

Studies in Estolides. I. Kinetics of Estolide Formation and Decomposition¹

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Abstract

A study has been made of the rate of formation of estolides from castor oil fatty acids and of their decomposition at different temps. Estolide formation appears to be optimum at the end of 5 hr at about 220C, beyond which estolides start decomposing, giving rise to DCO fatty acids. At about 300C, estolide decomposition is complete within an hour.

During estolide formation there is a linear increase in optical rotation which again decreases linearly, although at a different rate, during estolide decomposition. At optimum estolide formation, the optical rotation is as high as 25.5.

Introduction

SEVERAL INVESTIGATORS (1-8) have observed that ricinoleic acid and castor oil fatty acids show reduction in their acid value on keeping or heating. Rassow and Rubinsky (9) studied estolide formation in ricinoleic acid and found that the all important reaction taking place was polyester formation where in hydroxyl group of one molecule reacts with carboxyl group of another molecule and so on. Stefanescu and Stanescu (10) on the basis of IR spectra found that the polyesters formed were linear. However, Bolley (11) is of the opinion that the estolides are a mixture of lactones, lactides, simple esters, linear polyesters and cyclic polyesters. Rowe (12) observed that these estolides, like other esters, decompose at high temp at the ester group giving rise to a carboxyl group and a double bond. The above reaction is, in fact, the basis of several patents (13-15) for the manufacture of diunsaturated fatty acids from castor oil fatty acids.

Hawke and Kohll (16) have studied the kinetics of estolide formation from pure ricinoleic acid at 122C, 147C and 180C over reaction times of 32 hr. They also studied the catalytic dehydration of ricinoleic acid at a temp of 180C using anhydrous NaHSO₄ as the catalyst.

In the present work, a much higher range of temp (157-255C) has been used in the study of estolide formation from mixed castor oil fatty acids, and estolide decomposition has been studied at a still higher range (270-307C) in absence of a catalyst.

Experimental

Castor oil fatty acids were prepared by alkali saponification of the oil followed by acidification with dilute sulfuric acid. The acids were washed with water and dried. The characteristics of the oil and its fatty acids were, respectively: A.V. 2.6, 180.6; S.V. 180.0, 186.2; H.V. 163.5, 163.5; I.V. 84.6, 87.5 (acid value, saponification value, hydroxyl value, iodine value).

Estolide Formation

A three-neck, 1 liter round bottom flask having ground glass joints served as the reaction vessel. One

of the side necks carried a thermometer. The central neck carried a still-head through the top of which was inserted a tube for introducing nitrogen. The tube almost touched the bottom of the flask. A current of nitrogen served to agitate the mass and to maintain an inert atmosphere. The side end of the still-head was connected to a watercooled condenser which in turn was connected through a receiver to a vacuum pump. The third neck of the flask carried a sampling device for taking out samples without breaking the vacuum or stopping the reaction.

A heating mantle with a regulator was used to heat the fatty acids, the temp being controlled within ± 1 C. In each experiment an absolute pressure of 300 to 400 mm Hg was maintained during the estolide formation and this facilitated quick removal of water formed.

About 300 g of castor oil fatty acids were taken at a time in the flask for each experiment. Estolide formation was studied at 157, 187, 202, 220, 240, and 255C. At each temp maintained constant, samples were drawn at known intervals of time and analysed for some of their characteristics. The Analytical values are given in Table I.

Estolide Decomposition

A uniform sample of estolides was prepared and used throughout the present study. To prepare the

TABLE I
Changes in the Characteristics of Estolides During Their Formation^a

Reaction temp °C	Time of reaction hr, min	A.V.	H.V.	(A.V.-H.V.)
187	0-00	162.2	—	—
	1-00	124.9	—	—
	2-00	97.5	79.5	18.0
	4-00	73.1	—	—
	5-00	65.6	48.1	17.5
	7-00	54.0	37.4	16.6
	14-00	38.6	—	—
202	0-00	158.4	140.2	18.2
	1-00	106.5	90.4	16.1
	1-55	83.1	65.8	17.3
	2-55	68.7	52.5	16.2
	4-00	58.5	—	—
	6-55	44.1	—	—
	12-00	38.0	—	—
220	0-00	153.4	136.1	17.3
	0-30	108.0	91.0	17.0
	1-00	84.2	66.7	17.5
	1-30	72.2	54.5	17.7
	2-00	64.0	—	—
	3-00	50.8	—	—
	5-00	35.8	—	—
	7-50	36.4	—	—
	15-00	37.5	—	—
240	0-00	139.6	—	—
	1-00	67.6	—	—
	2-00	49.5	20.7	28.8
	3-32	43.4	18.1	25.3
	5-30	42.0	7.4	34.6
	6-30	42.7	—	—
255	0-00	117.6	99.2	18.4
	0-50	62.4	32.8	29.6
	1-35	56.7	18.7	38.0
	2-05	58.0	12.0	46.0
	2-20	58.8	6.2	52.6
	4-40	93.7	—	—
	10-00	125.7	—	—
	13-00	140.0	—	—

