

The heat of the reaction is thus 10.1 kcal. The 4 kcal. greater heat of reaction than that which accompanies the hydration of crotonaldehyde is ex-

plained by a lower loss of resonance energy in the hydration of crotonic acid.

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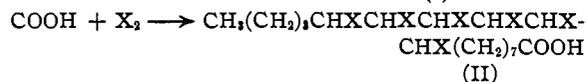
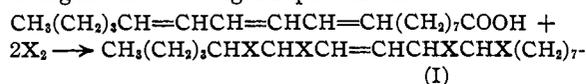
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[A CONTRIBUTION FROM THE YALE-IN-CHINA SCHOOL OF SCIENCE, HUA CHUNG COLLEGE]

The Reaction of Wijs Solution with Tung Oil

BY S. W. WAN AND D. B. HU

Tung oil contains mainly the glycerides of eleostearic acid and oleic acid and its drying power is due to the former unsaturated acid. In estimating the degree of unsaturation of tung oil with Wijs solution, the presence of eleostearic glyceride causes much uncertainty because the iodine value thus obtained varies with experimental conditions such as temperature, concentration and relative amount of reagent, and time of contact between reagent and oil.¹ Various methods have been tried for determining the percentage of eleostearic acid glyceride in tung oil, but have given no concordant results. Among the most recent methods may be mentioned the combined bromine vapor and Wijs method,² the differential halogen absorption method,³ the polymerization method,⁴ and the diene number method.⁵ The peculiar properties of eleostearic acid giving rise to analytical difficulties have been explained by Böeseken and co-workers by assigning to it the molecular constitution $\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CHCH}=\text{CHCH}=\text{CH}(\text{CH}_2)_7\text{COOH}$,⁶ which, in the light of Thiele's theory of partial valency, is expected to absorb halogens in two stages represented as



With Wijs solution, X_2 being a molecule of iodine monochloride, the first stage reaction is much faster and produces a chloro compound.⁶ On the other hand, compounds with non-conjugate double bonds take up the theoretical amount of iodine chloride in a short time, forming iodo-chloro compounds.

(1) Boughton, *Seventh Int. Congr. Appl. Chem.*, London (1909); Ho and co-workers, *Ind. Eng. Chem., Anal. Ed.*, **7**, 96 (1936).

(2) Toms, *Analyst*, **53**, 69 (1928).

(3) Croxford, *ibid.*, **54**, 445 (1929).

(4) Bolton and Williams, *ibid.*, **55**, 360 (1930).

(5) Kaufmann and Baltes, *Fette u. Seifen*, **43**, 93 (1936).

(6) Böeseken and Gelber, *Rec. trav. chim.*, **46**, 158 (1927); Böeseken, Hoogl, Broek and Smit, *ibid.*, **46**, 619 (1927).

This paper gives an account of the authors' attempt to apply the above-mentioned property of eleostearic acid to the determination of the concentration of its glyceride in tung oil, and an account of their investigation in the chemical kinetics of reaction (II).

Materials.—Glacial acetic acid, c. p., tested free from reducible substances. Iodine, c. p., twice resublimed. Sodium oxalate, c. p., giving an assay of 99.98%. Sodium thiosulfate, potassium iodide, carbon tetrachloride, oleic acid, potassium permanganate, all c. p. grade. Tung oil, supplied from the Chinese Vegetable Oil Corporation, Hankow. α -Eleostearic acid, prepared according to the method of Thomas and Thomson,⁷ m. p. 48.3°. Wijs solution, prepared according to the procedure given by Griffin⁸ with the important modification that the iodine and chlorine contents in the solution were adjusted to be exactly equivalent in amount.

The sodium thiosulfate solutions used in these experiments were standardized against potassium permanganate as a secondary standard and sodium oxalate as a primary standard.

Experimental

Part I.—Approximately equal weights of the carbon tetrachloride solution of a sample were placed in glass-stoppered conical flasks. To each was then added a weighed amount of Wijs solution and the mixture allowed to react for a definite length of time by shaking in a thermostat maintained at $25 \pm 0.1^\circ$. All reagents also had been allowed previously to reach temperature equilibrium in the same thermostat. The reaction in each mixture was stopped promptly by adding 20 cc. of 15% potassium iodide solution and the reaction mixture was immediately diluted with water and titrated with sodium thiosulfate solution from a weighing buret. A number of runs were made by following the above procedure and using samples of: (a) pure α -eleostearic acid with a reaction period of five minutes; (b) pure α -eleostearic acid with a reaction period of two minutes; (c) pure α -eleostearic acid with a reaction period of ten minutes; (d) pure oleic acid with a reaction period of ten minutes; (e) a known mixture of α -eleostearic and oleic acids with a reaction period of five minutes; (f) tung oil with a reaction period of five minutes.

