[Contribution from Hercules Powder Co.]

Preparation of Carboxylic Acids by the Carboxylation Reaction

D. R. LEVERING AND A. L. GLASEBROOK

Received March 17, 1958

Carboxylation of 1-pentene, 2-pentene, and *n*-amyl chloride with carbon monoxide and water in the presence of nickel catalyst gave the same two acids: hexanoic and 2-methylpentanoic. Carboxylation of 1-hexene gave hexanoic and 2-methylhexanoic acids and 2-methyl-2-butene gave at least three acids, 3-methylpentanoic, 4-methylpentanoic, and 2,3-dimethylbutanoic. The reactions went rapidly and in high yield when an iodide promoter was used. The promoted carboxylations of 1- and 2-pentene were more than 40 times faster than the unpromoted ones, while with 2-methyl-2-butene no reaction occurred without hydriodic acid present. The amount of straight-chain acids obtained varied from 30 to 47%. The promoted reactions gave the larger amount of straight-chain acids.

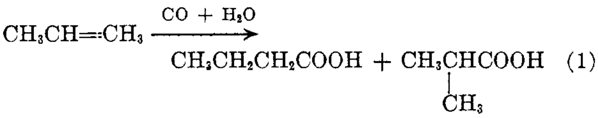
Alkyl halides are probably not intermediates in this reaction.

The preparation of carboxylic acids by the reaction of olefins with carbon monoxide and water in the presence of nickel catalysts is widely known as part of the field of chemistry developed by Reppe during the early forties.[1] The original work on this reaction, however, is reported by Schalch[2] some years earlier. More recently publications have appeared by workers from this country.[3]

In this laboratory pure 1-pentene, 2-pentene, 2-methyl-2-butene, and 1-hexene were studied both with and without the use of promoters to see the effect of the position of the double bond and structure on the rate, conversion, and type of products obtained.

DISCUSSION

Olefins react with carbon monoxide and water in the presence of nickel salts as catalysts at about 300° and 6000 pounds per square inch of carbon monoxide to give excellent yields of carboxylic acids. As in the case of the oxo reaction, two isomers are obtained from an olefin such as propylene.



$$CH_3CH{=}CH_3 \xrightarrow{CO\ +\ H_2O} CH_3CH_2CH_2COOH + \underset{\displaystyle CH_3}{CH_3\underset{|}{C}HCOOH} \qquad (1)$$

Nickel carbonyl when added in place of nickel salts is effective as the catalyst and is always present in reaction products. To get rapid reaction it is necessary to have an iodine promoter present in some form.

Effect of structure on rate. Unpromoted reaction. The unpromoted carboxylation reaction is most successful (*i.e.*, fastest rate and highest conversion) with ethylene. As the number of carbon atoms increase, the rate of conversion decreases. For example, 1-hexene reacts more slowly than 1-pentene. This is illustrated in Table 1 and Fig. 1 which show the gas absorbed as a function of time.

The over-all rate with 2-pentene was about the same as 1-hexene, but as shown in Fig. 1 this was due to a rather long induction period for 2-pentene. After the induction period the rate became approximately equivalent to that given by 1-pentene. The unpromoted carboxylation of 2-methyl-2-butene gave essentially no reaction under the conditions used for the other olefins.

The mechanism for the unpromoted reaction may be very similar to that proposed by Wender *et al.*[4] for the oxo reaction.

They argue that a rate controlling step is the reaction of the olefin with the carbonyl to form an intermediate complex. The rate of formation of the complex would vary with the structure of the olefins, terminal olefins reacting most readily and internal and branched olefins progressively less readily.

The ultimate structure of the complex may be intermediate between that which would be obtained from any of the individual olefin isomers. The structure is probably similar to that observed by Eischens and Pliskin[5] for olefins absorbed on metallic surfaces. Thus the types of products would depend upon the particular reaction. As in the case of metal surfaces when no reaction occurs the thermodynamic equilibrium mixture of olefins should be obtained.

The observed induction period for 2-pentene is not explained by this mechanism which predicts that 2-pentene should proceed at a slower rate than 1-pentene over most of the reaction period.

Promoted reaction. All three of the pentenes reacted very rapidly in the presence of hydriodic acid promoters. Reaction occurred with decreasing rate with the following olefins: 1-pentene, 2-pentene, and 2-methyl-2-butene. This is illustrated in Fig. 2 which shows the gas absorbed during similar promoted reactions as a function of time. It is

---

[1] J. W. Reppe and H. Kroper, *Ann.*, **582**, 38 (1953).

