n-Heptanoic Acid by the Caustic Oxidation of 2-Octanol

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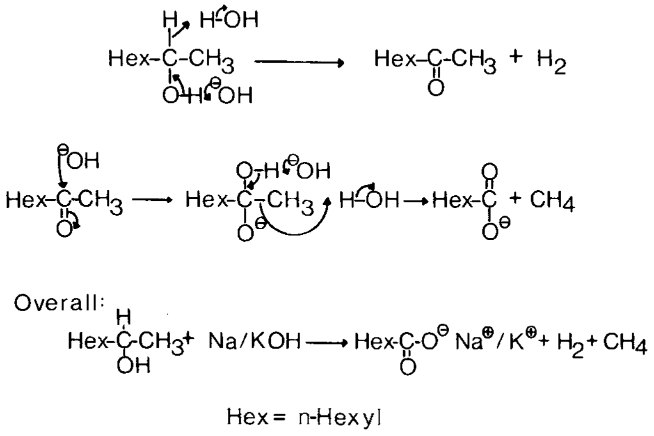
n-Heptanoic acid (97% pure) was prepared in 86% selectivity by the reaction of 2-octanol with molten 50:50 NaOH-KOH at 320 C using a meshing blade agitator and product heptanoic acid as an initiator.

n-Heptanoic acid is used to make pentaerythritol tetraheptanoate, an important component of polyol-ester synthetic lubricants and tetramethylene glycol diheptanoate, a plasticizer for the polyvinyl butyral layer in laminated safety glass (1). Heptanoic acid is made commercially by the air oxidation of heptaldehyde produced as a by-product of Nylon-11 manufacture and by the hydroformylation of hexene (1). The aim of the work to be reported in this paper was to develop a process to make pure heptanoic acid from 2-octanol (capryl alcohol). This is a co-product of the manufacture of sebacic acid by the reaction of castor oil with molten caustic. The caustic oxidation of 2-octanone from the sebacic process was briefly revealed in a patent to Keenan (2).

The oxidation of hydroxy-compounds with molten caustic to give carboxylic acid salts has been described in a number of publications (3-5) and patents (6-15). Based on these, we propose that 2-octanol reacts by the mechanism shown in Scheme 1.

This reaction scheme was useful because it indicated that:

(i) A small amount of water would have to be present in the hot reaction mixture.
(ii) Two moles of gas would be produced per mole of 2-octanol converted to heptanoate. Thus, a comparison of the gas produced to the feed converted would give a measure of any decomposition.
(iii) Crude 2-octanol, which is contaminated with 2-octanone, would be an acceptable feedstock.
(iv) The heat of reaction would be about -13.5 kcal mol^{-1} at 320 C by calculation. Thus, the reaction would not be excessively exothermic, but would supply part of its heat requirements.



SCHEME 1. Mechanism for the caustic oxidation of 2-octanol to heptanoic acid salts.

EXPERIMENTAL PROCEDURES

Apparatus. The apparatus used for these molten caustic reactions is shown in Figure 1.

The reactor was a two-l stainless steel resin kettle with the head modified with a glass viewing port. The "meshing blade" agitator was driven by a high torque 68 rpm motor. This was mounted on bearings and free to rotate but restrained by an arm connected to a spring balance. This assembly constituted a dynamomet whose readings indicated changes in viscosity of the reaction medium.

Procedure. A typical reaction run was carried out as follows: NaOH (sodium hydroxide 98%, 81.6 g, 2 mol) and KOH (potassium hydroxide 85%, 132.0 g, 2 mol) were charged to the reactor and heated to 320 C while the reactor was flushed with nitrogen. Heptanoic acid (36.5 g, 0.28 mol) was added as an "initiator."

If this initiator was absent, the reaction was slow to start and considerable dehydration occurred. 2-Octanol (98% pure) saturated with water (3.8 wt %) was then pumped into the reactor at such a rate that the reaction temperature could be maintained. Changing the feed rate did not appreciably change the amount of 2-octanol retained in the reaction mixture. That feed which did not react was flashed from the reactor and captured by the condenser system.

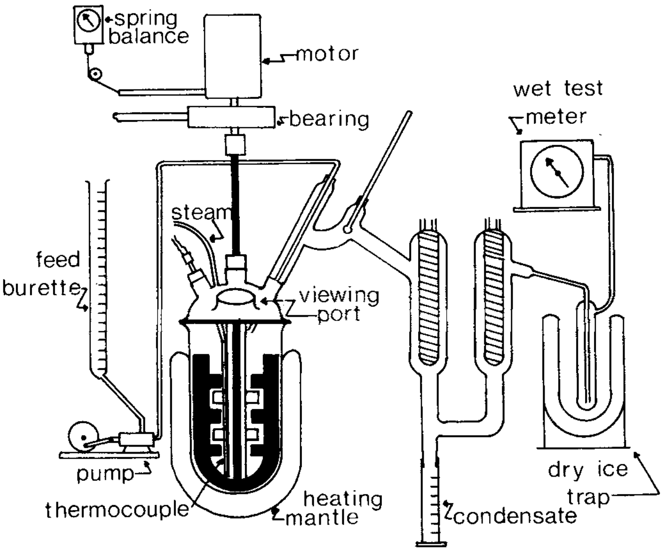


FIG. 1. Apparatus for the caustic oxidation of 2-octanol.

