STUDIES ON THE CONJUGATED FATTY ACIDS PART II THE THERMAL POLYMERIZATION OF THE CONJUGATED FISH OLL OBTAINED BY THE NICKEL-ON-CARBON CATALYST ISOMERIZATION

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PART II

THE THERMAL POLYMERIZATION OF THE CONJUGATED FISH OLL OBTAINED BY THE NICKEL-ON-CARBON CATALYST ISOMERIZATION

By

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Introduction

It has been widely recognized that the remarkable properties of Chinese tung oil can be ascribed to the fatty acid structure consisting largely of triglycerides of eleostearic acid which has three double bonds in the form of conjugation. The properties associated with this type of configuration in fatty oils are generally the rapidity of thermal polymerization and drying, and the ability to form tough films. Furthermore the fluctuations in price, and interruptions in the supply of the oil due to world conditions, have led to a considerable amount of investigation to find a substitute for tung oil by converting normal oils into conjugated isomers.

In order to isomerize the nonconjugated fatty acids in normal oils into conjugated forms, a number of catalysts have been invented and tested. The two methods among them have been approved for their excellency. The one is the alkali-isomerization(1) and the other is nickel catalyst isomerization(2, 9). Although the former has been soon evaluated and adopted in the spectrophotometrical oil analysis, it is laborious and economically inadequate for industrial procedure, since the technique saponificates the oil and uses much solvent. Hereupon the following experiments with two main objects were studied. For one aim, the investigation of nickel-on-carbon catalyst to isomerize the poly- and highly unsaturated fatty acids of fish oils which were little studied as raw materials in these researches; for the other, the mechanical studies of thermal polymerization of conjugated fish oils obtained by nickel-on-carbon catalyst were made.

Experimental and Results

1. *Preparation of Conjugated Fish Oils with Nickel Catalyst.*

Nickel-on-carbon catalyst.

One of the first proper descriptions of the conjugation itself is found in Moore's report (1d), which proved that alkaline saponification of linseed oil leads to the formation of conjugated systems, as was shown by the absorption in the ultraviolet spectrum of the substance. A technical application of this conjugation procedure has developed the alkali-isomerization method (3) in ultraviolet spectrophotometry for plant oil analysis. However the whole process including saponification and reesterification is very laborious.

It was obvious that after this discovery chemists energetically looked for other catalysts, which might conjugate the unsaturated double bonds of the oil without saponification. Such are oxide of metals(4), silicious materials(5), sulphur dioxide (6), organic compounds (7) of which the quinones showed marked activity, and iodine compounds(8). And Radlove, Teeter, Bond, Cowan and Kass(9) found that nickel-on-carbon catalysts were very effective even in the point of industrial views.

The preparation of nickel-on-carbon catalyst(9) is as follows. A solution of 116 grams of nickel nitrate in 160 ml of distilled water is ground with 100 g of activated carbon in a mortar. A solution of 68.0 g of powdered ammonium carbonate in 400 ml of water is added, and the ingredients are mixed thoroughly until the evolution of gas ceases. The mixture is filtered, and the filter cake is washed with about 200 ml of water in small portions. The filter cake is dried at 90°C overnight, powdered, and stored. The ratio of nickel to carbon is 0.234.

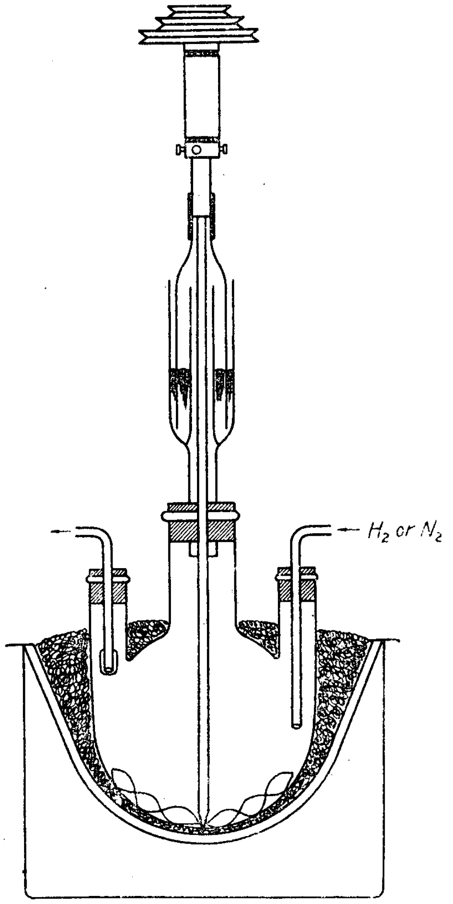


Fig. 1. Apparatus for activation and isomerization.