[2] J. W. S. Schalch, U. S. Patent **1,973,662** (1934).

[3] W. F. Gresham and R. E. Brooks, U.S. Patent **2,448,368** (1948). A. T. Larson, U. S. Patent **2,448,375** (1948). D. G. Hedberg, U. S. Patent **2,510,105** (1950). H. G. Hagemeyer, U. S. Patent **2,593,440** (1952).

[4] I. Wender, S. Metlin, S. Ergun, H. W. Sternberg, and H. Greenfield, *J. Am. Chem. Soc.*, **78**, 5401 (1956).

[5] R. P. Eischens and W. A. Pliskin, *Advances in Catalysis*, Volume X, Academic Press, Inc., New York, 1958.

TABLE I

CARBOXYLATION REACTIONS (Reaction conditions)

Run No.	Olefin	Mole	Ni(OAC)$_2$ Mole	H$_2$O Mole	HI Mole	Temp., °C.	Pressure P.S.I.	Time, Hr.	Conversion Based on Olefin, %	Space Time Yield, G. Mole/ Liter/Hr.
1	1-Pentene	1.5	0.05	2.0	...	300	5800–6000	8.0	93.5	0.5
2	1-Pentene	1.5	0.05	2.0	...	300	5800–6000	8.5	92.8	0.5
3	1-Pentene	2.0	0.07	2.6	0.013	300	5800–6000	0.2	87.0	20.5
4	1-Pentene	2.0	0.07	2.6	0.013	300	5800–6000	0.2	80.6	19.0
5	1-Hexene	1.2	0.05	1.6	...	296	5800–6000	13.0	82.0	0.2
6	1-Hexene	1.2	0.05	1.6	...	300	5800–6000	12.0	79.0	0.2
7	2-Pentene	2.0	0.05	2.5	...	300	5800–6000	12.5	66.0	0.2
8	2-Pentene	2.0	0.05	2.5	...	300	5800–6000	14.5	71.4	0.2
9	2-Pentene	2.0	0.05	2.5	0.013	300	5800–6000	0.4	88.0	10.0
10	2-Pentene	2.0	0.05	2.6	0.013	300	5800–6000	0.4	88.6	10.1
11	2-Methyl-2-butene	1.5	0.05	2.0	...	300	5800–6000	2.0	No reaction	
12	2-Methyl-2-butene	1.5	0.05	2.0	...	300	5800–6000	5.0	No reaction	
13	2-Methyl-2-butene	2.0	0.05	2.5	0.013	300	5800–6000	0.4	81.5	8.1
14	2-Methyl-2-butene	2.0	0.05	2.5	0.013	300	5800–0000	0.4	69.1	7.9
15	n-Amyl chloride	1.3	0.70[a]	3.0	0.009	295	7000	1.0	67.8	1.7
16	n-Amyl chloride	1.3	0.88[a]	3.0	0.009	295	7000	1.0	67.8	1.6
17	Mixed amyl chlorides	1.3	0.10	3.4	0.013	296	6000	2.0	10.5	0.1
18	Cyclohexene	1.7	0.05	2.2	0.013	320	6000	0.2	75.2	8.2
19	Mixed pentenes	2.0	0.074	2.3	0.01	300	6000	0.6	73.0	4.3

[a] Nickel carbonyl.

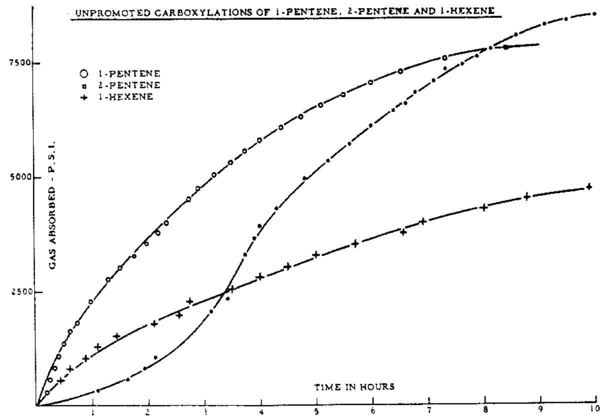


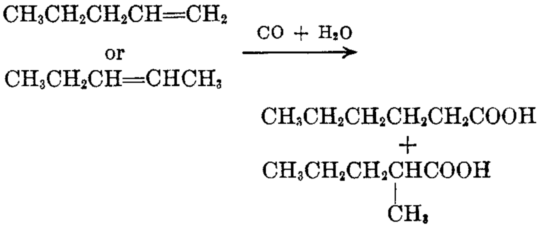
Fig. 1. Unpromoted carboxylations of 1-pentene, 2-pentene, and 1-hexene