^aTime of reaction was measured from the time (taken as zero time) the reaction temperature was attained. Additional pertinent observations include the following: at a reaction temp of 157C the A.V. was 134.6 after 3.5 hr and 64.7 after 17 hr; at 170C the acid value was 115.3 after 3 hr. Sap. values of a few intermediate samples taken at different reaction temps were in the range 193 to 199. I.V.'s of some of the samples taken at reaction temps below 240C ranged between 93 and 97; at 255C the I.V.'s of the last four samples were 112.4, 129.3, 135.0 and 147.4, respectively.

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estolides, castor oil fatty acids were heated at 255C for a period of 2½ hr in the way already described above. The above temp and time for estolide formation were so selected that the H.V. of the resultant estolides would be sufficiently low without much increase in their A.V. This ensured almost complete absence of estolide formation during the study of decomposition of estolides. Characteristics of the estolides were: A.V. 61.2; S.V. 200.0; I.V. 112.2; H.V. 45.

The procedure and equipment used in the study of estolide decomposition were the same as those used in the study of estolide formation. About 300 g of estolides were heated in the flask at the desired temp. Samples were removed at known intervals of time and analysed for A.V. and optical rotations. Estolide decomposition was studied at 257, 270, 280, 290 and 307.5C. The analytical values are given in Table II.

Methods of Analysis

A.V. It was observed that estolides of low A.V. were not soluble in 95% alcohol; therefore a 1:1 mixture of benzene and alcohol was used as a solvent and titrations were carried out using 0.5 N alcoholic potash.

S.V. A.O.C.S Cd.-325 procedure was followed. For estolides of low A.V. a refluxing time of 1 hr was sufficient.

I.V. For samples not containing appreciable amounts of conjugated fatty acids, the method of Sreenivasan et al (17) was followed. For samples containing conjugated fatty acids, the Woburn method of Von Mikusch and Frazier (18) was followed.

Conjugation. A.O.C.S method Cd-7-58 using absolute alcohol as a solvent was followed.

H.V. The method described by Burton and Robertshaw (19) was followed.

Optical Activity. Optical rotation was determined at 30C with the help of a Zeiss Winkel polarimeter and expressed as the angle of rotation for 1 dm length.

Density. This was determined by means of a sp gr bottle using thermostatic bath controlled to ± 0.1C.

Discussion

Estolide Formation

General. The extent of estolide formation is measured by a decrease either in A.V. or H.V. Obviously the former is easier to determine. At a temp of 157C, 17 hr is required for the A.V. to drop to about 65. At temps of 187C and 202C, the corresponding periods are 5 hr and 3 hr, respectively (Table I). At a still higher temp of 220C, a minimum A.V. of about 36 is obtained in about 5 hr. On further heating, acid and I.V. tend to increase. At the highest temp studied, viz. 255C, a minimum A.V. of about 57 only is reached in about 1 hr 30 min, beyond which both the A.V. and I.V. rise, indicating decomposition of estolides leading to the formation of more unsaturated acids, viz. DCO fatty acids.

An estolide sample prepared at 202C and having an A.V. of 44.1 was completely saponified and acidified to liberate the fatty acids. The characteristics of these (A.V., 182.5; I.V., 88.3; H.V., 167.4) were almost similar to those of the original castor oil fatty acids, thus showing that during estolide formation primarily no other reaction but esterification could have taken place. This is confirmed by the S.V.'s of a few intermediate samples.

