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**. Formánek and Grandmougin, "Untersuch. Nachweis Farbstoffe," **1908**, vol. I, p. 129. Meyer and Marx, *Ber.*, **40**, 3603 (1907); **41**, 2446 (1908). Formánek and Knop, *Z. anal. Chem.*, **56**, 273 (1917).

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

the sodium salt in water and of solutions of phenolphthalein in concd. sodium hydroxide solution and in concd. sulfuric acid. In the colorless sodium hydroxide solution they found no bands while we find two. In concd. sulfuric acid they reported two bands where we find five. Howe and Gibson[6] have published some work on the ultraviolet absorption of phenolphthalein in neutral alcohol and in colored alcoholic and aqueous potassium hydroxide solutions. Their results on the first two solutions check roughly with ours except that we have found an additional band in the extreme ultraviolet in the alcoholic solution of potassium hydroxide.

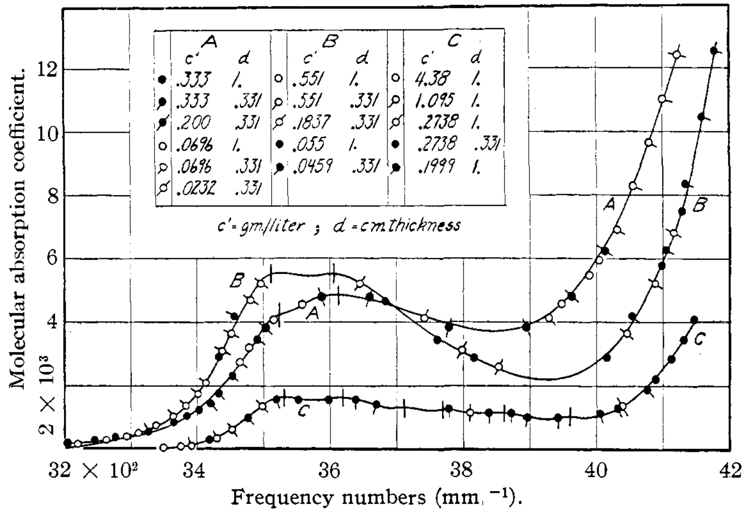

Fig. 1.—Neutral absolute alcohol solution. *A*. Phenolphthalein. *B*. Isophenolphthalein. *C*. Diphenylphthalide.

Moir[7] has reported on the absorption of a compound which he thought was *o*,*p*-dihydroxy-diphenylphthalide (our isophenolphthalein) in aqueous sodium hydroxide solution and in concd. sulfuric acid, but it is extremely doubtful, from his method of preparation, whether he really had that substance. Moreover, his data for the visible band in concd. sulfuric acid does not check with ours. Pratt[8] has studied the absorption of diphenylphthalide in neutral alcohol and in concd. sulfuric acid. He found only one band in the alcoholic solution, while we find six. He also reports three bands in concd. sulfuric acid, while we find four.

Our experimental procedure has been described in a previous article.[9] Fig. 1 shows the absorption curves of phenolphthalein (di-*p*-dihydroxy-diphenylphthalide), isophenolphthalein (*o*,*p*-dihydroxy-diphenylphthalide)

---

[6] Howe and Gibson, *Phys. Rev.*, **10**, 767 (1917).

[7] Moir, *Trans. Roy. Soc. So. Africa*, **7**, 111 (1918).

[8] Pratt, *Philippine J. Science*, **8A**, 399 (1913).

[9] THIS JOURNAL, **47**, 2767 (1925).

and diphenylphthalide in neutral absolute alcohol. Diphenylphthalide, Curve C, shows six bands in the ultraviolet, the first two of which at frequency numbers 3531 and 3620 correspond to the two bands for phenolphthalein, Curve A, at 3523 and 3613 and for isophenolphthalein, Curve B, at 3511 and 3606. It is interesting to note that while for diphenylphthalide and isophenolphthalein these two bands have equal intensities, in phenolphthalein the band at 3523 has a lower intensity than the one at 3613. The introduction of the two hydroxyl groups into the molecule of diphenylphthalide has markedly increased the intensity of absorption and at the same time has suppressed the weaker bands in the further ultraviolet. Benzaurin[9] and di-*p*-dihydroxy-triphenylmethane[9] in neutral alcoholic solution both show two bands in the same region as the two mentioned above for phenolphthalein, isophenolphthalein and diphenylphthalide.