Part II.— α -Eleostearic acid was weighed into a 100-cc. volumetric flask and carbon tetrachloride was added, mak-

(7) Thomas and Thomson, *THIS JOURNAL*, **56**, 898 (1934).

(8) Griffin, "Technical Methods of Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., p. 310.

ing up to volume at 25.0°. This solution was transferred into a glass-stoppered conical flask containing the Wijs solution previously set in the same thermostat maintained at 25.0 ± 0.1°. While beginning the delivery of the carbon tetrachloride solution of α -eleostearic acid two stop-watches were started simultaneously, one of them being stopped just when the delivery was completed, and the time of half delivery was taken as the starting point of the reaction. The flask containing the reaction mixture was well shaken at the start and also occasionally as the reaction went on. At definite intervals, 25-cc. portions of the reaction mixture were withdrawn with a pipet and each portion was delivered into one of a series of 120-cc. cork-stoppered conical flasks containing about 20 cc. of 15% potassium iodide solution. The duration for this delivery was noted and its half value was considered as the stopping point of the reaction. Each flask had been weighed with the potassium iodide solution in it and was again weighed after adding the reaction mixture. The exact volume of a portion of the mixture thus withdrawn was calculated from its weight and the density of the reaction mixture. (The densities of the eleostearic acid solution and that of Wijs solution were found to be additive.) The contents of the flask were transferred quickly and washed into a 300-cc. flask and titrated with sodium thiosulfate solution from a weighing buret. By following the above procedure the following investigations were performed: (g) reaction between α -eleostearic acid and Wijs solution in conventional proportions; (h) reaction between α -eleostearic acid and an equivalent amount of Wijs solution just sufficient for the first stage saturation; (i) reaction between α -eleostearic acid and an excess of Wijs solution; (j) comparison of halogen absorption by α -eleostearic acid and by tung oil.

Results

For experiments in part (I), solutions of α -eleostearic acid were of the concentration of about 0.015 millimole per gram of solution; solutions of oleic acid were of the concentration of about 0.022 millimole per gram of solution; the concentration of Wijs solution was 0.1450 millimole of iodine monochloride per gram of solution and 1 g. of the sodium thiosulfate solution was equivalent to 0.06295 millimole of halogen. All original data have been converted into millimoles of iodine monochloride used per millimole or gram of sample, and millimoles of halogen absorbed or left over per millimole or gram of sample, respectively; these results are given in Table I.

Results of Part II are given in Tables II to VI, where a is the molar concentration of α -eleostearic acid in the mixture or in other words the initial concentration of α -eleostearic acid tetrachloride at the beginning of the second stage reaction; b is the initial molar concentration of iodine monochloride at the beginning of the second stage; b' which is equal to $2a$ is the initial molar

concentration of free iodine liberated during the first stage; B is the sum of b and b' ; x' is the molar concentration of the iodochloride of α -eleostearic acid tetrachloride and x'' , that of the di-iodide of α -eleostearic acid tetrachloride formed during time t of the reaction; x is the sum of x' and x'' ; k_1, k_1^*, k_2, k_2^* , and k_3 are specific reaction rates described in another section of this paper (see Discussion).

