The Preparation of C_{19} Dicarboxylic Acid by the Koch Reaction

N.E. LAWSON and **T.T. CHENG**, Union Camp Corporation,
Research and Development Division, P.O. Box 412, Princeton,
NJ 08540, and **F.B. SLEZAK**, Mercer County Community
College, 1200 Old Trenton Rd., W. Windsor Twp., NJ 08690

ABSTRACT AND SUMMARY

This paper describes the preparation of C_{19} dicarboxylic acid by the Koch reaction with carbon monoxide and sulfuric acid of oleic, tall oil fatty, and partially hydrogenated tall oil fatty acids. The effects of changing reaction conditions upon the yield and purity of the product were examined. With the best conditions, it was possible to prepare light-colored, heat-stable C_{19} dicarboxylic acid in 83% overall weight yield at 96% purity, containing 75% tertiary isomers and 25% secondary.

INTRODUCTION

Unsaturated fatty acids have been converted to dicarboxylic acids by oxidative cleavage (1), alkali fusion (1), dimerization (2), Diels-Alder addition (3), hydrocarboxylation (4), hydroformylation-oxidation (4,5), and the Koch reaction; the latter process is the subject of this paper.

The Koch reaction is essentially a carbonylation of a double bond catalyzed by a large excess of a strong acid which acts as a protonating agent and reaction solvent, followed by the addition of water as shown in Scheme I. Rapid skeletal isomerization is believed to precede the addition of carbon monoxide, leading to the formation of many tertiary as well as secondary isomers (6). An excellent general review has been published by Falbe (6) and the more specific application of the Koch reaction to unsaturated fatty acids was reviewed by Pryde et al. (5).

Acid catalysts which have been used in the Koch reaction of unsaturated fatty acids include hydrofluoric acid (7), boron trifluoride (8), and sulfuric acid (9,10); the latter was chosen for our study since the spent acid could conceivably be used to acidulate tall oil soap. Repetition of previous work by Rowe and Swern (9) and Matubara et al. (10) showed that performing the Koch reaction at atmospheric pressure would require a large reactor because of considerable foaming. Further studies, reported in this paper, were therefore carried out under pressure, under which condition foaming ceased to be a problem.

EXPERIMENTAL PROCEDURES

Reagents

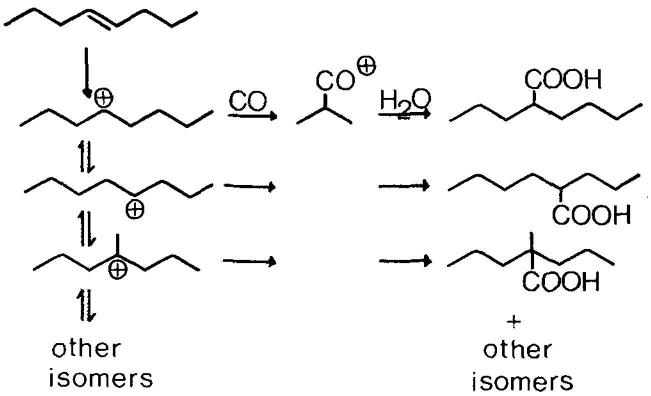
Fatty acid feedstocks analyzed by vapor phase chromatography (VPC) of the methyl esters on a column of 10% FFAP on Chromsorb W. Oleic acid (Armour Neo-Fat 90-04) had the following wt %'s: myristic–3.4; pentadecanoics–1.7; palmitic–3.6; margaric–1.4; stearic–1.1; myristoleic–0.7; palmitoleic–5.4; heptadecenoic–2.5; oleic–69.2; nonadecenoic + linoleic–6.8; linolenic–1.2; unknowns–3.3; acid value (AV)–200; iodine value (IV)–88. Tall oil fatty acids (Union Camp ACD grade): stearic–2.4; oleic–52.2; linoleic–41.1; AV–200; IV–130. Partially hydrogenated tall oil fatty acids were prepared by hydrogenation with a proprietary catalyst system and had the following analysis: monoene isomers–84; stearic–2.6; diene isomers–7.0; AV–195; IV–91. All other reagents were chemical grade.