TABLE II
Progressive Thermal Decomposition of Estolides at Different Temps^a

Temp. °C	Hr. min ^a	A.V.	O.R. ^b	Temp. °C	Hr. min ^a	A.V.	O.R. ^b
257	0-00	61.0	—	280	3-40	183.1	—
	1-00	71.1	—		5-40	180.5	—
	2-00	83.5	—		7-26	175.4	—
	3-15	93.7	—	290	0-00	68.6	20.7
	4-00	—	—		0-11	97.6	16.4
10-00	125.7	—	0-21		123.2	12.1	
			0-31		142.9	8.4	
270	0-00	59.1	—	0-53	168.6	4.3	
	0-32	78.0	19.1	1-24	182.0	1.7	
	1-01	95.5	—	1-17	185.1	—	
	1-31	110.9	13.7	2-25	184.7	—	
	2-02	125.6	—	2-55	182.0	—	
	3-05	144.9	—				
	4-07	158.7	5.1				
	6-10	174.9	2.2	307.5	0-00	96.4	16.7
7-10	177.3	—	0-08		114.9	—	
8-00	179.1	—	0-15		173.8	4.0	
			0-21		185.6	1.8	
280	0-00	62.4	—	0-27	189.3	1.0	
	0-21	91.2	17.0	0-37	190.5	0.5	
	0-42	116.3	13.1	0-58	187.0	—	
	1-03	137.2	9.3	1-08	184.3	—	
	1-31	156.3	6.2	1-29	183.2	—	
	2-07	172.4	3.7				

^a See the first sentence in the 'Note' under Table I.

^b Optical rotation (O.R.) was determined at 30C.

During estolide formation there is a regular decrease in the H.V. also. Up to a temp of 220C, the difference (A.V. - H.V.) remained fairly constant at about 17, indicating the simultaneous elimination of both carboxyl and hydroxyl groups. It is only when the decomposition reaction sets in at 240C and 255C that this difference tends to become larger.

Kinetics. There are no dicarboxylic acids in castor oil fatty acids. The small amount of dihydroxystearic acid present in them may be neglected. Since estolide formation is essentially an esterification reaction, the A.V. and H.V. of the estolides may be taken to be directly proportional to the moles containing carboxyl and hydroxyl groups, respectively. If in the above system a and b be the molar concns (g moles per liter) of the molecules containing a carboxyl and a hydroxyl group, respectively, then from the definition of A.V. and H.V., it can be seen that

$$\frac{a \times 56.1 \times 1000}{1000 \times d} = \text{A.V.} \quad [1]$$

$$\frac{b \times 56.1 \times 1000}{1000 \times d} = \text{H.V.} \quad [2]$$

where d is the density of the reaction mass, expressed as g per cc.

If A and B represent A.V. and H.V., respectively, then from the above

$$a = K'A \text{ and } b = K'B \quad [3]$$

$$\text{where } K' = \frac{d}{56.1}$$

Referring to Table III, density differences between estolides of different A.V.'s at 30C are small and so it can be assumed that during estolide formation at a constant temp, the density of the reaction mass would remain almost constant and hence K' would also remain practically constant.

If in the above system, a and b are the initial (at zero time, molar concns of the molecules containing a carboxyl group and a hydroxyl group, respectively, then for a second order reaction taking place between these molecules, the following equation will hold:

$$Kt = \frac{2.303}{a-b} \log \frac{(b)(a-x)}{(a)(b-x)} \quad [4]$$

TABLE III
Densities of Estolides

Sample	A.V.	Density 30C
Castor oil fatty acids.....	174.0	0.9344
Estolides prepared at 157C.....	60.8	0.9326
Estolides prepared at 170C.....	100.3	0.9320
Estolides prepared at 220C.....	128.1 92.3 37.0	0.9340 0.9333 0.9311

where x is the change in the molar concns a and b after time t and k is the rate constant.

When A and B are A.V. and H.V., respectively, at zero time and X , change in acid and hydroxyl values after time t , then as explained earlier, the molar concns a , b and x could be expressed as

$$a = K'A, b = K'B \text{ and } x = K'X$$

where K' is a constant the value of which would depend on the density of the reaction mass. Putting these values in equation 4,

$$KK't = \frac{2.303}{A-B} \log \frac{(B)(A-X)}{(A)(B-X)} \quad [5]$$

Equation 5 can also be put in the form:

$$\log \frac{(A-X)}{(B-X)} = KK' \frac{(A-B)}{2.303} t - \log \frac{B}{A} \quad [6]$$

In equation 6, $A-X$ and $B-X$ are acid and hydroxyl values, respectively, at time t .

In plotting $\log \frac{A.V.}{H.V.}$ against t for temps 157C to

220C, the A.V. and t are taken from Table I and H.V. is computed uniformly for all samples on the basis of the fact mentioned earlier that up to 220C the difference in A.V. and H.V. remains almost constant at an average value of 17 units. The straight line nature of the plots indicates the reaction to be of the second order.