Equipment and procedure for activation of catalyst and for conjugation isomerization.

The catalyst is activated by reduction of the catalyst composition in a current of hydrogen for a few hours at

350–370°C. Fig. 1 shows the apparatus used for activation and for conjugation isomerization. The three necked flask of 200 ml is charged with 7.2 g of catalyst. The apparatus is assembled, without stirring, and hydrogen is allowed to pass over the catalyst until 350–370°C. The stirrer is then started, and the catalyst is kept at 350–370°C for one or two hours. After the reduction of catalyst the flask and contents are cooled to below 170°C, and the hydrogen is replaced with nitrogen. The catalyst is then ready for use.

To the prepared catalyst, 80 g of oil are added, and the oil is heated, with stirring, at 170°C for a few hours. Then the isomerized oil is filtered through Büchner funnel under suction.

Conjugated fish oils.

The results obtained by the several experiments are given in Table 1. To determine the best condition and catalyst composition for conjugation isomerization of fish oils, the combination study of different activation and isomerization time, experiment on heat effect, and research for choice of activated carbon were examined.

First, heat alone isomerization at 170–180°C is shown in the column of experiment numbers 2, 3 in Table 1. Comparing these values with the data of unisomerized cod liver oil (exp. no. 1), there are no great differences on conjugation isomerization. So it is believed that the temperature of 170–180°C is too low to conjugate the oil, and a higher temperature is required for conjugation. It is true that the conjugation isomerization is fairly done under the condition of thermal polymerization temperature about 270°C, as seen in Table 2 or Table 3 in the following part.

Secondly, the problems of activation and isomerization time were examined. The same nickel-on-carbon catalyst made of the activated carbon of Kantô Chemicals is tested under different conditions and isomerization time as seen in exp. nos. 5, 6, 7, and 8 in Table 1. The most adequate activation time is determined under the equal isomerization time of three hours as given in exp. nos. 5, 6, and 7. Half an hour reduction is insufficient and two hours are excessive. One hour reduction, therefore, is enough for the activation time. Then the suitable isomerization time is conversely studied under the same reduction time as shown in exp. nos. 7 and 8. Three hours isomerization is adequate. The following condition, one hour reduction at 350–370°C and three hours isomerization at 170–180°C, is adopted as the standard condition of conjugation isomerization of fish oils in this experiment.

Thirdly, the experiments on difference of kinds of activated carbon were studied. The activated carbon used are the products of Kantô Chemical (A) and Kukita Chemical Co. Ltd. (B), Darco G-60, and Nuchar C-190-A and C-190-N, which were received through the kindness of the West Virginia Pulp

Table 1. Results of conjugation in specific extinction coefficients of conjugated fish oils obtained by nickel-on-carbon catalyst and alkali-isomerization.