Typical Procedure

Sulfuric acid (97.2% concentration, 350 ml) was charged into a 2-liter Parr 316 stainless steel reactor (Fig. 1). After purging with nitrogen and checking for leaks, carbon monoxide was introduced to the desired pressure. The acid was stirred for 30 min to saturate it with carbon monoxide, the reactor being cooled with a water or ice bath. Oleic acid

SCHEME I

Mechanism of the Koch reaction.



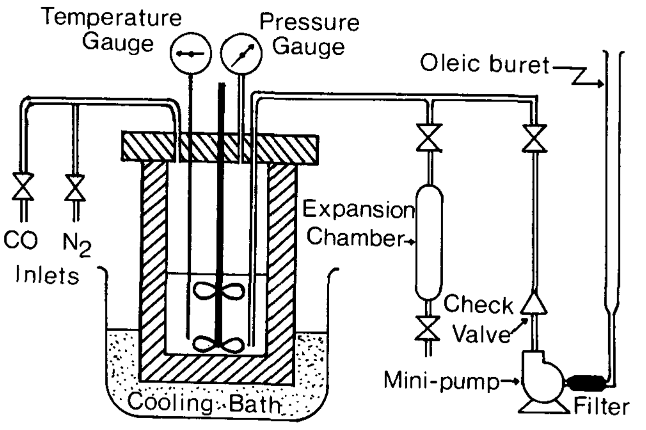


FIG. 1. Apparatus for Koch reaction under pressure.

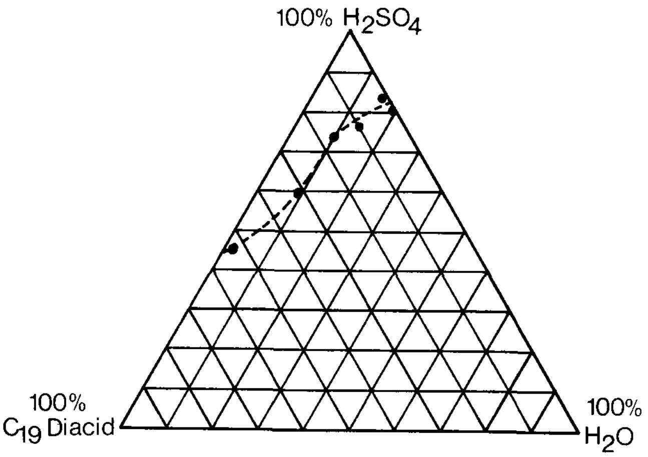


FIG. 2. Ternary phase diagram: C_{19} Dicarboxylic Acid-H_2SO_4-H_2O.

(114 g, 129 ml) was pumped from a buret over a period of 15 min by a 1000 psi Milton Roy mini-pump, carbon monoxide being added to maintain the desired pressure. Stirring was continued for an additional 2 hr after which the mixture was discharged into an ice-water bath and stirred for ca. 10 min. The organic material was extracted by an equal volume of heptane, and this solution was washed with water until the washings were neutral. The heptane was removed on a rotary evaporator under reduced pressure to yield the crude C_{19} dicarboxylic acid. Simple distillation through a short path head (head temp; 235 C at 0.2 Torr) was sufficient to purify the product.

