Branched Fatty Acids from the Caustic Oxidation of Isotridecyl Oxo Bottoms[1]

N.E. LAWSON[2] and M.J.C. HARDING[3], Union Camp Corporation,
Research and Development Division, Princeton, NJ 08540

ABSTRACT

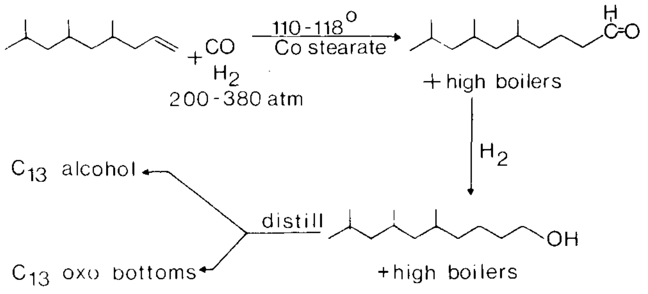
Caustic oxidation has been used to convert the complex residue from the isotridecyl alcohol process ("C_{13} oxo bottoms") to simpler mixtures of highly branched, liquid carboxylic acids in about 65% combined yield. One of the products, produced in 34% yield, was a mixture of isotridecanoic acids formed mainly from C_{13} alcohol and its ester. It was composed of 85% primary carboxylic acids and 15% secondary. The high boiling acids were largely C_{26} secondary carboxylic acids formed by oxidation of aldol dimers. The relative rates of esterification were stearic:C_{13} acid:high boiling acids–1:0.35:0.05. In addition, a 22% combined yield of neutrals consisting of saturated and unsaturated hydrocarbons and ethers was obtained.

INTRODUCTION

Branched-chain fatty acids are useful in many applications. As pointed out in a recent review by Kinsman (1), this is because they and their derivatives have the desirable stability of their saturated analogs but have melting points and tendencies to crystallize which are much lower due to the branching on the hydrocarbon chains and the large number of isomers, both of which inhibit the formation of regular crystal structures. This property is particularly important in additives for 2-cycle engine oil (2) which must withstand the cold temperatures to which chainsaws and snowmobiles are often exposed. The aim of the work to be described in this paper was to develop a process for making a mixture of liquid, saturated fatty acids by caustic oxidation of the bottoms by-product of isotridecyl (C_{13}) alcohol production. This process has been operated successfully at a plant scale.

The highest molecular weight alcohol produced by the simple oxo process (3) is C_{13} alcohol which is made from propylene tetramer as shown in Scheme I. From statistics on C_{13} alcohol production in 1970 (4), we estimated that about 3 million pounds of C_{13} oxo bottoms was produced. No published information specific to the composition of C_{13} oxo bottoms was available, although Bartlett et al. (5), commented that a C_{27} ether alcohol was a substantial component. By analogy to other oxo bottoms (6-10) we predicted that C_{13} oxo bottoms could contain undistilled C_{13} alcohol, C_{26} aldol dimer alcohols, esters, saturated and unsaturated ethers, ether alcohols, acetals and high molecular weight hydrocarbons. To prepare a simple product from such a complex mixture requires a vigorous process which can break down the many different structures into one simple functional group.

Such a process is caustic oxidation, which involves the heating of a compound or mixture of compounds in molten caustic at temperatures of 250-350 C. Under the correct conditions all oxygenated groups react to produce carboxylate salts and sometimes hydrocarbons which are easily removed. The definitive work on reactions in molten caustic was carried out by Weedon and coworkers and has been summarized by him an excellent review (11) to which the reader is referred for details on mechanisms.



SCHEME I. Formation of C_{13} alcohol and oxo bottoms by the oxo process.

At least five groups have caustic oxidized oxo bottoms: Mertzweiller (7), Bartlett et al. (8), Hill (9) and Ashworth (12) described the caustic oxidation of isooctyl oxo bottoms under various conditions. Diamond and Whitaker (10) applied the reaction to isodecyl oxo bottoms and Rehn and Theilig (8) to propionaldehyde oxo bottoms.

It is difficult to predict from the available literature what will happen to the ether functionality when it is caustic oxidized. The work of Ansell et al. (13) shows that facile β ether cleavage generates an olefin and a carboxylate. On the other hand, work by Bartlett and coworkers (6,14-16) indicates that ethers are not appreciably cleaved at temperatures of 293 C, close to the 300 C which we used.

