[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE CATALYTIC DECOMPOSITION OF SIMPLE GLYCERIDES

BY F. L. SIMONS[1]

RECEIVED APRIL 24, 1926 PUBLISHED JULY 6, 1926

In an attempt to open up our natural supplies of glycerides to further industrial use, Mailhe[2] adopted catalytic decomposition as his line of attack. He succeeded in preparing from a number of oils (cottonseed, rape, colza castor, etc.) a 20 to 30% yield of motor spirit, consisting of benzene, toluene, hexanes and other hydrocarbons. His process consisted essentially of a preliminary cracking of the glyceride over a copper-magnesia or copper-alumina catalyst, followed by hydrogenation of the low-boiling fraction of the product over nickel. Mailhe's work has been largely empirical, of course, as the high temperatures employed (600–650°) resulted in too profound a decomposition to justify any speculation as to reaction mechanism.

Our present knowledge of the behavior of glycerides at high temperatures is very meager. A review of the literature brings to light, outside of Mailhe's work, only a few scattered researches, such as those of Bussy,[3] Tilley[4] and Krafft[5] on the distillation of castor oil. Straight catalytic breakdown of a series of simpler glycerides seems to have been untried, although such research would be very useful in laying a foundation for future work along this line with the more complex natural compounds. It is, therefore, the purpose of this paper to present some of the results observed in the decomposition of triacetin and tripropionin over a thorium oxide catalyst, as a first step in the accumulation of systematic data for this series of glycerides.

Discussion

What to expect from the catalytic decomposition of even the simplest glycerides is largely a matter for conjecture. Acrolein, gaseous products, the glyceride acids and higher condensation products would probably be formed. By analogy with the esters of monohydric alcohols, we might also expect the ketone corresponding to the glyceride acid. Regarding the reactions that take place at elevated temperatures (over 600°), predictions are, of course, practically impossible. The data for the four runs thus far studied (given in Table I) show that these general expectations are fulfilled.

---

[1] Constructed from a dissertation presented by F. L. Simons to the Faculty of the Graduate School of Yale University in June, 1923, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy (T. B. Johnson).

[2] Mailhe, *Bull. soc. chim.*, **31**, 249 (1922), and later articles.

[3] Bussy, *Ann.*, **60**, 246 (1846).

[4] Tilley, *Ann.*, **67**, 105 (1848).

[5] Krafft, *Ber.*, **10**, 2034 (1877).

TABLE I

SUMMARY OF EXPERIMENTAL RESULTS

Run number	1	2	3	4
Glyceride	Triacetin		Tripropionin	
Temperature, °C.	460	525	420	510
Quantity used, g.	140	191.5	121	126.5
Liquid product, g.	97	134.5	98	78
Gases evolved, liters	16	21	11	31
PERCENTAGE COMPOSITION OF LIQUID PRODUCT				
Acrolein	21.0	14.1	4.0	6.7
Allyl alcohol	?	?	4.0	5.3
Crotonaldehyde	...	2.6	6.2	10.6
Water	...	?	?	6.6
Formic acid	7.0	20.0	...	...
Acetic acid	27.4	25.0	14.5	10.6
Propionic acid	...	...	17.5	33.5
Diacetin	24.2	?	...	...
Triacetin	4.6	...	...	...
Tripropionin	...	...	47.8	9.5
Tarry materials	10.1	30.6	4.0	13.3
PERCENTAGE COMPOSITION OF GASEOUS PRODUCT				
CO	not	36.6	34.9	18.5
CO_2	deter-	34.1	37.3	53.3
C_nH_{2n}	mined	13.0	8.2	9.0
H_2		6.8	10.7	17.2
C_nH_{2n+2}		present	present	present

It will be noted that decomposition of either glyceride is not complete unless the temperature is considerably over 500°. Preliminary trials also showed that decomposition does not begin, or rather does not take place to any great extent, until approximately 380° is reached. It is also notable that tripropionin is broken down at a slightly lower temperature than triacetin.

As might be expected, large amounts of tarry materials are formed, especially at the higher temperatures. Those runs that show unchanged glyceride in the product, show less tar than the others, and *vice versa*. Considerable amounts of this tar remained in the packing of the reaction tube at the end of each run. It had the general appearance of a very soft pitch, was insoluble in alcohol and soluble in benzene. It was not subjected to any study.

Careful search failed to reveal the presence of any dipropionin in the products from Runs 3 and 4. This is rather curious on the whole, and leads to the conclusion that under the particular conditions involved the triglyceride is more stable than the diglyceride. In the runs with triacetin, the contrary seems to be true.

Two quite unexpected substances appear in the products of decomposition, namely, the lower homolog of the glyceride acid, and hydrogen.

Formic acid appears in Runs 1 and 2, and acetic acid in Runs 3 and 4, in all cases in substantial quantities. Probably hydrogen is a product in Run 1, as well as in the others, although the gases unfortunately were not analyzed in this case. Whether or not the production of these substances is typical of all such decompositions remains to be seen.