Exp. No.	1 a)	2	3	4 b)	5	6	7	8	9 c)	10 d)	11	12	13	14	15 e)	16 f)	17	18 g)	19 h)
Fish Oil Materials	Cod Liver Oil	″	″	″	″	″	″	″	″	″	″	″	″	″	″	″	Saury Oil	″	″
Activated Carbons	—	—	—	—	A	″	″	″	″	″	B	Darco G-60	Nuchar C-190-A	Nuchar C-190-N	21%KOH-Glycol	11%KOH-Glycerol	Nuchar C-190-N	21%KOH-Glycol	11%KOH-Glycerol
Activation Time at 350-370°C in hours	—	—	—	—	1/2	1	2	2	2	2	1	1	1	1	—	—	1	—	—
Isomerization Time at 170-180°C in hours	—	3	5	5	3	3	3	5	5	5	3	3	3	3	1/4	3/4	3	1/4	3/4
N_D^{30}	1.4764	1.4779	1.4781	1.4786	1.4796	1.4802	1.4800	1.4805	1.4787	1.4793	1.4795	1.4813	1.4817	1.4822	—	—	1.4781	—	—
233 mμ	1.05	1.35	1.39	1.75	2.63	3.64	3.55	3.43	1.74	1.33	2.19	5.86	8.41	9.48	18.89	19.56	5.78	19.30	19.98
268	0.20	0.50	0.56	0.73	1.08	1.63	1.35	2.03	0.69	0.57	0.96	2.89	4.35	5.34	17.50	15.80	4.04	20.19	15.94
316	0.13	0.19	0.23	0.21	0.43	0.72	0.60	0.58	0.40	0.29	0.39	1.29	1.67	2.20	18.98	8.47	1.06	12.47	7.82
330	0.11	0.09	0.12	0.14	0.20	0.38	0.34	0.31	0.22	0.17	0.22	0.76	0.75	1.10	15.56	3.50	0.42	6.24	2.55
346	0.08	0.05	0.07	0.12	0.13	0.27	0.26	0.22	0.16	0.13	0.17	0.51	0.52	0.77	14.54	2.39	0.26	5.55	2.20
374	0.02	0.02	0.03	0.09	0.03	0.11	0.09	0.10	0.08	0.07	0.10	0.23	0.17	0.27	5.82	0.64	0.09	1.94	0.47
400	0.01	0.01	0.01	0.03	0.01	0.05	0.04	0.05	0.03	0.02	0.05	0.09	0.06	0.10	0.60	0.32	0.04	0.13	0.04

Remarks: a) Parent Oil, b) Nickel-Kieselguhr Catalyst, c) Activation of Carbon, d) Add Sustane, and e), f), g) h) Alkali-isomerization.

and Paper Company. The activities of nickel-on-carbon catalyst made of each activated carbon are indicated in the column of exp. nos. 6 (A), 11 (B), 12 (Darco G-60), 13 (Nuchar C-190-A) and 14 (Nuchar C-190-N) respectively. The most active catalysts are obtained when the Nuchar's activated carbons are used as components of the catalysts. In the experiment of Nuchar C-190-N (exp. no. 14), the highest specific extinction coefficients with the date of 9.48 at 233 mμ for diene, 5.34 at 268 mμ for triene, 2.20 at 316 mμ for tetraene, 0.77 at 346 mμ for pentaene, and 0.27 at 374 mμ for hexaene conjugation were respectively obtained in cod liver oil. Nevertheless, the activities of nickel-on-carbon catalyst are below half of 21 % KOH-glycol and 11 % KOH-glycol isomerization, also in saury oil(10), as shown in the column of exp. nos. 15 and 16. Especially, this tendency is found in the longer wave length.

Moreover, the activity of nickel-kieselguhr catalyst (exp. no. 4) used for hydrogenation of fatty oils was tested, but the isomerization activity was worse