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The water necessary for the reaction could also be provided by injection of steam into the reaction mixture; however, the use of water-saturated 2-octanol was more convenient. Preheating the feed reduced the rate of conversion because a greater proportion of it flashed from the reactor. The position of the outlet of the 2-octanol feed tube could be either above the surface of the molten caustic or below it; no major differences were noted. We concluded from an examination of several temperatures that 320 C was about optimum; below 300 C the reaction rate dropped sharply and above 340 C some decomposition of the heptanoate salts occurred.

After 2-octanol addition was complete, the reaction mixture was stirred at 320 C until gas evolution ceased. This was followed by steam purging for 15-30 min to remove volatile organic materials. One l of water was added (slowly at first) to dissolve the reaction mixture. The aqueous solution was discharged and then acidified with 50% sulfuric acid to liberate the heptanoic acid. This was combined with a small amount of ether, washed several times with water and dried over calcium sulfate (Drierite). The ether was removed under reduced pressure.

The purity of the crude heptanoic acid was determined by vapor phase chromatography of the trimethylsilyl ester (Sylon BT reagent from Supelco, Inc., Bellefonte, Pennsylvania) on a 12′ × 1/8″ stainless steel column, packed with 10% OV-17 on 100/120 mesh chromosorb W. Temperature programming was from 80 to 225 C at 5 C/min, and n-octanoic acid was the internal standard. The identity of the various components in the condensate was made by comparison of VPC retention times to those of authentic materials and by the use of $Hg(OAc)_2$ treatment prior to VPC to identify olefin peaks.

Pure sodium and potassium heptanoates were prepared by adding heptanoic acid to 2.3 molar NaOH or KOH in 90:10 methanol-water until the pH was about 7.5, and then slowly adding an equal volume of acetone. The precipitated salt was filtered, slurried with a small amount of methanol, refiltered, and thoroughly dried in a vacuum oven. All melting points of the salts and their mixtures were greater than the 359 C limit of the Thomas-Hoover melting point apparatus. Vorlander (16) gave a melting point of 350 C for sodium heptanoate, which is low compared to our value; however, he observed a change to a mesomorphic form at 240 C, which we confirmed.

Calculation of heat of reaction. This was calculated for the reaction of 2-octanol with NaOH to give sodium heptanoate, methane and hydrogen at 320 C using standard techniques (17, 18). An estimate for potassium hydroxide gave a similar result. Data used were: heats of formation (kcal mol^{-1}): NaOH, -101.9 (21); CH_4 -17.9 (17); H_2, O (by definition); 2-octanol, -105.2 (calculated from heat of combustion (21); sodium heptanoate -201.2 (calculated from heats of formation of heptanoic acid, -145.8 (17), and NaOH and the heats of neutralization of acetic and formic acids, -21.8 (17, 20), assuming they are the same as that of heptanoic acid, and also by the method of interseries increments (17). Average heat capacities (kcal mol^{-1} C^{-1}): solid NaOH, -25 C to 320 C, 0.0169 (PPG Industries, unpublished data); liquid 2-octanol -25 C to 179 C, 0.0884 (19), using heat capacity at 25 C of 0.0789 (21); 2-octanol vapor, 179 C to 320 C, 0.0755 (estimated from 1-octanol) (18); sodium heptanoate, 25 C to 320 C, 0.1233 ± 0.005 (measured by differential scanning calorimetry); and hydrogen, 25 C to 320 C, 0.00695 (18). Heat of fusion of NaOH (kcal mol^{-1}): 1.60 (22) and heat of vaporization of 2-octanol (kcal mol^{-1}): 12.27 (20).

RESULTS AND DISCUSSION

Table 1 shows the results of a typical reaction run under optimized conditions. Of the 2-octanol converted, 86% was accounted for by heptanoic acid, which was generally 97% or greater purity by GC analysis without distillation. The gas production was 105% of that expected on the basis of the proposed reaction mechanism.

As described in the experimental procedure section, the caustic fusion of 2-octanol was carried out in a semi-batch fashion; that is, the 2-octanol was added gradually to the full charge of molten mixed NaOH and KOH (containing 7 mol % of heptanoate salt initiator) until the conversion rate slowed.