TABLE I⁹

RESULTS OF EXPERIMENTS					
Run	Millimoles used		Run	Millimoles used	
	ICI per mmol. α -eleost. acid	Halogen abs. per mmol. acid		ICI per mmol. α -eleost. acid	Halogen abs. per mmol. acid
	Expt. (a)			Expt. (b)	
101	2.1306	1.0358	201	1.8173	0.9442
102	2.5400	1.2619	202	2.2790	1.1369
103	2.9461	1.4998	203	2.5285	1.2198
104	3.3753	1.7206	204	3.5789	1.6671
105	4.2076	2.0039	205	3.9596	1.8128
106	4.5855	2.0527	206	5.0272	2.0480
107	4.7605	2.1142	207	5.4495	2.0652
108	5.0209	2.1257	208	5.9313	2.0889
	Expt. (c)		209	6.4945	2.0940
301	3.856	2.008		Expt. (d)	
302	3.570	1.906		ICI per mmol. oleic acid	Halogen left per mmol. acid
303	3.187	1.715			
304	2.904	1.550	401	1.1358	0.1393
305	4.225	2.081	402	1.2372	.2208
306	4.505	2.100	403	1.3688	.3546
	Expt. (e)		404	1.4672	.4522
	ICI per g. acid mixt.	Halogen abs. per g. acid mixt.	405	1.5893	.5699
501	11.002	5.970	406	1.8165	.8001
502	11.318	6.116	407	2.0182	1.0000
503	11.743	6.292	408	2.2607	1.2370
504	12.168	6.415		Expt. (f)	
505	12.544	6.601		ICI per g. tung oil	Halogen abs. per g. of oil
506	13.505	6.799	601	8.962	5.052
507	12.956	6.808	602	9.290	5.239
508	13.830	6.844	603	9.558	5.397
509	14.231	6.888	604	9.936	5.610
510	14.696	6.904	605	10.216	5.751
511	13.078	6.683	606	10.546	5.925
	Actual compn. of mixt.:		607	10.886	5.994
	α -Eleostearic acid, 84.57%		608	11.161	6.186
	Oleic acid, 15.43%		609	11.582	6.353
	Calcd. compn. of mixt.:		610	11.958	6.461
	α -Eleostearic acid, 84.51%		611	12.262	6.537
	Oleic acid, 17.77%		612	9.352	5.351
			613	11.445	6.344
			614	12.533	6.583
				Calcd. % α -eleostearic acid glyceride, 72.2.	

(9) These data were obtained with the assistance of Miss K. L. Lu, while working on her undergraduate thesis in this College during 1937-1938.

TABLE II

RESULTS OF EXPERIMENT (g)

Original concentration of ICl, 0.07072 *M*; *a*, 0.007953 *M*; *b*, 0.038908 *M*; initial halogen concentration for second stage, $2a + b = 0.05481$ *M*.

<i>t</i> , minutes	Halogen concn.	<i>x</i>	<i>k</i> ₁	<i>k</i> ₁ [*]
30.7	0.05270	0.00211	0.211	89.2
68.5	.05198	.00283	.172	27.3
90.6	.05178	.00303	.142	26.5
125.5	.05161	.00320	.111	24.7
157.0	.05150	.00331	.0925	19.9
189.3	.05132	.00349	.0827	16.9
262.9	.05118	.00363	.0632	12.4

TABLE III

RESULTS OF EXPERIMENT (h)

Original concentration of ICl, 0.067891 *M*; *a*, 0.016972 *M*; *b*', 0.033944 *M*.

<i>t</i> , minutes	Concn. of I ₂	<i>x</i> '	Log $\frac{(b' - x)}{(a - x)}$	<i>K</i> ₂ × 10 ³
23.95	0.033807	0.000137	0.3028	9.99
47.45	.033679	.000265	.3045	9.81
80.45	.033546	.000398	.3062	8.74
117.5	.033365	.000579	.3086	8.78
160.2	.033260	.000684	.3101	7.64
204.8	.033035	.000909	.3132	8.03
351.3	.032604	.001340	.3198	7.23
466.0	.032371	.001573	.3227	6.18

Calculated log *b*'/*a* = 0.3010.
Extrapolated log *b*'/*a* = 0.3022.

TABLE IV

RESULTS OF EXPERIMENT (i)

Original concentration of ICl, 0.11960; *a*, 0.0(5303 *M*; *b*, 0.098390 *M*.

<i>t</i> , minutes	Halogen concn.	<i>x</i> '	Log $\frac{(b - x)}{(a - x)}$	<i>k</i> ₂ × 10 ³	<i>k</i> ₂ [*] × 10 ³
50.1	0.10742	0.00156	1.413	7.13	6.42
78.3	.10712	.00186	1.448	5.69	1.52
105.6	.10694	.00205	1.471	4.76	1.66
142.1	.10667	.00231	1.493	3.92	1.62
186.2	.10674	.00224	1.497	3.04	1.00
230.1	.10658	.00240	1.520	2.71	1.29
269.1	.10653	.00245	1.527	2.38	1.17
329.7	.10608	.00290	1.600	2.49	1.50
377.1	.10597	.00301	1.620	2.31	1.44
512.6	.10585	.00313	1.642	1.81	1.17
632.1	.10549	.00349	1.724	1.79	1.27

Calculated log *b*/*a* = 1.268.
Extrapolated log *b*/*a* = 1.400.