EXPERIMENTAL

Caustic oxidation of C_{13} oxo bottoms was performed in the apparatus shown in Figure 1. This was set up in a normal laboratory hood, but the controls were located outside to permit remote operation. The diagram is self-explanatory and only the foam detection and water quenching system needs comment: Caustic oxidations are often accompanied by foaming problems; in such an event the hot foam would

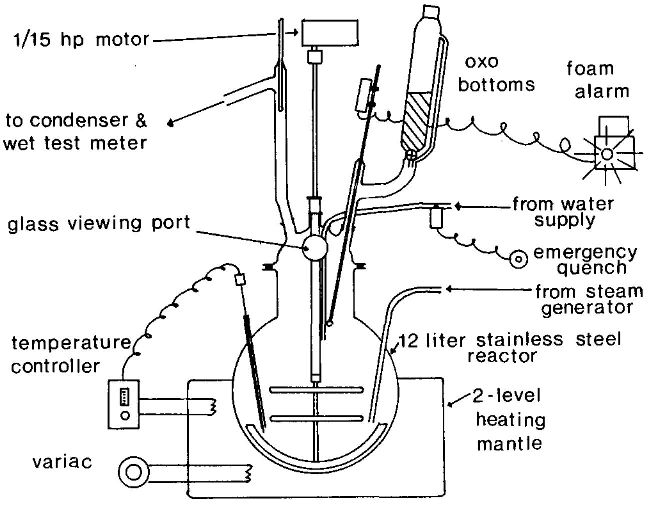


FIG. 1. Apparatus for caustic oxidation of C_{13} oxo bottoms.

---

[1] Presented at the ISF-AOCS World Congress, New York, April 1980.

[2] To whom correspondence should be addressed.

[3] Presently at FMC Research, Princeton, NJ 08540.

touch the thermometer, causing the alarm to sound. By activating the solenoid valve a small amount of water could be added to the reactor, causing an immediate suppression of the reaction and the foaming.

The following procedure was optimum: 476 g of sodium hydroxide pellets were poured into the reactor, which was sparged with a stream of nitrogen and heated to 300 C. After the caustic melted, the agitator was started and 1715 g of oxo bottoms dripped into the reactor over 1 hr while dry steam was passed over the surface of the melt. During the addition stage 101.4 g of a volatile organic material, referred to as condensate, distilled from the reactor and was condensed. The volume of hydrogen evolved and the volume of condensate collected were monitored throughout the reaction.

After addition was completed the reaction mixture was "baked" at 300 C for 30 min. During this time both the gas and condensate evolutions decreased to almost nothing, but after 30 min condensate evolution started to increase, at which point the baking stage was terminated by the introduction of steam below the surface of the reaction mixture. Steaming was continued for 4 hr to remove 280 g of the less volatile neutral material, which was referred to as steam distillate.

Finally, the reaction mixture was cooled below 200 C and water added slowly. The aqueous salt solution was poured from the reactor and acidified with a 10% excess of dilute 30% sulfuric acid. The crude acids were washed two to three times with hot water and heated to 60 C under water aspirator vacuum to dry the product. The Gardner color of the crude acids could be improved from 18 to 7 by adding 0.6% of H_3PO_4 and then bleaching with 3% Impact 100RR clay at 120 C for 2 hr.

The crude acids were distilled using a 5-plate Oldershaw column at 4.5 Torr and a 0.5 reflux ratio.

RESULTS AND DISCUSSION

Composition of Isotridecyl Oxo Bottoms

Table I summarizes the analytical data for three representative samples of C_{13} oxo bottoms. They are consistent with the aforementioned functional groups except that no infrared (IR) or proton magnetic resonance (PMR) absorptions due to acetals could be detected; according to Exxon personnel (17) no acetals are present in C_{13} oxo bottoms. Urea adduction followed by gas liquid chromatography (GLC) of the adduct showed the presence of about 1% palmityl/stearyl alcohols probably derived from the cobalt stearate oxo catalyst. By analogy with the work of Bartlett et al. (6) and Mertzweiller (7) one would expect the presence of isotridecyl isotridecanoate esters in the oxo bottoms, formed from Tischenko reaction of the C_{13} aldehydes. However, we found that heating the oxo bottoms with 2 mol of powdered NaOH per mol of saponifiable material and distilling the liberated alcohols produced only 4% more C_{13} alcohol than that which could be distilled with no caustic. These results indicate that most of the ester is a combination of a high boiling alcohol with (probably) a C_{13} acid; this ester could have been formed from the C_{13}-C_{13} ester by transesterification during the distillation of the isotridecyl alcohol.