Figure 2 shows some of the physical changes which occurred over the course of a typical run. The viscosity of the reaction mixture increased to a maximum when 25-35% of the caustic was reacted (calculated from the moles of gas produced plus the moles of heptanoic "initiator" added). This was accompanied by erratic temperature readings caused by poor heat conductivity through the semi-solid reaction mixture. The viscosity then decreased quickly and rose slowly to the end of the reaction. The reason for the viscosity maximum is not known, but it is possible that a heptanoate salt-caustic complex may be responsible.

The percentage of the 2-octanol feed retained in the reactor also increased sharply near the viscosity maximum (Fig. 2), corresponding to the increased formation of a mushy, semi-solid mixture of heptanoate salts and molten caustic. 2-Octanol will not dissolve easily in molten caustic at a temperature far above its boiling point. However, we observed that if the feed was stopped after the reaction was well under way, gas production would continue for several minutes. Steaming the mixture caused more 2-octanol to be distilled than could be accounted for by vapor alone. We conclude, therefore, that the heptanoate salts play an important part in the overall process by dissolving and holding the 2-octanol

TABLE 1.

Results of Typical Reaction Run

Caustic charge	4 mol
Conversion of caustic[a]	81 mol %
Conversion of 2-octanol	48 mol %
Overall conversion rate	0.58 mol/hr
Maximum conversion rate	1.31 mol/hr
Gas evolution	105% of theoretical
Crude product purity	97% heptanoic acid
Selectivity[b]	86 mol %

[a] Includes that neutralized by "initiator."

[b] Yield of heptanoic acid based on reacted 2-octanol.

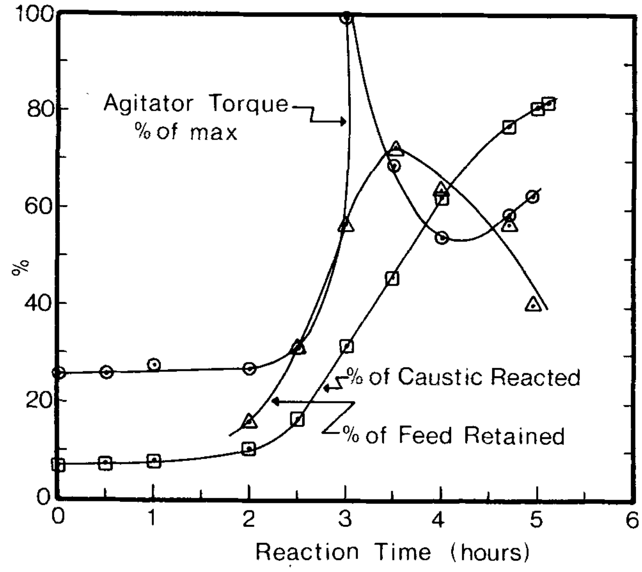
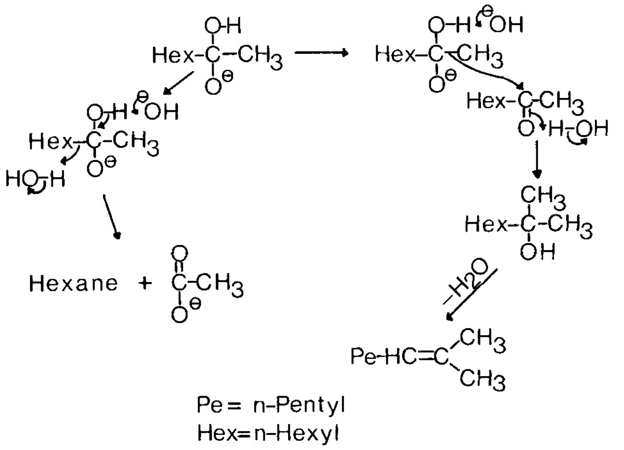


FIG. 2. Typical reaction profile.



SCHEME 2. Mechanism for the formation of hexane and 2-methyloctenes.

in the reaction mixture long enough for it to react with the molten caustic. This is why it is necessary to start the reaction with some heptanoic acid "initiator."

After about 50% of the caustic was reacted, the proportion of the 2-octanol feed retained started to decrease. This was due to the decreasing concentration of caustic in the reaction mixture, and when 80-90% of the caustic was used, the reaction rate became too slow to be useful.

The composition of the volatile materials flashed from the reactor also changed as the reaction proceeded (Table 2). This has some importance because in a commercial process the condensate would be recycled to the reactor. During the first stages, the condensate was largely 2-octanol with lesser amounts of 2-octanone and small amounts of an octene mixture (1- and 2-octenes and 2-methyloctenes). The "others" fraction contained mainly hexane. We believe the 2-octanone was formed by dehydrogenation of the 2-octanol in the first step of the reaction mechanism; the octenes from dehydration of the 2-octanol; and the 2-methyloctenes and hexane from side reactions of the dianion intermediate of Scheme 1 (Scheme 2).