TABLE V

RESULTS OF EXPERIMENT (g)

Showing the relation between *t* and log $\frac{(B - x)}{(a - x)}$, where $B = b + b' = 0.038908 + 0.015906 = 0.054814$.

<i>t</i> , minutes	Log $\frac{(B - x)}{(a - x)}$
30.7	0.9554
68.5	1.007
90.6	1.021
125.5	1.037
157.0	1.045
189.3	1.060
262.9	1.075

TABLE VI

RESULTS OF EXPERIMENT (j)

Weight of tung oil sample, 1.7286 g.; original concentration of ICl, 0.07775 *M*.

<i>t</i> , minutes	Halogen concn.
16.0	0.04647
37.3	.04606
85.0	.04553
138.3	.04528
187.8	.04503
235.2	.04470
353.0	.04429
450.0	.04414

Discussion

The interpretation of the results from the experiments of part (I) is based on the following consideration. When *x*, representing the number of millimoles of iodine monochloride added to one millimole of acid, is plotted against *y*, the number of millimoles of halogen absorbed, then in the case of α -eleostearic acid, a linear relation, $y = x/2$, will be obtained until the point, $y = 2$, $x = 4$, is reached, because this acid absorbs chlorine and not iodine in the first stage reaction, each millimole of acid requiring two of chlorine obtainable from four of iodine monochloride. Beyond this point the plot will become a horizontal straight line, $y = 2$.

However, the above relation is valid only when the reaction period is long enough for completing the first stage absorption but not too long lest the second stage reaction become appreciable. If the second stage reaction takes place to an appreciable extent along with the first stage reaction, the plot will not be linear; if the reaction period is too short for the first stage saturation, the first part of the plot will have a slope less than $1/2$; and if the reaction period is too long for the first stage saturation, the first part of the plot will have a slope greater than $1/2$. Furthermore, if the second stage reaction can be detected in the presence of excess iodine monochloride, the second part of the plot will not be horizontal and not necessarily linear. These phenomena are clearly illustrated by Figs. 1, 2 and 3, in which are plotted the results of experiments (a), (b) and (c).

The results obtained from the reaction of oleic acid and iodine monochloride when treated in the same manner give a decisive answer to the question whether oleic acid absorbs chlorine alone or a whole molecule of iodine monochloride. Since oleic acid contains one double bond, the plot, in the former case, will be $y = 1/2x$ up to $x = 2$,

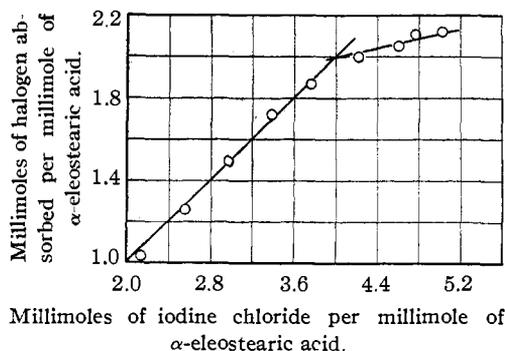


Fig. 1.

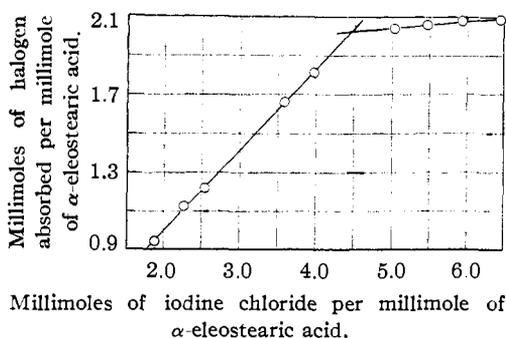


Fig. 2.