significant that the promoted carboxylations of 1-pentene and 2-pentene were more than 40 times faster than the unpromoted ones, while 2-methyl-2-butene which had not reacted previously, reacted at a rate about one-half that of the other two pentenes.

In all cases the promoted reactions were exothermic and the temperature was difficult to control (control was within 5°). The iodide promoter can be added in the form of methyl iodide, potassium iodide, hydriodic acid, or nickel iodide.

Effect of structure on type of products. Analysis of the products by analytical fractionation was carried out when infrared and mass spectrometer methods proved unsatisfactory for quantitatively determining the various isomers present.

From the normal olefins, two compounds were formed: hexanoic acid and 2-methylpentanoic acid from 1- and 2-pentenes, and the corresponding heptanoic acids from 1-hexene. It is possible that by the method of analysis small amounts of the 2-ethyl isomers could have been present and not detected. Infrared spectra, however, of the lower boiling acids obtained from 1- and 2-pentenes by both promoted and unpromoted carboxylation proved to be almost identical, showing that the same acid or mixture of acids was formed in each case.



$$\begin{array}{l} CH_3CH_2CH_2CH{=}CH_2 \\ \text{or} \\ CH_3CH_2CH{=}CHCH_3 \end{array} \xrightarrow{CO + H_2O} \begin{array}{c} CH_3CH_2CH_2CH_2CH_2COOH \\ + \\ CH_3CH_2CH_2\underset{\underset{\displaystyle CH_3}{|}}{CH}COOH \end{array} \qquad (2)$$

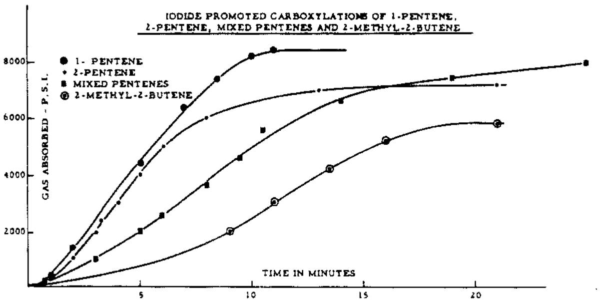
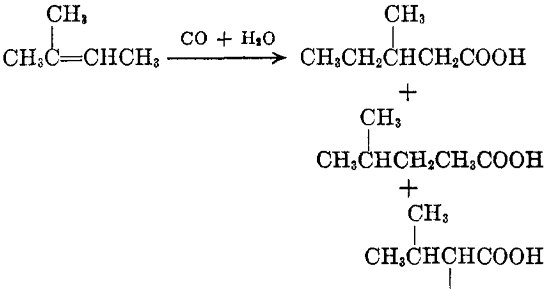


Fig. 2. Iodide promoted carboxylations of 1-pentene, 2-pentene, mixed pentenes, and 2-methyl-2-butene

At least three acids, 3-methylpentanoic, 4-methylpentanoic, and 2,3 -dimethylbutanoic, were obtained from 2-methyl-2-butene. The fourth



$$CH_3\overset{CH_3}{\overset{|}{C}}=CHCH_3 \xrightarrow{CO + H_2O} CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2COOH + CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_3COOH + CH_3CH\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}HCOOH \quad (3)$$

possible acid would be formed only by reaction at the tertiary carbon, which is known to occur with difficulty under these conditions, if at all. Thus it must be present in only small amounts. If no isomerization of the double bond occurred, 2,3-dimethylbutanoic acid would be the sole product. If isomerization to the terminal position occurs sometime during reaction, twice as much 3-methylpentanoic acid as either of the other two acids should be formed. That is roughly what occurred. A similar set of products were reported by Keulemans *et al.*[6] when they reacted these olefins under the conditions of the oxo reaction.

Either the dehydration mechanism proposed by Adkins and Rosenthal[7] for the carboxylation of alcohols or their analytical data are in error since they claim to obtain only one acid while at least two acids are obtained from straight-chain olefins.