The following analytical methods were used. AV: AOCS-Te-2A-64 using 0.1N NaOH; SV: AOCS-Cd-3-25 with a 3 hr reflux time; IV: AOCS-Tg-1A-64T using Fisher Scientific Company (Fairlawn, NJ) Wijs reagent; heat stability: AOCS-Td-3a-64 (205 C, 2 hr, N_2). Analytical VPC of the crude C_{19} dicarboxylic acid trimethylsilyl esters was carried out on a Perkin-Elmer Model 900 chromatograph equipped with a 10 ft by 1/8 in. stainless steel column packed with 10% OV-17 on Chromosorb W. The helium flow was 25 ml/min and the temperature program was 230 C for 20 min followed by a 32°/min rise to 300 C, where the final temperature was held for 10 min. The internal standard was margaric acid. VPC-mass spectroscopy was obtained on a Hitachi-Perkin Elmer RMU-6 mass spectrometer connected to the above chromatograph.

Kinetic studies of the esterification of distilled C_{19} dicarboxylic acid followed the procedure of Roe et al. (11). VPC of the methyl esters was done on a 6 ft x 1/4 in. column of 10% OV-17 on chromosorb W. Helium flow was 65 ml/min and the temperature was programmed to rise 4°/min from 180 C to 280 C with a final 10 min at 280 C. The internal standard was stearic acid.

Since one of the objectives of our study was to determine whether the spent sulfuric acid from the C_{19} dicarboxylic acid process would be concentrated enough for use in tall oil soap acidulation, it was necessary to measure how much water should be added to the sulfuric acid-C_{19} dicarboxylic acid solution to cause phase separation. This was done by preparing various blends of C_{19} dicarboxylic acid with concentrated sulfuric acid and "titrating" them with water until turbidity was observed. The amount of sulfuric acid in the aqueous phase was determined by titration with standard alkali solution. The results were plotted in a ternary phase diagram shown in Figure 2.

The phase equilibrium diagram indicates that for a reaction mixture containing five to six parts of sulfuric acid to one part of the crude C_{19} dicarboxylic acid, it is necessary to add 10 to 20% of water (based on the total weight) to separate the C_{19} dicarboxylic acid from the sulfuric acid. This would leave the spent sulfuric acid at a concentration of between 70 to 80% which is strong enough to acidulate tall oil soap.

RESULTS AND DISCUSSION

The initial study of the effects of changing reaction variables on the C_{19} dicarboxylic acid product utilized commercial oleic acid as the feedstock. All reaction runs were sampled at least three times and the worked-up crude products analyzed by acid, saponification, and iodine values (AV, SV, and IV). The data reported in Table I correspond to samples taken 2 hr after the end of feed addition, at which point no further reaction was observed.

TABLE I

Koch Reaction of Oleic Acid—Study of Reaction Variables

Run No.	1	2	3	4	5	6	7	8	9
Pressure (psi)	100	250	250	250	250	250	250	250[a]	250
Temperature (°C)	10-15	10-15	10-15	20-25	20-25	20-25	20-25	20-25	20-25
Mole ratio H_2SO_4/oleic	32	32	16	16	8	8	8	16	8
Mole ratio H_2O/oleic	1.33	1.33	1.33	1.33	1.33	2.0	3.3	1.33	1.33
Agitator speed (rpm)	600	600	600	600	600	600	600	600	1000
Crude Product[b]									
AV	296	317	307	317	292	289	232	212	303
SV	–	327	313	323	312	309	280	231	330
IV	8	4	4	5	11	8	7	18	6
Gardner color (neat)	9	11	8	7	10	>18	17	>18	14

[a] No presaturation of H_2SO_4 by CO.

[b] AV = acid value; SV = saponification value; IV = iodine value.

TABLE II

Standard Reaction Conditions for C_{19} Dicarboxylic Acid Synthesis

Temperature:	20-25 C
Presaturation:	30 min at 250 psi CO pressure
CO pressure:	250 psi
Stirring rate:	1000 rpm
Ratio of H_2SO_4 to oleic acid:	16 (molar) or 5.7 (weight)
Oleic acid feeding time:	15 min
Reaction time:	120 min (measured from end of addition)
Quenching media:	ice
Quenching temperature:	0 C
Extraction solvent:	heptane

The conclusions from our study of the reaction variables were as follows:

(a) A pressure of 250 psi was preferable to 100 psi for producing crude C_{19} dicarboxylic acid with higher AV and lower IV (compare runs 1 and 2).
(b) A reaction temperature of 20-25 C is preferable to 10-15 C (compare runs 3 and 4).
(c) The mole ratio of sulfuric to oleic acids should be as high as practical (compare runs 2 with 3 and 4 with 5); the upper limit would be placed by the available utilization of the spent sulfuric acid.
(d) A mole ratio of water to oleic acid of 1.33 is superior to higher ratios in giving light-colored products of higher AV (compare runs 5, 6, and 7); this ratio was conveniently provided by the 97% sulfuric acid used in the remainder of the study.
(e) Presaturation of the sulfuric acid by the carbon monoxide before the oleic addition was essential (compare runs 8 and 4); a 60 min presaturation offered no advantage over the 30 min normally used.
(f) A faster agitation rate of 1000 rpm appeared superior to the 600 rpm used in the other runs (compare runs 9 and 5).

Based on these conclusions a standard set of reaction conditions (Table II) was chosen for further work with oleic acid, tall oil fatty acid (TOFA), and partially hydrogenated TOFA. Data from typical reaction runs are shown in Table III.

These data indicate that TOFA is not a suitable feedstock for production of C_{19} dicarboxylic acid by the Koch reaction. The AV of the crude product was considerably lower than that from oleic acid even though the SVs are identical, possibly due to the greater concentration of lactone functionality. Lactone formation has been observed by other authors (9) and probably occurs by carboxylation of one of the double bonds of linoleic acid present in the TOFA, followed by protonation of the other double bond and attack by the carboxyl group.

In contrast to TOFA, partially hydrogenated TOFA was an acceptable feedstock yielding both crude and distilled C_{19} dicarboxylic acids of at least as good quality (AV 96% of theoretical) as oleic acid.

VPC of the distilled C_{19} dicarboxylic methyl esters revealed that the product was a complex mixture of isomers. At least five distinct peaks were evident (Fig. 3), each of which gave a molecular ion in the mass spectrogram of m/e 359, and the pattern was identical regardless of whether oleic acid, TOFA, or partially hydrogenated TOFA was the feedstock, indicating that the same mixture of secondary and tertiary C_{19} dicarboxylic acid isomers was formed in all cases. This is consistent with the assumption of a rapid equilibration of the first-formed carbonium ions to the same isomeric mixture before the addition of carbon monoxide (6).

TABLE III

Properties of Products from Koch Reaction of Oleic Acid, Tall Oil Fatty Acid (TOFA), and Partially Hydrogenated TOFA

	Oleic Acid	TOFA	Part. Hydrog. TOFA
Crude Product[a]			
AV	322	300	326
SV	325	325	–
IV	5	17	2
Gardner color (neat)	9	12	11
Sulfur content (ppm)	870	–	880
VPC Analysis (wt %)			
Monobasic acids	4.8	–	3.7
Short chain dicarboxylic acids	4.2	–	2.1
C_{19} dicarboxylic acids	66.3	–	78.4
Post C_{19} products	6.6	–	4.3
Distilled C_{19} Dicarboxylic Acid			
Overall yield (wt %)	83	–	83
AV	330	–	333
IV	4.0	–	4.0
Sulfure (ppm)	260	–	220
Heat Stability			
Initial Gardner color	3	–	5
Final Gardner color	5	–	6

[a]See Table I for identification of abbreviations.