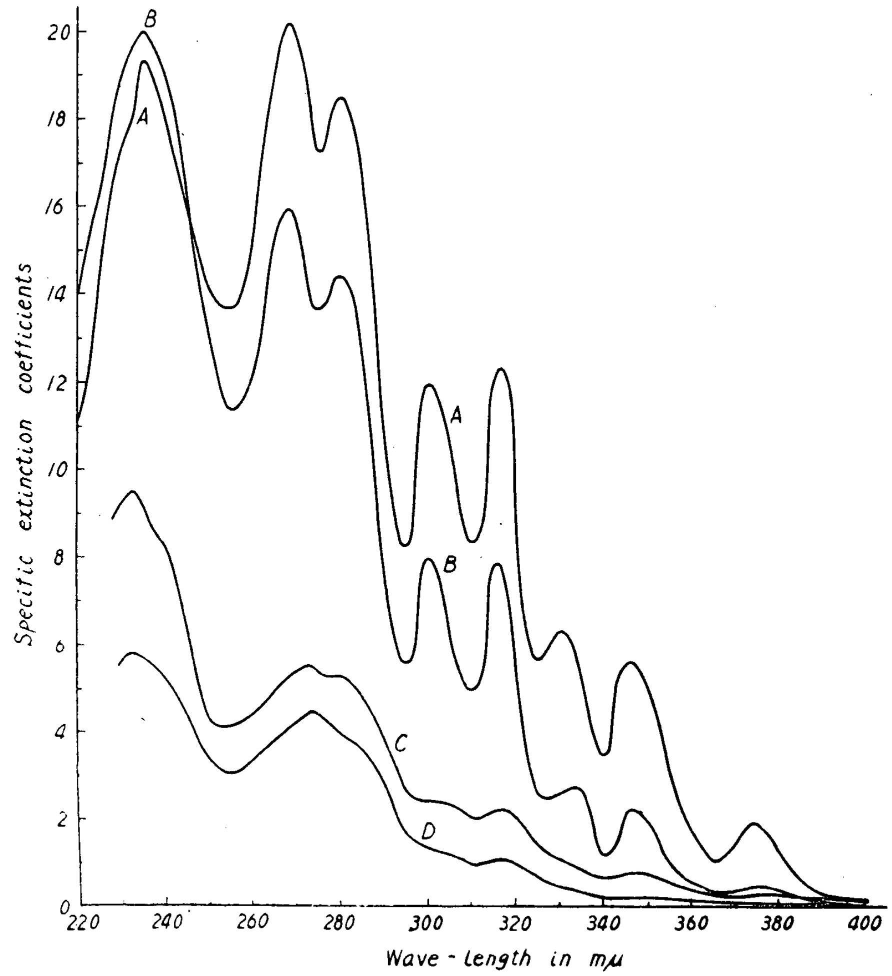


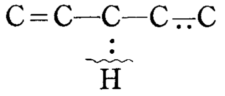
Fig. 2. Absorption curves of conjugated acids obtained by 21% KOH-glycol (A), 11% KOH-glycerol (B) alkali-isomerization and of conjugated oil by nickel-on-carbon catalyst (D) using saury oil as material, and conjugated cod livr oil by nickel-on-carbon catalyst (C).

than the nickel-carbon catalyst. And the effects of activation of activated carbon (11) and the use of antioxidant sustane were examined as seen in exp. nos. 9 and 10. In any case minor results were obtained.

Finally, the comparison between the nickel-on-carbon catalyst isomerization and alkali-isomerization were determined, using saury oil as the sample. The data are shown in the column of exp. nos. 17, 18, and 19 in Table 1, and the spectrophotometric curves are illustrated in Fig. 2. The data concerning the specific extinction coefficients were measured by the Beckman DU Spectrophotometer.

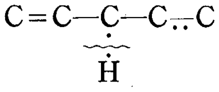
2. *Mechanism of Conjugation Isomerization by Catalyst.*

The 1, 4 to 1, 3-isomerization of dienes may occur by either a polar or a free radical mechanism(12). A hydrogen of the active methylene group shifts as a proton if the cleavage of the C–H bond is heterolytic (A) and as a hydrogen atom if it is homolytic (B). The driving force for this reaction is the greater stability through resonance of the congugated structure.



$$\mathrm{C{=}C{-}\underset{\underset{H}{\vdots}}{C}{-}C\cdots C}$$

(A)

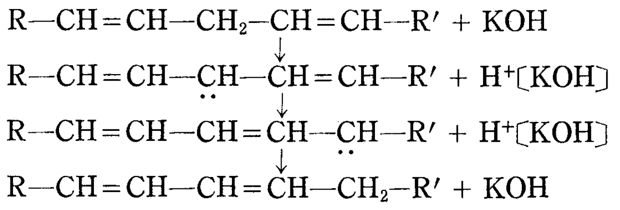


$$\mathrm{C{=}C{-}\underset{\underset{H}{\cdot}}{C}{-}C\cdots C}$$

(B)

That is to say in fatty oils, shifting in unsaturated fatty acids to form isomeric compounds containing conjugated unsaturation appears to depend on either the removal of a proton or a hydrogen atom.

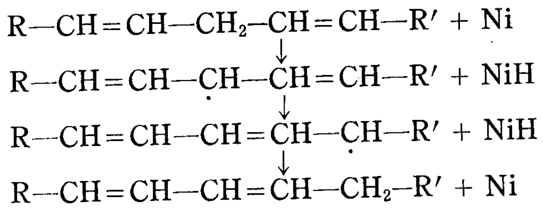
The highly polar nature of aqueous potassium hydroxide undoubtedly catalyses a polar isomerization through the nucleophilic activity of the hydroxide ion. So alkali acts as a proton acceptor (13) as below.