The ratio of straight-chain to branched acids varied with the rate of reaction (Table II). The unpromoted carboxylation of 1-olefins gave a 40 to 60 ratio of straight-chain to branched acids acids while 2-pentene gave a 30 to 70 ratio. Iodide promotion increased the amount of straight-chain acids to 47 and 44%, respectively.

TABLE II

RATIO OF STRAIGHT-CHAIN TO BRANCHED ACIDS OBTAINED IN CARBOXYLATION REACTION

Reactant	Promoter	Parts of Normal Acid	Parts of Branched Acid
1-Pentene	. . .	40.2	59.8
1-Pentene	HI	47.4	52.6
1-Hexene	. . .	39.9	60.1
2-Pentene	. . .	28.8	71.2
2-Pentene	HI	44.3	55.7
2-Methyl-2-butene	. . .	0	0
2-Methyl-2-butene	HI	0	100.0
n-Amyl chloride	HI	52.7	47.3

The role the promoter plays has not been defined. Halogen promoters are effective and necessary in reactions catalyzed by nickel carbonyl but not those catalyzed by cobalt or iron carbonyls. It is possible that the promoter forms an unstable compound with nickel carbonyl. This compound then reacts more readily with the olefins resulting in a greatly increased over-all rate of reaction. The intermediate may be an iodine bridged compound such as has been suggested for ruthenium and iron.[8] This would explain the decreasing effectiveness of the halogens as promoters as you go from iodine to bromine to chlorine since iodine is more willing to share its electrons and should form a bridge more readily.

The change of isomer distribution to a more nearly 50/50 ratio with the increase in rate probably reflects the greatly increased ease with which both isomers are formed rather than any directive effect of the iodine.

Reaction with alkyl halides. The fact that halogens are good promoters for this reaction suggested that alkyl halides might be primary intermediates. Thus from a pure isomer, such as *n*-amyl chloride, only one acid should be obtained if isomerization of the halide is not an important factor.

Amyl chlorides react with carbon monoxide and water to give carboxylic acids in yields equivalent to the amount of nickel carbonyl present. The reaction rate was slower for *n*-amyl chloride than for 1-pentene but the product was similar except that more of the straight-chain acid was obtained (Table II). Therefore the alkyl halide as such was probably not an intermediate in this reaction.

Reaction variables. The iodide promoted reactions were very corrosive and it was necessary to use inert metal liners for the autoclaves. Traces of iodine markedly affected the rate. The optimum concentration was not determined. The molar ratio of nickel to olefin of 0.12 was found to give the fastest rate. Excess of water was found to be detrimental, probably due to solvent effects.

CONCLUSIONS

The carboxylation of 1- and 2-pentenes, 1-hexene, 2-methyl-2-butene, and *n*-amyl chloride was carried out to give carboxylic acids in excellent conversions (about 90%). The reaction with carbon monoxide and water in the presence of nickel carbonyl as catalyst proceeded at 300° and 6000 pounds per square inch. The unpromoted carboxylation of 1-pentene proceeded most rapidly, 1-hexene somewhat slower, 2-pentene still slower, and 2-methyl-2-butene gave essentially no reaction. The hydriodic acid promoted carboxylation of 1- and 2-pentene and 2-methyl-2-butene all proceeded very rapidly in the order named. The promoted carboxylations of 1- and 2-pentene were more than 40 times faster than the unpromoted ones, while with 2-methyl-2-butene no reaction occurred without hydriodic acid present. With *n*-amyl chloride it was necessary to use a stoichiometric amount of nickel carbonyl and the rate was

---

(6) A. I. M. Keulemans, A. Kwartes, and Th. Van Bavel, *Rec. trav. chim.*, **67**, 298 (1948).

(7) H. Adkins and R. W. Rosenthal, *J. Am. Chem. Soc.*, **72**, 4550 (1950).

(8) R. H. Irving, *J. Chem. Soc.*, 2879 (1956).

markedly less than with the olefins. Therefore alkyl halides are probably not intermediates. Cyclohexene reacts at about the same rate as the branched olefins.