Drawing upon the earlier work by other authors (5-10), we postulate that C_{13} oxo bottoms contains the major components shown in Table II. Their modes of formation, expected reactions in molten caustic, and probable products are also listed there. In summary, one might expect caustic oxidation of C_{13} oxo bottoms to produce acids with an average carbon number of 13 from free C_{13} alcohol and the cleavage-oxidation of esters, ethers and ether alcohols; higher acids (C_{26}) from the C_{26} aldol dimer alcohols and possibly uncleaved C_{27} ether alcohols; and a neutral product composed of ethers and hydrocarbons.

Condensate

After half the oxo bottoms had been added to the reactor, condensate distilled at a fairly constant rate; evolution stopped when addition was complete, indicating that the condensate was one of the products of caustic oxidation. After 30 min of baking, condensate again began to form, probably due to decomposition of the reaction mixture. About 6 lb of condensate was produced per 100 lb of oxo bottoms reacted.

IR and PMR spectroscopy indicated that the condensate was a mixture of branched hydrocarbons, both saturated and unsaturated. An absorption peak at 909 cm^{-1}, strong relative to peaks at 962 and 885 cm^{-1}, indicated that the unsaturation was primarily due to monosubstituted α-

TABLE I

Analysis of C_{13} Oxo Bottoms[a]

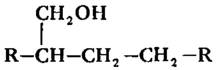
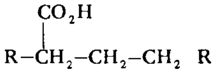
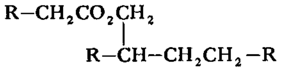
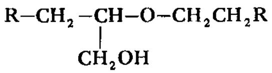
	IR (cm^{-1})	PMR[b] (ppm)
Functional groups by:		
Primary alcohol	3,260, 1,047	4.2
Ether	1,104	3.4
Ester	1,728	2.2, 4.0
AN 0.4-0.5	IV	8
Saponification number 32-45	Specific gravity	0.860-0.865
Hydroxyl number 121-155	Gardner color	6-8
		Content (%)
Free C_{13} alcohol (by distillation)		10-20
Simple ethers (by alumina column chromatography		7.5
Ethers + ether alcohols (by PMR)		20-25
Esters (as $C_{13}CO_2C_{26}$)		35-45
Palmityl/stearyl alcohols		1
Ash		0.007
Ash components (emission spectroscopy)		Fe, Co

[a] Based on 3 samples.

[b] After reaction of the oxo bottoms with trichloroacetyl isocyanate.

TABLE II

Probable Components of C_{13} Oxo Bottoms and Their Caustic Oxidation Products, $R = C_{11}H_{23}$

Component	Mode of formation	Probable reaction with NaOH	Probable products
(a) C_{13} alcohol $R{-}CH_2{-}CH_2OH$	Incomplete stripping of residue	$R{-}CH_2CH_2OH{+}NaOH \rightarrow R{-}CH_2CO_2^-{+}2H_2\uparrow$	C_{13} primary acid $R{-}CH_2{-}CO_2H$
(b) C_{26} alcohol  $R{-}\overset{CH_2OH}{\overset{\vert}{C}}H{-}CH_2{-}CH_2{-}R$	Aldol dimerization of C_{13} aldehyde during oxo reaction, elimination of H_2O, hydrogenation of double bond and aldehyde	Similar to (1)	C_{26} secondary acid  $R{-}\overset{CO_2H}{\overset{\vert}{C}}H_2{-}CH_2{-}CH_2\ R$
(c) C_{26} ester of C_{13} acid  $R{-}CH_2CO_2CH_2$ $R{-}\overset{\vert}{C}H{-}CH_2CH_2{-}R$ (C_{27} ether alcohol may also form part of the ester.)	Tischenko reaction of C_{13} aldehydes during oxo process to give C_{13}-C_{13} ester followed by transesterification with C_{26} alcohol or C_{27} ether alcohol during distillation.	Saponification of ester and oxidation of alcohol portion to acid	C_{13} primary acid C_{26} secondary acid
(d) Palmityl and stearyl alcohols	Esterification of stearic acid from cobalt stearate oxo catalyst with alcohols, followed by hydrogenation of ester to the alcohols	Similar to (3)	Palmitic/stearic acid
(e) C_{26} ether $R{-}CH_2CH_2{-}O{-}CH_2CH_2{-}R$	Acetal formation of C_{13} aldehyde and 2 C_{13} alcohol, followed by alcohol elimination to unsaturated ether and hydrogenation of double bond (6)	No reaction or β-elimination of ether	C_{26} ether (unreacted) C_{13} olefin C_{13} acid
(f) C_{27} ether-alcohol  $R{-}CH_2{-}\underset{CH_2OH}{\underset{\vert}{C}}H{-}O{-}CH_2CH_2R$	Oxo addition to unsaturated ether followed by hydrogenation to alcohol (5)	Oxidation to ether acid followed by β-ether cleavage and/or decarboxylation	C_{13} acid C_{13} olefins C_{26} ethers