Substance	1st band	2nd band	Difference
Phenolphthalein	3523	3613	90
Isophenolphthalein	3511	3606	95
Diphenylphthalide	3531	3620	89
Benzaurin	3526	3630	104
Benzaurin, faded	3520	3613	93
Di-*p*-dihydroxy-triphenylmethane	3465	3571	106

Di-*p*-dihydroxy-triphenylmethane also shows three more bands in the further ultraviolet comparable with three of the remaining four bands of diphenylphthalide.

Diphenylphthalide	3711	3769	3861	3960
Di-*p*-dihydroxy-triphenylmethane	3695	3782	3877	....

Fig. 2 shows the absorption curves for phenolphthalein, isophenolphthalein and diphenylphthalide in concd. sulfuric acid (93%). Diphenylphthalide, which gives a yellow solution in concd. sulfuric acid, shows two prominent bands (Curve C), one at either end of the spectrum, a phenomenon characteristic of the triphenylmethane derivatives, such as benzaurin,[9] *o*-cresol benzein, aurin, triphenylcarbinol, fuchsone and *o*-cresolsulfonephthalein[10] in this solvent. Fluorescein, sulfonefluorescein[10] and resorcinol-benzein[11] show the same phenomenon, except that the band in the extreme ultraviolet is resolved into two components.

The color of the freshly prepared sulfuric acid solutions of phenolphthalein and isophenolphthalein is due to the formation of quinoid sulfates. With these phthaleins, however, difficulties were encountered because of the progressive sulfonation of the substances in the cold, sulfuric acid solution. This is apparent from the color of the solutions—both are a deep *red* at the moment of forming the solution, but fade shortly, the phenolphthalein solution becoming *deep orange*, while the isophenol-

[10] Unpublished data.

[11] THIS JOURNAL, **48**, 1327 (1926).

phthalein solution changes rapidly to a pale *yellow*. In both cases in order to obtain consistent results, it was necessary to wait until equilibrium had been established and no further fading took place. In the case of phenolphthalein, one day was sufficient while for the isophenolphthalein, probably due to the greater degree of sulfonation, three to four days were required to reach complete equilibrium. The spectra of these *faded* solutions are shown in Curve A for phenolphthalein and in Curve B for isophenolphthalein. In the visible and near ultraviolet these two substances yield strikingly different results, the absorption of phenolphthalein being 120 times as intense as that of isophenolphthalein in the region of the band at 2025. Further in the ultraviolet the absorption becomes very similar for both substances. An attempt was made to measure the visible absorption of a fresh (*deep-red*) solution of isophenolphthalein. By working very rapidly, immediately after the material had gone into solution, data were obtained showing a molecular absorption coefficient of about 18 × 10^3 in the region of frequency number 2200, this value being about 60 times as great as that shown on Curve B for the solution which had reached equilibrium. However, even this provisional value is too low, as fading was taking place during the short interval of time necessary to fill the cell and make the measurement.

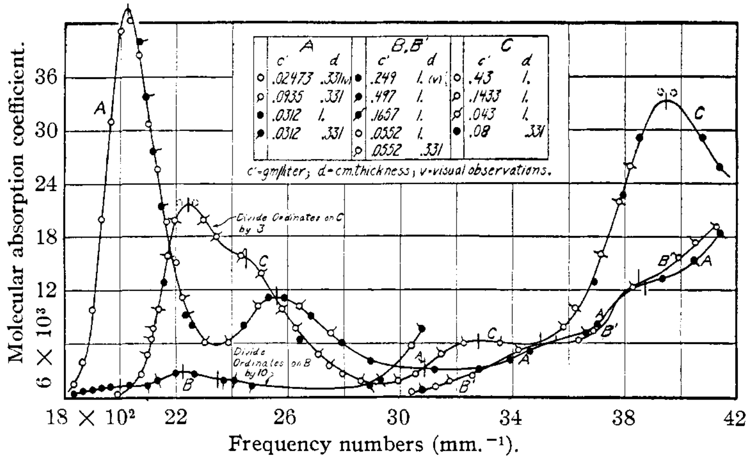

Fig. 2.—Concentrated (93%) sulfuric acid solution. *A*. Phenolphthalein. *B*, *B'*. Isophenolphthalein. *C*. Diphenylphthalide.