$$\begin{aligned}
&\mathrm{R{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}R' + KOH}\\
&\qquad\qquad\qquad\downarrow\\
&\mathrm{R{-}CH{=}CH{-}\underset{\cdot\cdot}{C}H{-}CH{=}CH{-}R' + H^{+}[KOH]}\\
&\qquad\qquad\qquad\downarrow\\
&\mathrm{R{-}CH{=}CH{-}CH{=}CH{-}\underset{\cdot\cdot}{C}H{-}R' + H^{+}[KOH]}\\
&\qquad\qquad\qquad\downarrow\\
&\mathrm{R{-}CH{=}CH{-}CH{=}CH{-}CH_2{-}R' + KOH}
\end{aligned}$$

Thus the alkali-isomerization is to be held, owing to the coming and going of proton resulting from the heterolytic cleavage of the C–H bond of active methylene group.

For the nickel-on-carbon catalyst a free radical mechanism may be the most logical. A hydrogen atom from the active methylene group adds to reduced nickel, which acts as a strong hydrogen acceptor (13) as follows.



$$\begin{array}{l}
R{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}R' + Ni\\
\qquad\qquad\qquad\quad\ \downarrow\\
R{-}CH{=}CH{-}\underset{\cdot}{C}H{-}CH{=}CH{-}R' + NiH\\
\qquad\qquad\qquad\quad\ \downarrow\\
R{-}CH{=}CH{-}CH{=}CH{-}\underset{\cdot}{C}H{-}R' + NiH\\
\qquad\qquad\qquad\quad\ \downarrow\\
R{-}CH{=}CH{-}CH{=}CH{-}CH_2{-}R' + Ni
\end{array}$$

Thus the homolytic cleavage of the C–H bond of active methylene group by nickel catalyst causes the conjugation isomerization with the driving force of resonance stability of the conjugated structure as shown diagrammatically above.

3. *Thermal Polymerization of Conjugated Fish Oil.*

The conjugated cod liver oil obtained by the nickel-on-carbon catalyst isomerization as stated above was compared with the bleached, alkali-refined parent cod liver oil of contrast in the thermal polymerization experiment to elucidate the one of the properties the conjugated fatty acids or conjugated oils especially possess. Polymerizations were done by heating the sample sealed in evacuated glass ampoules on one hand, and by the sample introduced in three necked flask under nitrogen on the other. The former results are shown in Table 2, and the latter in Table 3. The data in the table were obtained in the following way, refractive index (N_D^{30}) with Abbé's refractometer, specific gravity (d_4^{30}) with pycnometer, specific viscosity with Ostwald's viscometer, iodine value (I. V.) with Wij's method, hydrogen iodine value (H. I. V.) with catalytic hydrogenation (14), saponification value (S. V.) with the usual method, and specific extinction coefficients with the Beckman DU Spectrophotometer. The specific viscosity was relatively calculated by defining the oil at the initial one. In addition the comparative data with initial parent oil of nonconjugation are put in parentheses.

Both specific gravity and viscosity increase their value with the polymerization time. And not merely iodine value in nonconjugation column but also hydrogen iodine value in conjugation column decrease in the course of time. It is easy to find that there are considerable discrepancies of data between nonconjugated and conjugated oil. The rate of increase in the viscosity would be seen as the result corresponding to the diminution of iodine value and hydrogen iodine value. Both the increment and decrease in nonconjugation are more gentle and smaller, however, the inclinations of conjugated oils are much rapid and larger. Therefore these results explain well that the conjugated oils must be more reactive than the nonconjugated ones in addition and other polymerization reactions.

Still more the following data of specific extinction coefficients prove the reactiveness of conjugated oil, and they elucidate the mechanism of the thermal

Table 2. Change of oil characteristics and specific extinction coefficients with thermal polymerization time in evacuated ampoule at 270°C.