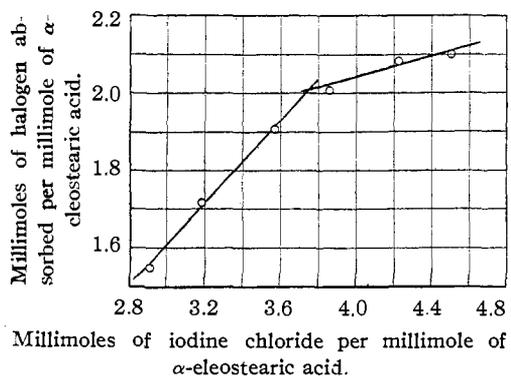


Fig. 3.

$y = 1$, and become $y = 1$ beyond that, while in the latter case it will be simply $y = x$ up to $x = 1$, $y = 1$ and then become $y = 1$ beyond that. On the other hand, if u represents the millimoles of iodine monochloride added to one of acid, and v , the millimoles of halogen left over, the plot will be $u = 2v$ up to $u = 2$ and $v = 1$, and become $u = v$ further on, in the former case; in the latter case, $u = v + 1$ throughout. The intercept of 1 on the u -axis is clearly brought out in Fig. 4.

With a mixture of the two acids, the results have been plotted on the basis of x millimoles of iodine monochloride added per gram of sample against y millimoles of halogen absorbed. Let r

and s be the weight fractions; m_e and m_o , the millimolecular weights of α -eleostearic acid and oleic acid, respectively; p , the point at which just enough iodine monochloride has been used to satisfy both the oleic acid and the eleostearic acid first stage saturation. From the knowledge gained in these experiments concerning the behavior of iodine monochloride toward the two acids, it is evident that

$$x_p = 4\frac{r}{m_e} + \frac{s}{m_o} \quad \text{and} \quad y_p = 2\frac{r}{m_e} + \frac{s}{m_o}$$

Hence r and s can be solved for simultaneously from the above equations.

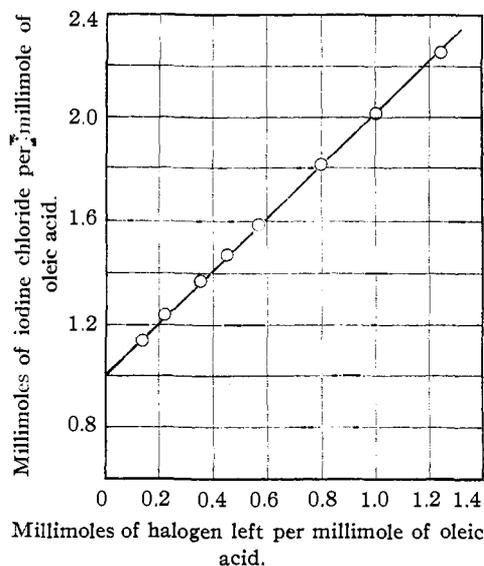


Fig. 4.

In our analysis of a known mixture by this method, there has been good agreement between the actual and the calculated values for α -eleostearic acid (see Fig. 5). Only one determination

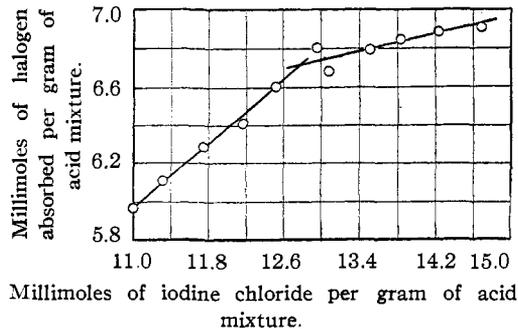


Fig. 5.

has been made with tung oil (see Fig. 6) but further investigation is in progress because on the

whole the method thus developed seems very promising.

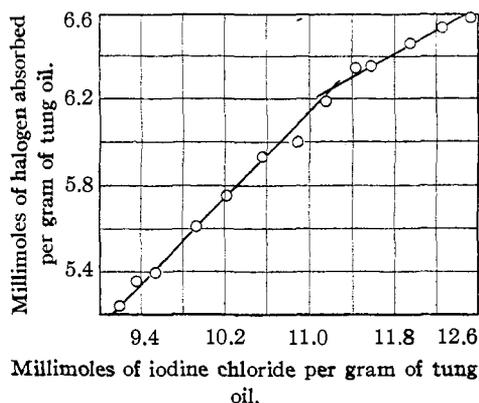


Fig. 6.