An attempt was made to measure the absorption of alcoholic solutions of phenolphthalein and isophenolphthalein containing various amounts of hydrogen chloride gas, but the plates obtained showed that no reaction had occurred as the absorption was exactly the same as that of the neutral solutions of the phthalein in alcohol, even with the addition of hydrochloric acid in the ratio of 11,500 molecules to one of the phthalein. This agrees with the observation of K. Meyer and Hantzsch[12] who found that phenolphthalein takes up hydrochloric acid at —30°, turning red, but on warming, all the hydrogen chloride splits off, leaving the phenolphthalein colorless.

Fig. 3 shows the effect of adding various amounts of potassium hydroxide to the alcoholic solution of phenolphthalein. Curve A for 23 molecules of potassium hydroxide shows the development of two new bands at 1785 and 2730 due to the formation of the di-potassium salt. On diluting the solution with alcohol, in order to obtain the further ultraviolet spectrum, the absorption gradually reverted to the neutral type of absorption (Curves A′ and A″), the bands at 3523 and 3625 corresponding in intensity and position to the neutral bands at 3523 and 3613. In other words, the solution at this dilution consists almost entirely of free phenolphthalein and free potassium hydroxide. On increasing the ratio of potassium hydroxide to 232 molecules (Curve B) the two bands at 1785 and 2730 have increased in intensity while in the extreme ultraviolet a new band has appeared at 3950 together with a broad shoulder at 3400. These two new bands correspond to those found in the colorless 33% aqueous potassium hydroxide solution of phenolphthalein (see Fig. 5). With this higher ratio of potassium hydroxide, an even greater dilution with alcohol failed to bring about the type of reversion noted above. A similar behavior was noted in hydrochloric acid solutions of resorcinol-benzein.[11] In the visible there is evidence of fading with time (see tailed, solid circles) due to the slow formation of the colorless tripotassium salt of the carbinol-carboxylic acid at this concentration of potassium hydroxide.

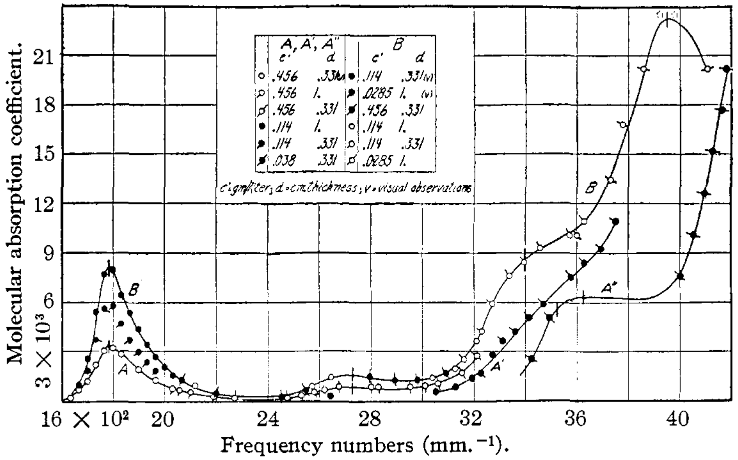

Fig. 3.—Phenolphthalein in alc. KOH. *A*, *A′*, *A″*. 23 molecules KOH:-1 Phenolphthalein. *B*. 232 molecules KOH: 1 Phenolphthalein.

---

[12] Meyer and Hantzsch, *Ber.*, **40**, 3479 (1907).

Fig. 4 shows the effect of adding varying amounts of potassium hydroxide to an alcoholic solution of isophenolphthalein. On adding two molecules of potassium hydroxide the solution is a pale *yellow* with a very weak absorption in the blue and near ultraviolet. On adding 23 molecules of potassium hydroxide the color changes to green and Curve A represents the absorption with weak bands at 1695, 2525 and 2855. On diluting this solution with alcohol the absorption reverts to the neutral type (Curves A′ and A″), the bands at 3525 and 3615 on A″ being similar in position and intensity to the bands at 3511 and 3606 for the neutral solution of isophenolphthalein. The addition of 171 molecules of potassium hydroxide produces a blue solution with the absorption bands at 1695, 2440, 3400 and 4060, the last two bands being broad shoulders which correspond in position with the two bands in the colorless solution of isophenolphthalein in 33% aqueous potassium hydroxide at 3400 and 4115 (see Fig. 5). As in the case of phenolphthalein, a greater dilution with alcohol can be made for this higher ratio of potassium hydroxide without bringing about reversion to the neutral type of absorption. Since the monosodium salt of isophenolphthalein is *yellow* and the disodium salt is *blue*,[2] while the sodium salts of phenolphthalein are red we are inclined to think that the salts of isophenolphthalein have an *o*-quinoid structure[2] while those of phenolphthalein are *p*-quinoid. This probably is the explanation of the difference in the absorption spectra of the two substances in alkaline solution.

