane and carbon dioxide, in approximately equal proportions, in the gaseous products suggest that formation and thermal decomposition of propionic acid occur simultaneously. In the early part of the reaction, the rate of acid formation would exceed that of its decomposition and the quantity surviving in the product would increase. Towards the end of the reaction, decomposition would occur faster than synthesis and eventually little or no acid would remain.

That propionic acid undergoes decomposition at 300° has been confirmed by a series of experiments in which the pure acid was maintained at this temperature for 2 hours in contact with a reduced-nickel catalyst. The results for a range of initial pressures are summarised in Table II. The small quantities of hydrogen found in both series of experiments are probably formed by decomposition of ethane. Whereas Hardy showed that both formation and polymerisation of alcohol occurred over phosphoric acid, no alcohol and only a small amount of polymer were produced in our experiments over nickel.

TABLE II.

Thermal decomposition of propionic acid at 300°, in contact with a reduced-nickel catalyst.

Pressure of acid, atms.	Acid decomposed, %.	Gaseous products, % by vol.			
		CO_2 .	CO.	C_2H_6 .	H_2 .
26.5	9.7	49.0	1.2	49.4	0.4
50.0	6.8	50.4	1.8	47.1	0.7
79.5	5.7	48.1	2.7	49.0	0.2
106.0	4.7	48.8	2.2	48.4	0.6

TABLE III.

Products from the reaction of a $\text{C}_2\text{H}_4 + \text{CO} + \text{H}_2\text{O}$ mixture at 248 atmospheres and various temperatures.

Reaction temperature.	Duration of reaction, hrs.	Gaseous products, % by vol.					Yield of acid, %, based upon C_2H_4 in reactants.
		C_2H_4 .	CO.	CO_2 .	C_2H_6 .	H_2 .	
250°	1	49.0	48.1	2.9	—	—	4.9
	2	42.6	47.6	7.8	2.0	—	28.8
300	1	32.0	34.0	16.2	17.4	0.4	20.6
	2	23.6	34.7	16.2	24.8	0.7	46.6
330	1	20.0	4.1	51.4	23.8	0.7	9.9

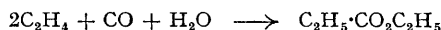
(ii) *The effect of temperature.* Experiments were carried out at 250°, 300°, and 330°, the initial pressure of reactants being 248 atmospheres. The results summarised in Table III

indicate that, at the lower temperatures, although the synthetic reaction is slow, thermal decomposition of the acid is still taking place. At 330°, both reactions proceed rapidly and very little acid survives after 1 hour. The drop in the percentage of carbon monoxide in the products of this experiment, combined with a large increase in the ratio of carbon dioxide to ethane, suggest that some decomposition of carbon monoxide is taking place; a considerable amount of carbon was in fact deposited on the catalyst during this experiment.

(iii) *The effect of pressure.* A series of experiments carried out at 300° and pressures of 1, 150, 248, and 400 atmospheres showed that, whilst at the lower pressure no detectable reaction took place, at 150 atmospheres the yield of acid was 10.4% and at 248 atmospheres had risen to 46.6%. At 400 atmospheres, the yield, contrary to expectation, dropped suddenly, an effect attributable to deposition of carbon on the catalyst resulting from decomposition of the carbon monoxide.

It would appear from the above results that the reduced-nickel catalyst is active in promoting both the synthesis and the thermal decomposition of propionic acid and also the decomposition of carbon monoxide. Increase of pressure favours the synthesis and the reaction $2\text{CO} \longrightarrow \text{CO}_2 + \text{C}$, and tends to prevent decomposition of the acid. Increase of temperature lowers the yield of acid and favours decomposition of carbon monoxide. The optimum conditions in respect of yield of acid are a reaction temperature of 300° and a pressure of 250 atmospheres.

The Synthesis of Esters.—In the above experiments, stoichiometric proportions of the reactants were used for the synthesis of acid. Further experiments were carried out to ascertain whether, by employing an excess of olefin, esters could be produced, according to the reaction



With a reduced-nickel catalyst, only traces of ester were found in the products. When, however, a mixed catalyst consisting of reduced nickel and phosphoric acid, containing 2% of copper phosphate was used, yields of ester representing about 5% of the ethylene in the initial gases were obtained. The results for several mixtures of various compositions are given in Table IV.

TABLE IV.
Synthesis of ethyl propionate.

Reaction temperature.	Total pressure, atms.	Composition of initial mixture. $\text{C}_2\text{H}_4 : \text{H}_2\text{O} : \text{CO}$.	Free acid, %.	Ester, %.
255°	173	6 : 3 : 2	3.2	5.4
300	165	6 : 2 : 2	7.3	2.1
300	221	6 : 3.5 : 4	25.0	5.4
325	221	6 : 3.5 : 3.5	6.4	0.8

Synthesis of isoButyric Acid.—A stoichiometric mixture of propylene, carbon monoxide, and steam in the presence of a reduced-nickel catalyst at 300° and 220 atmospheres gave 2.8% of isobutyric acid. When the amount of olefin in the initial mixture was doubled and all other conditions were kept constant, the yield was raised to 5.2%. *n*-Butyric acid and isopropyl alcohol were not found in the products.