The data of experimental part (II) are the first of the kind making possible a study of the chemical kinetics for the reaction between α -eleostearic acid and iodine monochloride. For this reaction Böeseken⁶ has proposed the scheme

$$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CHCH}=\text{CHCH}=\text{CH}(\text{CH}_2)_7\text{COOH} + 4 \text{ ICl} \rightarrow \text{CH}_3(\text{CH}_2)_3\text{CHClCHClCHCl}=\text{CHCHClCHCl}(\text{CH}_2)_7\text{COOH} + 2 \text{ I}_2 \xrightarrow{+\text{ICl}} \text{CH}(\text{CH}_2)_3\text{CHClCHClCHClCHClCHClCHCl}(\text{CH}_2)_7\text{COOH} \quad (\text{II})$$

The second stage reaction according to the above scheme is bimolecular and therefore its reaction rate k_1 can be expressed by the second order relation

$$k_1 = 1/t(a - b) \ln b(a - x)/a(b - x) \quad (\text{IV})$$

However, if the absorption involves the addition of chlorine or iodine (from iodine monochloride), instead of iodine monochloride itself, the specific reaction rate k_1^* of a third order reaction would be obtained from the equations

$$dx/dt = k_1^*(a - x)(b - 2x)^2 \quad (\text{V})$$

and

$$k_1^* = 1/t(b - 2a) \{ 1/(b - 2a) \ln a(b - 2x)/b(a - x) - 1/(b - 2x) + 1/b \} \quad (\text{VI})$$

There is still another possibility, namely, the absorption of iodine (liberated in the first stage) and iodine monochloride simultaneously in the second stage. In this case, the reaction rate would be governed by the relation

$$dx/dt = k_2(a - x)(b - x') - k_3(a - x)(b' - x'') \quad (\text{VII})$$

The integration of equation (VII) would be a laborious process but as a first approximation the calculation may be simplified by either one of the following conditions. (1) The iodine monochloride concentration is just sufficient to complete the

first stage absorption, so that $b = 0$ and $x' = 0$ and equation (VII) reduces to

$$\begin{aligned} dx/dt &= k_2(a - x)(b' - x'') \\ &= k_3(a - x)(b' - x) \end{aligned} \quad (\text{VIII})$$

and

$$k_3 = 1/t(b' - a) \ln a(b' - x)/b'(a - x) \quad (\text{IX})$$

(2) When excess of iodine monochloride is used, the relatively small amount of iodine liberated in the first stage may be disregarded so that equation (VII) becomes

$$\begin{aligned} dx/dt &= k_2(a - x)(b - x') \\ &= k_2(a - x)(b - x) \end{aligned} \quad (\text{X})$$

and

$$k_2 = 1/t(b - a) \ln a(b - x)/b(a - x) \quad (\text{XI})$$

The fact that values of k_1 and k_1^* given in Table II fail to correlate with equations (IV) and (VI), respectively, indicates that the mechanism suggested by Böeseken for the second stage reaction between iodine monochloride and α -eleostearic acid is incorrect, and that it is neither bimolecular nor trimolecular but most probably a combination of two simultaneous bimolecular reactions, one between the acid and the iodine liberated in the first stage and the other between the acid and iodine monochloride. This statement is supported by the data given in Table III and Table IV and plotted in Fig. 7 and Fig. 8 to show the linear relation between t and $\ln(b' - x)/(a - x)$ and between t and $\ln(b - x)/(a - x)$, respectively. It should be noted that when the

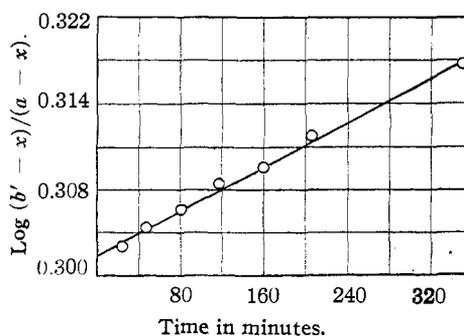


Fig. 7.