Characteristics / Polymerization Time in hours	N_D^{30}		d_4^{30}		η^{30}		I. V.	H. I. V.	S. V.	
	Nonconjugated	Conjugated	Non.	Conj.	Non.	Conj.	Non.	Conj.	Non.	Conj.
0	1.4774	1.4803	0.9174	0.9212	1	1 (1.2)	172.4	167.2	183	185
1/2	1.4795	1.4816	0.9209	0.9260	1.2	1.4(1.7)	158.8	145.0	182	170
2	1.4820	1.4832	0.9321	0.9436	3.2	6.2(7.1)	136.3	72.7	172	175
6	1.4822	1.4845	0.9322	0.9453	3.2	8.3(9.6)	133.7	58.4	185	167

Wave-length in mμ / Polymerization Time in hours	Specific Extinction Coefficients													
	Nonconjugated							Conjugated						
	233	268	315	330	346	374	400	233	268	315	330	346	374	400
0	1.16	0.26	0.14	0.12	0.08	0.03	0.00	3.18	1.50	0.54	0.31	0.19	0.09	0.03
1/2	2.92	3.86	0.19	0.09	0.02	0.03	0.00	4.36	3.92	0.31	0.14	0.07	0.03	0.01
2	5.65	2.88	0.23	0.12	0.01	0.03	0.00	5.17	1.51	0.26	0.14	0.07	0.02	0.00
6	5.79	2.93	0.19	0.07	0.03	0.01	0.00	4.05	1.65	0.23	0.07	0.06	0.01	0.00

Table 3. Change of oil characteristics and specific extinction coefficients with thermal polymerization time in three necked flask under nitrogen at 270°C.

Characteristics / Polymerization Time in hours	N_D^{30}		d_4^{30}		η^{30}		I. V.	H. I. V.	S. V.	
	Nonconjugated	Conjugated	Non.	Conj.	Non.	Conj.	Non.	Conj.	Non.	Conj.
0	1.4764	1.4802	0.9179	0.9237	1	1 (1.5)	168.9	167.3	182	177
1/2	1.4770	1.4815	0.9181	0.9340	1.2	2.8(4.3)	165.3	134.5	183	175
1	1.4777	1.4821	0.9203	0.9391	1.5	4.4(6.7)	158.6	105.9	183	185
$1^1/_2$	1.4784	1.4824	0.9214	0.9403	1.8	5.6(8.4)	153.0	101.4	185	182
2	1.4790	1.4828	0.9239	0.9439	2.2	6.7(10.3)	145.7	93.7	185	176
$2^1/_2$	1.4797	1.4832	0.9258	0.9446	2.4	8.1(12.6)	141.4	92.3	187	181
3	1.4801	1.4836	0.9282	0.9454	2.7	9.4(14.1)	138.3	90.2	186	182
$3^1/_2$	1.4805	1.4839	0.9304	0.9477	3.1	10.9(16.3)	134.4	85.8	186	184
4	1.4809	1.4842	0.9335	0.9505	3.7	12.5(19.1)	132.5	81.0	187	185
5	1.4814	1.4850	0.9371	0.9510	4.8	14.3(21.8)	126.8	77.3	188	185
6	1.4817	1.4853	0.9403	0.9528	5.9	15.8(23.7)	117.2	68.8	185	186

Wave-length in mμ / Polymerization Time in hours	Specific Extinction Coefficients													
	Nonconjugated							Conjugated						
	233	268	315	330	346	374	400	233	268	315	330	346	374	400
0	1.26	0.47	0.12	0.08	0.05	0.01	0.00	3.68	1.89	0.50	0.21	0.12	0.04	0.02
1/2	1.82	2.09	0.18	0.07	0.04	0.01	0.00	5.78	2.48	0.40	0.14	0.05	0.02	0.01
1	2.13	2.65	0.24	0.06	0.04	0.01	0.00	6.01	1.88	0.33	0.13	0.06	0.03	0.01
2	2.98	3.34	0.37	0.07	0.03	0.01	0.00	6.59	1.37	0.30	0.12	0.07	0.02	0.01
3	3.61	3.28	0.35	0.08	0.05	0.02	0.00	5.36	1.24	0.21	0.11	0.06	0.02	0.01
4	2.57	2.31	0.33	0.07	0.06	0.02	0.00	4.94	1.13	0.23	0.12	0.07	0.02	0.01
5	2.40	2.33	0.32	0.08	0.05	0.01	0.00	4.88	1.15	0.24	0.14	0.08	0.03	0.00
6	2.39	2.35	0.31	0.11	0.05	0.02	0.00	4.25	1.13	0·25	0.15	0.06	0.02	0.00

polymerization. The specific extinction coefficients in Table 2 and Table 3 show respectively the results of polymerization in evacuated ampoule and in three necked flask under nitrogen.