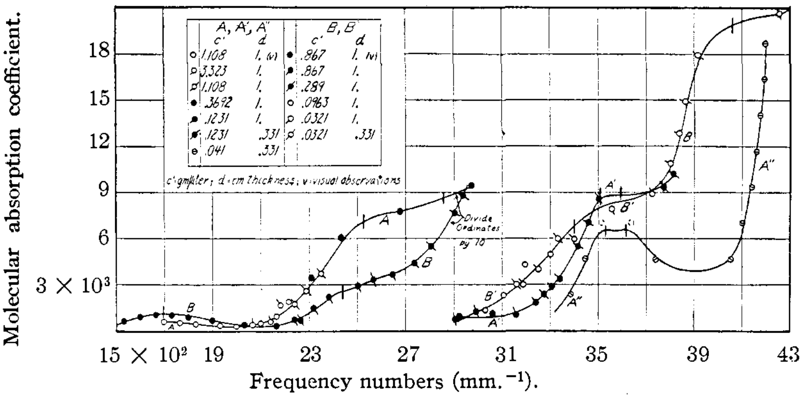

Fig. 4.—Isophenolphthalein in alc. KOH. *A*, *A′*, *A″*. 23 molecules KOH:-1 Isophenolphthalein. *B*, *B′*. 171 molecules KOH: 1 Isophenolphthalein.

Benzaurin[9] in alcoholic potassium hydroxide solution (60 molecules of potassium hydroxide: 1 of benzaurin) shows bands analogous to those reported above for phenolphthalein with 232 molecules of potassium hydroxide and for isophenolphthalein with 171 molecules of potassium hydroxide.

	Bands at			
Phenolphthalein and 232 molecules of KOH	1785	2730	3400	3950
Isophenolphthalein and 171 molecules of KOH	1695	2440	3400	4060
Benzaurin and 60 molecules of KOH	1765	2640	3380	4005

The bands at 3380 and 4005 for benzaurin with 60 molecules of potassium hydroxide correspond with the bands at 3380 and 4050 for benzaurin in 33% aqueous potassium hydroxide solution. This is the same relationship that we noted above for phenolphthalein and isophenolphthalein in these two solvents.

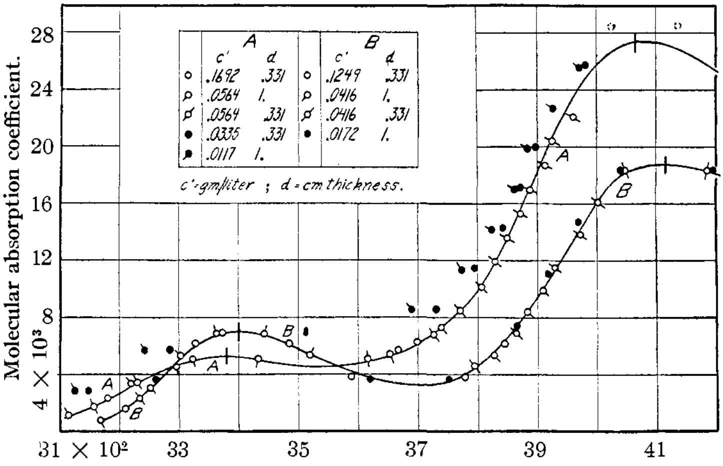

Fig. 5.—33% KOH solution. *A*. Phenolphthalein. *B*. Isophenolphthalein.

Fig. 5 shows the absorption curves for phenolphthalein and isophenolphthalein in 33% aqueous potassium hydroxide. Both substances give colorless solutions in this concentration of the potassium hydroxide. Phenolphthalein (Curve A) shows two prominent bands at 3380 and 4065. On diluting this solution with 33% potassium hydroxide in order to measure the extreme ultraviolet, the absorption tends to increase somewhat, as indicated by the solid black circles. This may be due to the formation of more of the tripotassium salt of the carbinol-carboxylic acid caused by the relatively greater concentration of the potassium hydroxide. Curve B for isophenolphthalein also shows two bands at 3400 and 4115, while the effect produced by the addition of more potassium hydroxide solution is much less pronounced, although still perceptible. Benzaurin[9] shows three bands in 33% aqueous potassium hydroxide solution, the latter two corresponding to those of phenolphthalein and isophenolphthalein.