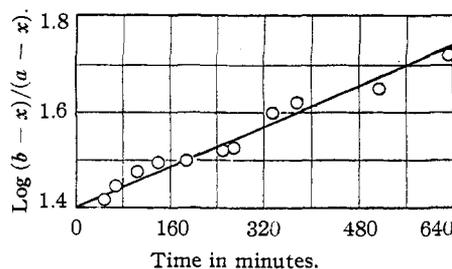


Fig. 8.

above plots are extrapolated to zero time, the values of $\ln(b/a)$ and $\ln(b'/a)$ are higher than the corresponding computed values. This may be accounted for by the presence of the beta form of eleostearic acid produced from the alpha acid on standing, the beta acid having a lower halogen-absorption rate.¹⁰ Furthermore, the prompt stopping of a reaction in these experiments was done through adding to the reaction mixture, an excess of potassium iodide solution which might react with the iodo-chloride of α -eleostearic acid addition product forming a di-iodide which in turn might liberate iodine and restore the last-saturated double bond.⁶

The specific reaction rates k_2 and k_3 of the above-mentioned simultaneous bimolecular reactions are both small and of the same order of magnitude. If they could be assumed equal, equation (VII) would become

$$\begin{aligned} dx/dt &= k_4(a-x)(b+b') - (x'+x'') \\ &= k_4(a-x)(B-x) \end{aligned} \quad (\text{XII})$$

which is equivalent to a second order equation. As a matter of fact, a linear relation is obtained between t and $\log(B-x)/(a-x)$ as shown in Fig. 9, which apparently confirms the contention made previously on the absorption of halogen by α -eleostearic acid in Wijs solution that the mechanism of the reaction is bimolecular.

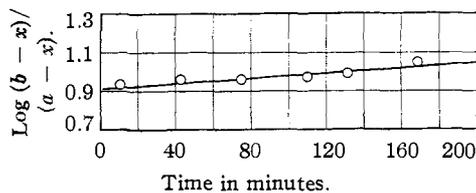


Fig. 9.

The similarity of the two curves in Fig. 10 serves to indicate that the reaction of halogen in Wijs solution with tung oil is much of the same nature as that with α -eleostearic acid. This property also has been applied in experimental part (I).

The increase of iodine value of the oil with increase of temperature or time of contact with Wijs solution can be explained easily in the light of what has been found from these experiments. The absorption of chlorine from iodine monochloride in the first stage explains the requirement of a minimum excess of Wijs solution for obtaining a normal iodine value.¹ The slight decrease of iodine value with increased amount of oil when the

(10) Van Loon, *Chem. Umschau, Feise, Oele, Wachse, Harze*, **37**, 269 (1930).

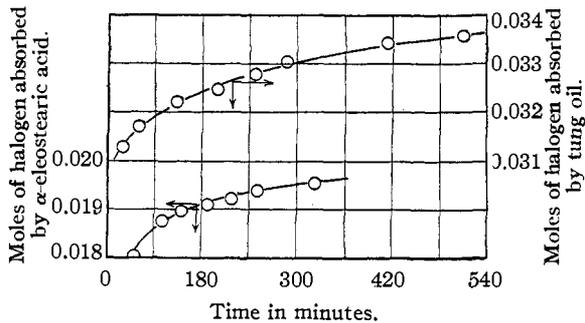


Fig. 10.

same amount of Wijs solution is used¹¹ may be accounted for by the fact that a relatively larger amount of α -eleostearic acid glyceride absorbs a correspondingly larger amount of iodine monochloride in the first stage and leaves a smaller excess of halogen which because of the kinetic relations mentioned above decreases the rate of halogen absorption in the second stage.

Finally, attention should be called to the fact that although experiment (i) was aimed at using a large excess of iodine monochloride relative to α -eleostearic acid so that b' and x'' might become insignificant compared with b and x' , yet practical limitations made it possible to realize only a ratio of about 10 to 1 between b and b' . This ratio may not justify the process of simplifying equation (VII) to equation (X). Most probably errors have been introduced into the values of k_2 by this simplifying process which makes it necessary to use an extrapolated value for $\log(b/a)$ in order to obtain a fairly constant k_2^* . A more direct and accurate determination of both k_2 and k_3 is highly desirable. The authors are making this investigation.

Summary

1. The behavior of Wijs solution toward α -eleostearic acid, oleic acid and a mixture of the two acids has been studied by varying the proportion of Wijs solution to acid and the time of contact.

2. The two-stage halogen absorption from Wijs solution by α -eleostearic acid forming a tetrachloro addition product in the first stage, and the addition of iodine monochloride to oleic acid have been quantitatively established.

3. The difference in halogen absorption between α -eleostearic acid and oleic acid has been applied to the analysis of a mixture of the two acids and to the analysis of α -eleostearic acid

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