The data of the specific extinction coefficients in Table 2 are plotted in Fig. 3 to make clear the transfiguration of conjugated double bonds in the process of polymerization. The increase at each wavelength shows the rise in conjugation rate corresponding to the conjugation number. The drops of value gives the decrease of conjugation.

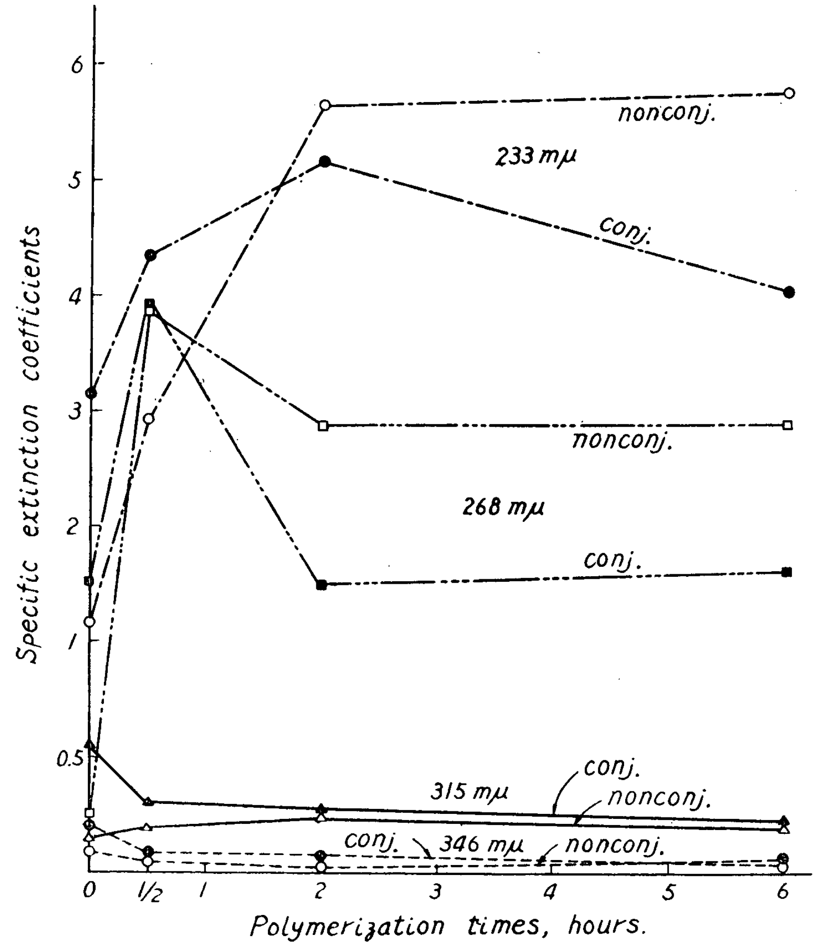


Fig. 3. Change of specific extinction coefficients at each wave-length with thermal polymerization time in evacuated ampoule at 270°C.

For instance, the increment at 233 mμ of nonconjugated oil with the lapse of time, a half an hour, two hours, and six hours, denotes the increase of diene conjugation resulting from heat effect at 270°C. While the falling-off at 315 mμ of conjugated oil with the time, a half an hour, two hours, and six hours, indicates the decrease of tetraene conjugation already present, caused by thermal polymerization. Observing the data between the nonconjugated and conjugated oils at 233 mμ (diene), the conjugated oil which has been previously conjugated with nickel catalyst ascends slowly with the lapse, zero to a half an hour, and a half an hour to two hours, and falls abruptly from two to six hours, whereas the nonconjugated oil which has not yet been isomerized ascends rapidly with the time, zero to a half an hour, and one to two hours, followed by a little increase from two to six hours. The fairly similar phenomena are also observed at 268 mμ (triene), but at the longer wavelength above 315 mμ, namely, 315 mμ (tetraene), 346 mμ (pentaene), 374 mμ (hexaene) in conjugated oil drops respectively from the beginning. That means the more reactiveness of highly conjugated acids and isomerization hardness of highly unsaturated acid to highly conjugated forms. The conjugated oils consisting of the diene, triene, tetraene, pentaene, and hexaene conjugated fatty acid are definitely polymerized more quickly than nonconjugated oil which has corresponding unsaturation in the form of nonconjugation. And polymerization of nonconjugated oils are considered to occur by thermal conjugation, followed by a Diels-Alder addition between conjugated and nonconjugated acids.