The two olefins, 1- and 2-pentene, and *n*-amyl chloride gave as major products the same two compounds, *n*-hexanoic acid and 2-methylpentanoic acid. The ratio of normal to branched acids varied depending upon the conditions and the starting materials. For example, the unpromoted carboxylation of 1- and 2-pentene gave 7 to 14% more branched acids than the promoted reaction. In both cases the amount of branched acids was greater than the amount of normal acids. With *n*-amyl chloride more normal than branched acids were obtained. At least three acids, 3-methylpentanoic, 4-methylpentanoic, and 2, 3-dimethylbutanoic, were obtained from 2-methyl-2-butene in the ratio 2 to 1 to 1.

EXPERIMENTAL

Materials. The reactions were carried out in a 500-ml. autoclave containing an inert metal liner. The pure olefins were obtained from the Phillips Petroleum Co. and were Pure Grade (99 mole %). Mixed pentenes were obtained from Enjay Co. (85%). The *n*-amyl chloride was obtained from Matheson Co. and was Research Grade (b.p. 106–108°). The nickel carbonyl was also Research Grade from Matheson Co. The nickel acetate tetrahydrate was obtained from J. T. Baker Chemical Co. and the hydriodic acid (55–58% HI) was obtained from Merck and Co.

Procedure. The same general procedure for charging and discharging the reactor was used for the experiments shown in Table I. The reactor was charged with solid catalyst (if used) and pressure tested with nitrogen. The nitrogen was vented slowly and the bomb was evacuated with an oil pump (when nickel carbonyl was used, the autoclave was previously cooled). The liquid reagents were drawn into the evacuated reactor.

The autoclave was placed in the rocker, the lines to the reactor flushed with carbon monoxide, and the autoclave pressured to 600 pounds per square inch with carbon monoxide. The reactor was then heated to 300° and the pressure raised to 6000 pounds per square inch and maintained between 5800 and 6000 pounds per square inch throughout the reaction period. After reaction, the autoclave was cooled and vented through a Dry Ice trap to condense any nickel carbonyl before the product was removed.

Analysis of product. The crude reaction product was analyzed for acid by titrating it with alcoholic potassium hydroxide and calculating the results as per cent hexanoic or per cent heptanoic acid. The results of the various experiments are shown in Table I.

The crude products were separated from the nickel compounds by distillation. The main fraction was analytically fractionated on a 50-plate, $^3/_{32}$-in. glass helix packed column at 50 mm. at a 40 to 1 reflux ratio.

Identification of products. The distillation cuts from each plateau in the fractionation were combined and examined by infrared. The spectra for those compounds boiling in the same range were almost identical. The curves were similar to those expected for carboxylic acids and there were no unaccounted for bands. The boiling points of products from various experiments are compared in Table III.

TABLE III

BOILING POINTS OF ACID OBTAINED IN CARBOXYLATION REACTION

Olefin	Promoter	2-Methyl-pentanoic Acid, °C.	Hexanoic Acid, °C.
1-Pentene	. . .	120.6–122.4	130.0–130.2
1-Pentene	HI	120.6–122.4	129.6–129.7
2-Pentene	. . .	120.1–122.0	129.7–129.9
2-Pentene	HI	120.2–122.4	130.0–130.2

The chemical and physical properties of representative samples are compared below.

Hexanoic Acid

	Found	Literature (Value)
B.p., °C.	129.6–129.7/50 mm.	205.3/760[9]
d_4^{20}	0.9276	0.929[10]
n_D^{20}	1.4170	1.4170[9]
Acid number	482	483 (theory)

2-Methylpentanoic Acid

	Found	Literature[11]
B.p., °C.	120.6–122.4/50 mm.	195–196/760 mm.
d_D^{20}	0.9233	0.9230
n_4^{20}	1.4141	1.4136
Acid Number	482.8	483 (theory)

Derivatives. The amides of various acids were prepared by converting the acids to the acid chloride and then reaction with concentrated ammonium hydroxide.

Acid	Melting Point of Amide, °C. Found	Melting Point of Amide, °C. Literature[11]
Hexanoic	99–100	100
2-Methylpentanoic	78–79	79.6
Heptanoic	95–96	96

WILMINGTON, DEL.

---

(9) J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier Publishing Co., Inc., New York, 1950.

(10) *Handbook of Chemistry and Physics*, 39th ed., Chemical Rubber Publishing Co., Cleveland, 1957.

(11) E. H. Huntress, and S. P. Mulliken, *Identification of Pure Organic Compounds*, Order I, John Wiley and Sons, Inc., New York, 1941.