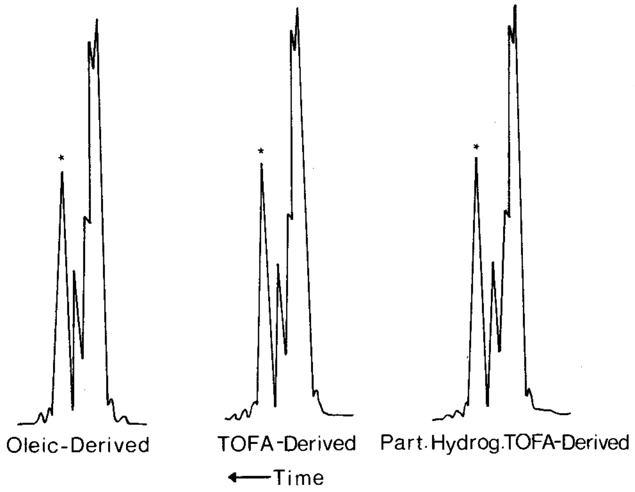


FIG. 3. VPC of C_{19} dicarboxylic methyl esters.

It was of considerable interest to determine which of the five VPC peaks corresponded to secondary carboxylic acid isomers and which to tertiary, since the reactivity of the C_{19} dicarboxylic acid in many applications would depend upon its composition. A kinetic study of the esterification of the distilled C_{19} dicarboxylic acid with methanol according to the procedure of Roe et al. (11) was carried out, samples being removed at increasing time and analyzed by VPC. It was found that the asterisked peak in Figure 3 (ca.

25% of the total area) appeared in the chromatogram of samples removed early in the reaction whereas the other peaks were very slow to appear. We concluded that the asterisked peak corresponded to C_{19} dicarboxylic acid isomers in which the new carboxyl group was secondary (no skeletal rearrangement), and the other peaks would correspond to rearranged tertiary isomers.

Additional evidence that the asterisked peak corresponded to secondary isomers was provided by VPC of C_{19} dicarboxylic methyl esters prepared by the Reppe reaction (12) and obtained from the BASF Company (Ludwigshafen, West Germany). It is known that the Reppe process does not isomerize the hydrocarbon chain to which the carboxyl group is added (13); therefore the Reppe C_{19} dicarboxylic acid must be secondary. Since the VPC retention time of its methyl ester was identical to that of the asterisked peak in Figure 3, we concluded that this peak must represent secondary isomers, Our Koch C_{19} dicarboxylic acid thus consists of ca. 25% secondary isomers and 75% tetiary isomers.

ACKNOWLEDGMENTS

We thank Dr. Henry Hollifield for the gas chromatographic analyses, Dr. Thomas Farina for the methyl ester kinetic study, and the Union Camp Chemical Products Division Technical Laboratory at Savannah for the preparation of partially hydrogenated tall oil fatty acids.

REFERENCES

1. Sreenivasan, B., Indian Oil Soap J. 31:234 (1966).
2. Cowan, J.C., JAOCS, 39:534 (1962).
3. Ward, B.F., U.S. Patent 3,753,968 (1973).
4. Frankel, E.N. and F.L. Thomas, JAOCS 50:39 (1973) and references cited therein.
5. Pryde, E.H., E.N. Frankel, and J.C. Cowan, Ibid. 49:451 (1972).
6. Falbe, J., "Carbon Monoxide in Organic Synthesis," Chapter III, Springer-Verlag, New York, (1970).
7. Miller, E.J., and A. Mais, U.S. Pat 3,481,977 (1969).
8. Kirkpatrick, E.C., U.S. Pat. 2,372,090 (1945).
9. Roe, E.T. and D. Swern, JAOCS 37:661 (1960); U.S. Pat. 3,270,035 (1966); and Brit. Pat. 960,011 (1964).
10. Matsubara, M., M. Sasaki, and H. Ohtsuka, Kogyo Kagaku Zasshi, 71:1179 (1968).
11. Roe, E.T., G.R. Riser, and D. Swern, JAOCS 38:527 (1961).
12. Reppe, W., N. von Kutepow, and H. Detzer, Ger. Pat. 1,006,849 (1957).
13. Falbe, J., "Carbon Monoxide in Organic Synthesis," Chapter II, Springer-Verlag, New York, 1970.

[Received March, 10, 1977]