Discussion

The growth of polymer molecules during the thermal treatment of triglyceride oils results from the presence of double bonds which are situated in the fatty acid chains in the form either conjugated or normally nonconjugated. Although the structures of the thermally formed linkages between chains are not yet known with absolute certainty, Diels-Alder mechanism has been supported by the majority of authors (15) in the field. Diels-Alder reaction takes place by the addition of a double bond in one chain to the ends of a conjugated diene system already present or formed by heating in another chain so that the linkage consists of a cyclohexene ring.

In this study the hypothesis of Diels-Alder mechanism can explain quite well that the conjugated oils are polymerized more rapidly, assuming the thermal conjugation followed by a Diels-Alder addition between conjugated diene and normal or conjugated double bond of dieneophile. And it is suggested that the conjugation isomerization in unsaturated acids becomes the slow rate determining step as Paschke and Wheeler report (16).

The isomerization of nonconjugated acids to conjugated isomers by heat takes place in the first place as slow rate determining step. The conjugated acids isomerized in such way contain at least one diene structure in its chain, and add together or with normal double bond which exists in the state of free double bond. Thus dimerization proceeds with fast speed as the principal reactions. Then dimer adds to conjugated monomer or dimer which possesses conjugated structure adds to nonconjugated double bond to form trimer. Thereby thermal polymerization grows with time. The cyclization may occur to some extent, and other isomers incapable of participating in polymerization may be produced during thermal polymerization.

Also the other principal differences may be considered between polyunsaturated and highly unsaturated acids, and between cis and trans configuration. The highly unsaturated acid develops conjugation isomer more readily, since it has more abundant methylene group between two double bonds. Accordingly it polymerizes more rapidly. Moreover the trans isomerization taking place during conjugation isomerization(17) makes it easy to polymerize. A trans-trans acyclic conjugated diene is much more reactive as diene in the Diels-Alder reaction than a cis-trans diene (18). The trans, trans, trans conjugated β-isomer of eleostearic acid has two pairs of trans-trans conjugated dienes is more active than the cis, trans, trans conjugated α-isomer (19) which has only one trans-trans conjugation in the molecule. However, the α-eleostearate is faster than the trans, trans conjugated linoleate, because of the former has one more cis double bond in the configuration of cis-trans form.

Thus the conjugated isomers are all much faster and depend greatly on the conjugation number and cis-trans configuration. The relative rates between conjugated and nonconjugated oils are explainable by the rate determining step of conjugation isomerization and followed Diels-Alder addition, considering the effect of cis, trans isomers on the diene activity of conjugated isomers.

Although we must still pay more attention on the excellency of Nuchar products as component of nickel catalyst, we know just only the activated carborn, finely pulverized, prepared from the residue of sulfite waste liquors, with superior property in absorbity.

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Summary

In order to isomerize the normal fish oil to the conjugated forms the nickel-on-carbon catalysts, with some kinds of activated carbon, have been prepared. Among them the catalyst made of Nuchar type carbon was most favorable. The activation for one hour at 350–370°C and isomerization for three hours at 170–180°C were adopted as an adequate condition to prepare conjugated fish oils. Although the high isomerization was gained in the case

of nickel-on-carbon catalyst consisting of Nuchar C-190-N activated carbon, its specific extinction coefficients were no more than below a half of the alkali-isomerization.

The conjugated fish oils gained in such way were thermally polymerized in the evacuated ampoule and the three necked flask under nitrogen at 270°C. Much rapid polymerization resulting from conjugation already present were observed in the conjugated oil, showing fast decrease of hydrogen iodine value and specific extinction coefficients, and great increase of viscosity. The thermal polymerization of nonconjugated oils was considered to occur by thermal conjugation followed by a Diels-Alder addition. And the rapid increment of specific extinction coefficients of nonconjugated oil at an early step in polymerization proved clearly this mechanism.

As a result the conjugated oils react more rapidly in the polymerization reaction than the nonconjugated oils due to the slow rate determining step from the nonconjugated to conjugated forms. Furthermore the effect of cis-trans configuration on polymerization was also discussed.

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