Synthesis of Propionanilide.—A 2 : 4 : 1 mixture of ethylene, carbon monoxide, and aniline at 300 atmospheres and 325° in the presence of a reduced-nickel catalyst gave 46.2% of propionanilide (based upon the aniline used). The product consisted of a semi-solid mass from which the anilide was obtained by recrystallisation.

Synthesis of Benzyl Propionate.—A 3 : 3 : 1 mixture of ethylene, carbon monoxide, and benzyl alcohol at 250 atmospheres and 300°, in the presence of a reduced-nickel catalyst, gave 9.2% of ester (based upon the alcohol used). At 335° and 275°, the yields were 6.4 and 3.4% respectively.

Synthesis of Phenyl Propionate.—A 2 : 2 : 1 mixture of ethylene, carbon monoxide, and phenol at 230 atmospheres and 275°, in the presence of a reduced-nickel catalyst, gave 8.9% of phenyl propionate. At 300° and 250°, the yields were 4.9 and 2.0% respectively.

EXPERIMENTAL.

The apparatus employed was similar to that described previously (*J.*, 1937, 1666). The reaction vessel was constructed of stainless steel and was capable of withstanding an internal pressure of 400 atmospheres; its capacity was 145 c.c.

In carrying out an experiment, the usual procedure was first to introduce the requisite quantity of water, alcohol, ammonia, or phenol into the reaction vessel by means of compressed nitrogen, and then

to add separately the ethylene and carbon monoxide, the quantities being determined by means of a Bourdon gauge. Allowance was made for the known compressibilities of the vapours and gases.

At the conclusion of the reaction, the contents of the reaction vessel were in general allowed to expand suddenly into a second steel vessel of large capacity, at room temperature. In this way, the reaction was frozen. The pressure of the expanded cold products was measured, and samples were taken and analysed as described below.

Materials.—Ethylene and propylene were purchased in cylinders, and their purity was checked by analyses before use. Carbon monoxide was prepared by dropping formic acid into warm concentrated sulphuric acid, scrubbing the gas with concentrated aqueous potassium hydroxide, and compressing it into cylinders to 400 atmospheres.

Reduced Nickel Catalyst.—45 G. of AnalaR nickel nitrate were dissolved in 100 c.c. of water, and 50 g. of washed granular pumice added. The mixture was boiled and evaporated to about one-fifth of its original volume. The residual liquid was then drained off and ammonia gas passed over the saturated pumice for some 30 minutes. Finally, 1–2 c.c. of aqueous ammonia were added. The mass was dried in a steam-oven and was then reduced in a current of dry hydrogen for 2 hours at 290°.

Phosphoric Acid Catalyst.—To a weighed quantity of 87% phosphoric acid sufficient copper oxide was added to give 2% of copper phosphate. The mixture was heated until a clear solution was obtained. Activated charcoal was added, and the mixture was boiled for some time and allowed to cool. After draining overnight, it was ready for use.

Analysis of Gaseous Products.—Samples were collected over mercury and analysed in a constant-volume apparatus, using the conventional reagents for absorbing ethylene and the oxides of carbon. Ethane and hydrogen were determined together by explosion with oxygen and absorption of the carbon dioxide formed.

Propionic Acid.—This was identified by preparation of the *p*-toluidide (m. p. 123°; mixed m. p. 123–124°). It was determined by titration with *N*/10-sodium hydroxide.

isoButyric Acid.—This was identified by preparing the *p*-toluidide (m. p. 104°; mixed m. p. 104–105°) and was similarly determined.

Ethyl Propionate.—The products from the reaction vessel were passed through a glass coil cooled to –78° to condense out the acid and ester. In one part of the condensate free acid was determined; the other was hydrolysed with excess of sodium hydroxide solution. Ethyl alcohol and propionic acid were then identified by preparing iodoform and the *p*-toluidide, respectively.

Propionanilide.—The product consisted of a semi-solid mass. It was extracted with benzene and recrystallised from water (m. p. 102–103.5°; mixed m. p. 102–104°).

Propionamide.—The product was condensed, warmed with animal charcoal, and filtered. The amide was separated by crystallisation (m. p. 79°; mixed m. p. 79°).

Benzyl Propionate.—The product was condensed at –78° and the ester determined by hydrolysing it with potassium hydroxide solution.

Phenyl Propionate.—The product was condensed, warmed with animal charcoal, and distilled. The distillate was hydrolysed as above.

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[Received, June 11th, 1949.]