olefins. Analysis by PMR confirmed the unsaturation with absorption at 4.98 ppm and no protons on carbons α to ether oxygen. The condensate distilled over a boiling range of 165-185 C at 760 Torr which was similar to that expected for a mixture of hydrocarbons with an average carbon number of 10 to 12, and this, combined with an iodine value (IV) of 66, indicated that the condensate was roughly 40% unsaturated.

It is possible that some of the olefins are formed by β elimination of ethers and ether acids (derived from ether alcohols) since an α-olefin is one of the expected products (13). However, at least some of the condensate is formed by decarboxylation of the C_{13} salts since the condensate yield increases with the temperature of the baking stage as does the difference between the acid number (AN) of the crude product relative to that calculated from the wet chemical analysis of the oxo bottoms (Fig. 2). Also, those runs which produced the largest yield of condensate also evolved the most carbon dioxide when the salts were acidified; sodium carbonate is a product of decarboxylation.

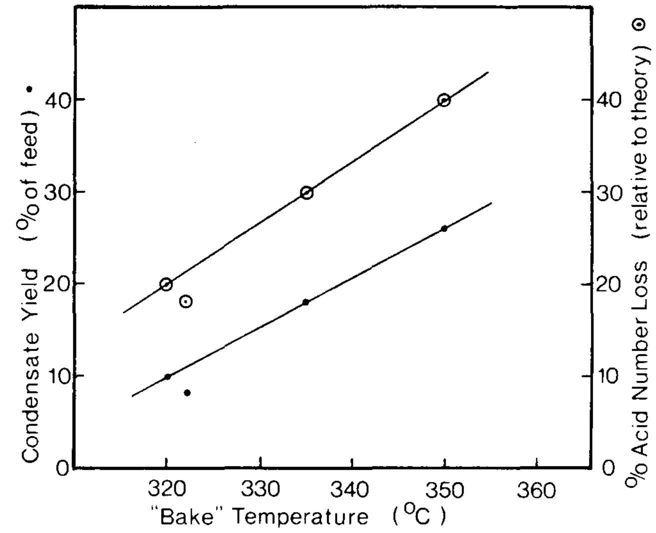


FIG. 2. Effect of "bake" temperature on condensate and acid number loss.

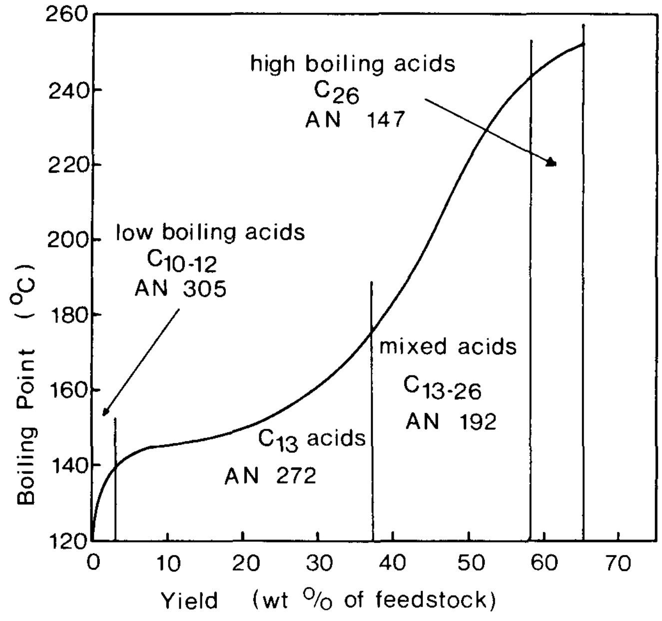


FIG. 3. Distillation curve for C_{13} oxo acids.