As more of the caustic was converted to heptanoate salts, the concentration of the 2-octanol in the condensate decreased and that of the octene by-products increased. We believe that again this is due to the decreasing concentration of caustic in the reaction mixture, which leads to a slower rate of reaction to form heptanoate salts, allowing base-catalyzed dehydration to become significant. This was especially true of the condensate derived from steaming the final reaction mixture.

Although it would be economically preferable for the caustic to consist of only NaOH, it is necessary to include an equimolar amount of the more expensive KOH. This conclusion is supported by the data shown in Figure 3. When the proportion of KOH in the molten caustic was decreased, the conversion rate and selectivity dropped significantly, and decomposition of the heptanoate salts increased.

KOH is plainly desirable for the caustic fusion of 2-octanol, but why it is so, is less obvious. It does not reduce the melting points of the heptanoate salts which were shown to melt at temperatures of greater than 359 C, both alone and in a 50-50 mixture. This is considerably above the 320 C reaction temperature. We believe that the function of the KOH is to retain in the molten caustic the small amount of water required by the reaction mechanism and which also suppresses decomposition of the heptanoate salts. It has been shown that at 300 C, molten NaOH saturated with steam contains 5.7 wt % of water; KOH contains three times as much. Mixtures contain water in proportion to their compositions (Pelton, E.L., preprint of paper presented to Midland Section of American Chemical Society, April

TABLE 2

Condensate Composition

Source	% Caustic reacted	% Of Total	Composition (wt %) 2-Octanol	2-Octanone	Octenes[a]	Others[b]
Reaction	7-39	39	90	6	3	1
Reaction	39-62	37	84	10	6	-
Reaction	62-81	22	84	8	8	-
Steaming	81	1	38	6	24	32
Dry Ice Trap	7-81	1	73	6	7	14

[a] 1- and 2-Octenes and 2-methyloctenes.

[b] Hexane and non-volatiles.

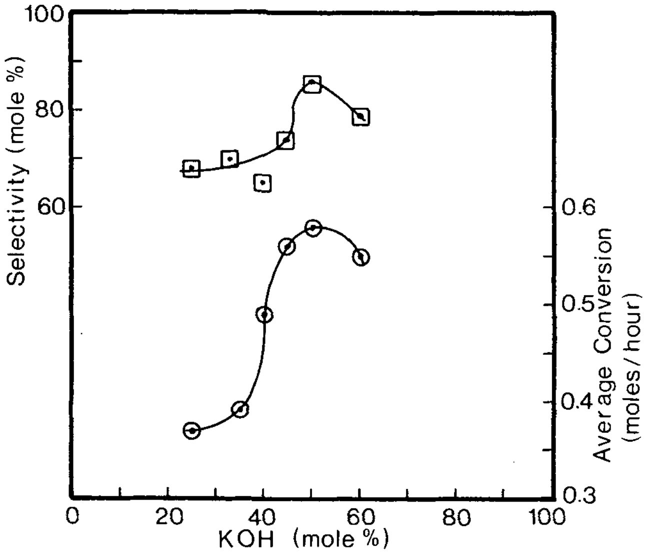


FIG. 3. Conversion rate and selectivity as a function of KOH content of the caustic.

1951). At 320 C, molten NaOH probably cannot hold enough water for the reaction to proceed, whereas an equimolar mixture of NaOH and KOH can.

A major problem encountered during this study was foaming. Foaming was observed as the physical rising of the semi-solid reaction mixture up the reaction vessel and, if not quenched by water addition, through the reactor outlet, frequently plugging it. Foaming occurred more often when a simple horseshoe agitator was used and was aggravated by excessively high feed rates. Also, it appeared to occur about the time when 25–35% of the caustic had been reacted.

How foaming occurred became clearer when it was observed that sodium and potassium heptanoates were insoluble in molten caustic at 320 C and simply floated as a solid layer. At 25–35% conversion of the caustic, sufficient salts were formed for the "cover" to be complete. Gases formed by the reaction then acted as the driving force to push the solid heptanoate layer up the reactor.

Initial efforts to overcome the foaming problem were based on the premise that if the melting point of the heptanoate salts could be reduced, or if the salts could be made more miscible with the caustic, the "cover" of solid product would not form. Adding mineral oil, branched-chain "iso-acids" (such as tridecanoic acid), dodecylphenol, or myristyl alcohol with the 2-octanol feed were all tried. None worked well.

A more successful way around the foaming problem in the laboratory was to modify the agitator design to break up the solid heptanoate salts and blend them into the molten caustic. This led to the "meshing blade" agitator shown in Figure 1. We have concluded that the appropriate reactor and agitator design is the key to successful operation of this process to convert 2-octanol to heptanoic acid.

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