Phenolphthalein	....	3380	4065
Isophenolphthalein	....	3400	4115
Benzaurin	2900	3380	4050

Table I gives the frequency numbers of the peaks of the bands in the various solutions of phenolphthalein, isophenolphthalein and diphenylphthalide.

Table I

Frequency Numbers of Bands

Solvent	Diphenyl-phthalide	Phenol-phthalein	Isophenol-phthalein
Neutral absolute alcohol	3531	3523	3511
	3620	3613	3606
	3711		
	3769		
	3861		
	3960		
Concd. sulfuric acid		2025	2000
	2243		2225
	2450	2560	2350
		3085	
	3277	3555	3500
	3946	3875	3850
Alcoholic KOH—23 molecules		1785	1695
		2730	2525
			2855
		3523	3525
		3625	3615
Alcoholic KOH (Phenolphthalein—232 molecules) (Isophenolphthalein—171 molecules)		1785	1695
		2730	2440
		3400	3400
		3950	4060
33% aqueous KOH		3380	3400
		4065	4115

We are much indebted to Mr. C. V. Shapiro[13] for his assistance in the preparation of our data for publication.

Summary

1. The absorption curves of phenolphthalein, isophenolphthalein and of diphenylphthalide (the mother substance of the two phthaleins) in neutral absolute alcohol have been determined and their relation pointed out.

2. The absorption curves for the three above-mentioned substances in concd. sulfuric acid solution have been determined and their resemblances and differences indicated.

3. The effect of the addition of various amounts of potassium hydroxide to the alcoholic solutions of phenolphthalein and isophenolphthalein due to the formation of the potassium salts has been studied. It has been suggested that the salts of isophenolphthalein have an *o*-quinoid structure while those of phenolphthalein are *p*-quinoid.

---

[13] Heckscher Research Assistant in Physics and Chemistry, Cornell University, 1923–26.

4. The absorption curves for the colorless solutions of phenolphthalein and isophenolphthalein in 33% aqueous potassium hydroxide have been determined. The absorption is due to the presence of the colorless tripotassium salt of the carbinol-carboxylic acid.

5. A table showing the frequency numbers of the peaks of the bands of the various solutions studied has been prepared.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE POLARIMETRY SECTION OF THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE][1]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XVI.[2] CONVERSION OF CELLOBIOSE TO ANOTHER DISACCHARIDE, CELTROBIOSE, BY THE ALUMINUM CHLORIDE REACTION. CHLORO-ACETYL CELTROBIOSE

BY C. S. HUDSON

RECEIVED MAY 22, 1926 PUBLISHED JULY 6, 1926

The new method of chlorinating sugar acetates by aluminum chloride which Kunz and the writer have described in the preceding article has been applied to cellobiose octa-acetate with the result that a considerable yield of the well-known crystalline α-chloro-acetyl cellobiose has been obtained, and in addition a yield of about 13% of an isomeric crystalline substance, the properties of which show that it is the chloro-acetyl derivative of a new disaccharide. It has been carefully purified by repeated crystallizations until its rotation became constant at $[\alpha]_D^{20} = +59.2$ in chloroform solution. The melting point was 137–138°. Its chlorine content was found to be 5.43% by heating it in acetic anhydride solution with silver acetate and 5.40% by Bacon's directions[3] for the Stepanoff method. The theoretical value for a chloro-hepta-acetyl dihexose, $C_{26}H_{35}O_{17}Cl$, is 5.41%. Its saponification by potassium hydroxide at 0° according to Kunz' method (see preceding article) shows its acid equivalent to correspond closely with that calculated. The alkaline saponification of the new chloro-acetate yields a dextrorotatory solution from the reading of which it is evident that the parent sugar is weakly dextrorotatory. After hydrolysis of the new chloro-acetate with 0.5 N hydrochloric acid for two and a half hours at 98°, by which treatment it is to be expected that the chlorine and acetyl groups are split off and the parent disaccharide largely hydrolyzed to its component hexoses, the solution is strongly levorotatory. These analytical, melting-point, rotation and hydrolysis data differentiate the sugar from all

---

[1] Published by permission of the Director of the Bureau of Standards.

[2] See preceding Article XV.

[3] Bacon, THIS JOURNAL, **31,** 49 (1909).