Steam Distillate

About 16 lb of less volatile neutrals was steam distilled from the reaction. Fractional distillation gave roughly equal cuts boiling from 145 to 235 C and 265 to 310 C (corrected to 760 Torr). The first was similar to the condensate hydrocarbons by IR. The second was composed mainly (80%) of ethers by IR and PMR analysis. This calculates to about 8% ethers based on oxo bottoms which is close to the 7.5% ethers originally present. Mixtures of combined condensates and steam distillates were caustic oxidized under several different conditions, but the best yield of acid products from these experiments was only 4.5%. It was concluded that under our caustic oxidation conditions much of the ethers was not cleaved in agreement with the results of Bartlett and coworkers (14-16).

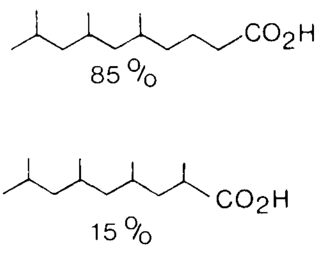
Acid Products

Provided that the caustic melt was steamed for at least 4 hr, the crude oxo acids contained 1% or less of neutrals by chromatography on an alumina column with elution of neutrals by ethyl acetate. An IV of 3.7 showed that unsaturated compounds had been reacted or removed.

Fractional distillation of the crude acids at 4.5 Torr generated a distillation curve (Fig. 3) which was fairly broad as would be expected by the large number of different isomers in the product.

Arbitrarily, the first cut, the low boiling acids, consisted of all material boiling at less than 145 C and represented about 3% yield based on starting oxo bottoms. The AN was 305 corresponding to an average carbon chain length of about C_{11}.

The C_{13} cut distilled next at 145 to 175 C and was obtained in 34% yield. The AN of 272 corresponded to an average chain length of C_{12} to C_{13}. Analysis by PMR inciated four methyl groups per molecule and integration of the absorption of protons α to the carboxyl group showed that about 15% of the acids was branched at the α-carbon. This indicates that the major products are primary and secondary branched carboxylic acids, with the following typical structures expected from the oxo reaction on propylene tetramer (Scheme II):



SCHEME II.

The next cut, the mixed acids, boiling between 175 to 244 C, comprised about 21% of the yield. An AN of 192 indicated that it was a mixture of acids of chain lengths from C_{13} to C_{26}. It consisted of a mixture of liquid with a crystalline solid (about 1-2% yield based on oxo bottoms). The solid was easily filtered and recrystallized from methanol (melting point of 51.5 to 54 C and an AN of 186). GLC indicated that the solid was largely palmitic and stearic acids formed by caustic oxidation of the respective alcohols in the oxo bottoms.

The high boiling acids, produced in about 10% yield, had a boiling range of 244 to 252 C and an AN of 147—

TABLE III

Relative Rates of Esterification of Acids in Excess Methanol

Conditions: H_2SO_4 catalyst, temperature
64.7 ± 0.2 C (reflux) (18,19)

Acid	Rate relative to stearic acid
Stearic	1
Isostearic	0.95
C_{13} acids	0.35
C_{26} acids	0.05

close to that expected for a C_{26} secondary acid from the caustic oxidation of the C_{26} aldol dimer alcohol. IR and PMR spectra of this fraction indicated only traces of ether functionality; it seems that ether alcohols, in contrast to simple ethers, must be either cleaved to acids and olefins or oxidized to ether acids which decarboxylate.

The total yield of distillable acids from the caustic oxidation of C_{13} oxo bottoms is thus about 65% (the distillation residue amounted to 11%). Depending upon the particular end-use contemplated, any one or combination of the three acid cuts can be used. All have colors of Gardner 1 or less and the C_{13} acid cut has a titer of approximately -50 C.