It seems doubtful whether any particular significance is to be attached to the presence of allyl alcohol and crotonaldehyde in the products, although from the value for crotonaldehyde in Run 4 we might judge that its production was favored by higher temperatures. The water produced in Run 4 seems to indicate a considerable stability for tripropionin toward hydrolytic agents. This is also true in the case of hydrolysis with aqueous alkali, as far more drastic conditions are required for tripropionin than for triacetin.

Present theories of catalysis, or analogies with other known reactions seem quite inadequate to account for the fact that triacetin is decomposed into a product containing 10% of the weight of the glyceride as formic acid. The presence of hydrogen is similarly unaccounted for, although when formic acid is present, it may proceed from its decomposition.

However, two steps in these decompositions may be traced with some degree of plausibility. The first is a complete breakdown of a portion of the glyceride which liberates water and a variety of other products. The débris of the glycerol chain appears as acrolein, and some of the glyceride acid is set free as such. At the higher temperatures, this profound decomposition predominates, as would be expected. The second step is probably a simple hydrolysis of other portions of the glyceride through the agency of water previously formed, whereby the acid and a lower glyceride are produced. The results for triacetin indicate the truth of this and, although lower homologs do not appear in the runs with tripropionin, the high acid content points in this direction. The mode of formation of formic acid and other products may be made clear only by further work with other members of the series and with mixed glycerides.

Experimental Part

The glycerides used in the work were prepared with special care, the method for triacetin being straight acetylation of glycerol with acetic anhydride and sodium acetate, and for tripropionin, simple refluxing of pure propionic acid with dry glycerol in the presence of anhydrous potassium bisulfate at 110° for 60 hours.

Curiously enough, tripropionin is not reported in the literature. The product obtained boiled at 130–132° (3 mm.); attempts to distil at pressures above 20 mm. resulted in partial decomposition. The material is a colorless and practically odorless liquid, less mobile than triacetin, but slightly soluble in water, and very slow to hydrolyze with aqueous alkali; d_{18}^{20}, 1.100; n_{D}^{15}, 1.434.

Anal. Subs.: 1.0114, 1.0013: 17.42, 17.14 cc. of 0.6719 *N* NaOH used on hydrolysis. Calcd. for $(CH_2OCOC_2H_5)_2CHOCOC_2H_5$: NaOH equiv.: 0.4682, 0.4607. Found: 0.4669, 0.4621.

The method employed in the decompositions was a simple one, consisting essentially of a means of dropping the glyceride directly onto the heated catalyst, with suitable provision for condensing and collecting the gaseous and liquid products. The catalyst in all cases was thorium oxide, prepared by ignition of the nitrate, and supported on finely cracked, porous tile. The reaction chamber, containing the catalyst, was a vertical silica tube, 76 by 3.8 cm., electrically heated. Analysis of the liquid products presented considerable difficulty, but the results are believed to be reasonably accurate. The determination of fatty acids was greatly facilitated by the use of their benzyl pseudothio-urea salts, a method suggested by the paper of Johnson and Donleavy.[6] The results for the four runs thus far completed have been given under the discussion.

Summary

1. The catalytic decomposition of triacetin and of tripropionin over thorium oxide has been studied at a maximum temperature of 525°.

2. Acrolein, acids, oxides of carbon, hydrocarbons and tarry condensation compounds are uniform products of decomposition. Unexpectedly, hydrogen and the lower homolog of the glyceride acid are also formed.

3. The production of the latter substances makes it impossible at present to deduce a reaction mechanism.

4. Tripropionin, prepared for this work, is a new representative of the glyceride series.

BROWN UNIVERSITY
PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE BAKER CHEMICAL AND THE ROCKEFELLER PHYSICAL LABORATORIES OF CORNELL UNIVERSITY]

THE ABSORPTION SPECTRA OF PHENOLPHTHALEIN, ISOPHENOLPHTHALEIN AND OF DIPHENYLPHTHALIDE[1,2]

BY W. R. ORNDORFF, R. C. GIBBS AND S. ALICE MCNULTY[3]

RECEIVED MAY 10, 1926 PUBLISHED JULY 6, 1926

Much of the work reported on the absorption spectra of phenolphthalein has been done with alkaline solutions and in the visible region only.[4] R. Meyer and O. Fischer[5] have reported on the ultraviolet absorption of

[6] Reported at the New Haven Meeting of the American Chemical Society, April, 1923.

[1] The assistance of a grant made to the first two authors from the Heckscher Research Foundation of Cornell University which enabled them to make the measurements described in this report is gratefully acknowledged.

[2] For a preliminary report on the absorption of phenolphthalein and isophenolphthalein, see THIS JOURNAL, **46,** 2483 (1924). In that report the frequency numbers should be divided by 10, to conform with the unit used in the present article.

[3] Heckscher Research Assistant in Physics and Chemistry, Cornell University, 1921–1923. (Now Mrs. H. F. Vieweg.)

[4] Vogel, "Praktisches Spectralanal," **1889.** Formânek and Grandmougin, "Untersuch. Nachweis Farbstoffe," **1908,** vol. I, p. 129. Meyer and Marx, *Ber.*, **40,** 3603 (1907); **41,** 2446 (1908). Formânek and Knop, *Z. anal. Chem.*, **56,** 273 (1917).

[5] Meyer and Fischer, *Ber.*, **44,** 1944 (1911); **46,** 70 (1913).