Esterification of Acid Products

Since the rate of formation of derivatives such as esters or amides is strongly dependent upon the structure of the acids, it was desirable to have a measure of the reactivities of the C_{13} acids and high boiling acids relative to straight-chain fatty acids. Table III shows that the C_{13} and high boiling acid products are considerably more hindered about the carboxyl group than stearic and isostearic acids.

ACKNOWLEDGMENTS

We thank D.H. McMahon for making the analytical determination.

REFERENCES

1. Kinsman, D.V., JAOCS 56:823A (1979).
2. Benoit, G.F., Jr., U.S.Patent 3,110,673, 1963.
3. Falbe, J., "Carbon Monoxide in Organic Synthesis," Springer-Verlag, New York, 1970, p. 71.
4. Glauz, R.L., Chemical Economics Handbook, 609.5022, June 1977.
5. Bartlett, J.H., I. Kirshenbaum and C.W. Muessig, Ind. and Eng. Chem. 51:257 (1959).
6. Bartlett, J.H., A.J. Morway, L.A. Mikeska and S.G. Galto, U.S. Patent 2,801,971, 1957.
7. Mertzweiller, J.K., U.S. Patent 2,802,846, 1957.
8. Rehn, K. and G. Theilig, Ger. Prov. Patent 1,061,770, 1959.
9. Hill, P., U.S. Patent 2,766,267, 1956.
10. Diamond, H.L., and A.C. Whitaker, U.S. Patent 3,370,074, 1968.
11. Weedon, B.C.L., Techniques of Chemistry, 4:325 (1973).
12. Ashworth, P.J., U.S. Patent 3,227,737, 1966.
13. Ansell, M.F., I.S. Shepherd and B.C.L. Weedon, J. Chem. Soc. C:1840 (1971).
14. Bartlett, J.H., A.J. Morway and J.C. Munday, U.S. Patent 2,801,970, 1957.
15. Morway, A.J., and J.H. Bartlett, U.S. Patent 2,801,969, 1957.
16. Bartlett, J.H., A.J. Morway and L.A. Mikeska, U.S. 2,801,972, 1957.
17. Private communication from J. Reich and C. Savini of Exxon Research and Engineering Corp.
18. Smith, H.A., J. Am. Chem. Soc. 61:254 (1939).
19. Loening, K.L., Ibid. 74:3929 (1952).

[Received May 30, 1980]

High Resolution Glass Capillary Columns with Chemically Bonded Stationary Phases: Application to the Gas Chromatographic Analysis of Sterols and Steroids in Biological Extracts

C. MADANI and **E.M. CHAMBAZ**, Laboratoire d'Hormonologie,
C.H.U. de Grenoble, 38700 La tronche, France

ABSTRACT

A new approach has been developed for the preparation of highly stable glass capillary columns using irreversible bonding of polysiloxane polymers to the glass surface. The general procedure involves (a) synthesis of reactive linear polysiloxanes from variously (alkyl, aryl) substituted dichlorosilanes through homologous or heterologous polymerization under alcaline aqueous conditions, and (b) covalent condensation of the polymers to a properly prepared glass capillary surface at high temperature. The principle has been first applied to the successful preparation of apolar gas chromatographic systems (methylpolysiloxanes), then extended to the obtention of polar systems (methyl phenyl polysiloxanes). The flexibility of the approach is demonstrated by the possibility of obtaining stationary phases of various and controlled polarity (i.e., extent of phenyl substitution), tailor-made to a given analytical problem. These gas chromatographic systems appear to be remarkably stable both with time and temperature up to 300 C and compare favorably to existing systems for their high resolution properties. These columns have been satisfactorily used in the last years for the analysis of sterols and steroids of biological origin and most extensively in the study of urinary steroid metabolite in humans under pathological conditions.

INTRODUCTION

In the last ten years, glass capillary gas chromatography has been widely accepted as one of the most powerful analytical tools in biochemical separations. However, manufacture of long-lived, thermostable high resolution systems remains a challenging problem, especially if polar stationary phases are needed. The major recognized problem is the wettability of the glass surface which limits the production of a regular and stable coating. Commercially available polymers have generally been used as stationary phases and