Referring to equation 6, it is seen that knowing the slopes $\frac{KK'(A-B)}{2.303}$ of the different straight lines

and densities of estolides at the corresponding temps, the reaction rate constant K can be calculated. In order to obtain densities at different temps, the temp coefficient of density of the estolide having an A.V. 100.3 (Table III) was determined and was found to be $-0.006 \text{ g/cc}/^\circ\text{C}$. It was also assumed that this coefficient would be the same for all estolides. Table IV gives the calculated values of slope m , density d

TABLE IV

Values of m , d and K , at Different Temps of Estolide Formation

Temp. of estolide formation $^\circ\text{C}$	$m \times 10^4$	d	$K \times 10^3$
157	0.819	0.8558	0.758
170	1.346	0.8480	1.207
187	2.823	0.8378	2.563
202	3.979	0.8288	3.654
220	7.041	0.8180	6.551

Units of K are litre mol $^{-1}$ min $^{-1}$

and reaction rate constant K at different temps of estolide formation.

According to the Arrhenius equation, $\log K = \frac{-E}{2.303 RT} + \text{constant}$, where K is the rate constant,

E , activation energy, R , the gas constant and T , the absolute temp of reaction. On plotting values of $\log K$ against $1/T$, the activation energy calculated from the slope of the curve was found to be 14.7 cal.

Hawke and Kohll (16) from their study of the kinetics of estolide formation have shown the reaction to be of second order which agrees with the experimental results of the present work.

The value of k , the velocity constant, at 180C, viz. 14.0×10^{-4} obtained by Hawke and Kohll agrees in magnitude with the values of k at 170C and 187C (12.1×10^{-4} and 25.6×10^{-4} , respectively) obtained in the present work.

Estolide Decomposition

General. Decomposition of primary alcohol esters of fatty acids to terminal olefins has been known as a synthetic tool since 1842 (20). Liquid phase pyrolysis of cetyl palmitate (21) to cetylene and palmitic acid illustrates the use of the reaction for the preparation of either olefins or fatty acids. In the present study, estolides could be looked upon as esters of a secondary alcohol and fatty acids and decomposition of estolides as decomposition of secondary esters.

As a result of decomposition of the estolides at the ester group, there are simultaneously formed a double bond and a carboxyl group. This is illustrated in Figure 1 in which a simple estolide is shown to decompose, giving rise to one molecule of octadecadienoic acid and one of ricinoleic acid. Estolide decomposition can therefore be estimated through A.V. or I.V. In the present study, A.V. and not I.V. was taken as a measure of decomposition because during the study of decomposition, especially at higher temps, the I.V. is bound to be affected by polymerisation of the products of decomposition.

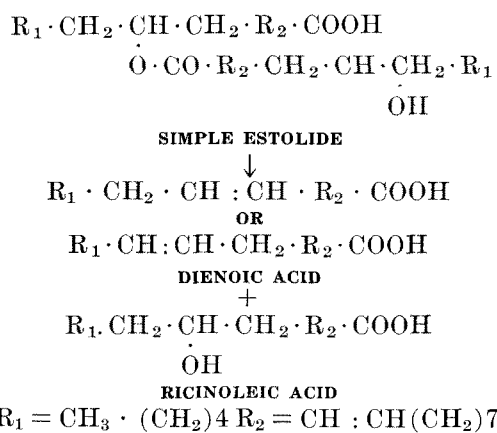


FIG. 1. Decomposition of Estolide

From Table II it is seen that the A.V. also is affected to a certain extent, especially at higher temps and after prolonged heating. This could be due to anhydride formation and decarboxylation. Samples taken at 2 hr 37 min and 3 hr 40 min during decomposition at 280C were found to have S.V.'s of 194.8 and 192.3, respectively, indicating some decarboxylation.

Kinetics. The rate of decomposition of estolides as measured by rate of increase in A.V. at a certain

time and fixed temp would depend on concn of ester groups in the estolides at the time under consideration. The concn of ester groups could be represented by the ester value. If S be the saponification value and X , the acid value of the estolide at time t , then $(S-X)$ would be the ester value. Since during decomposition of the ester there is no loss of weight in the system (see diagram above), saponification value S should remain the same.

The equation for the first order reaction is

$$Kt = 2.303 \log \frac{a}{a-x} \quad [7]$$

where K is the rate constant of the reaction, a , the molar concn of the reactant at zero time and x , change in concn of the reactant after time t . Applying the above equation to estolide decomposition it is seen that $(S-X_0)$ and $(S-X)$ would correspond to a and $(a-x)$, respectively, where X_0 and X are acid values of estolides at zero time and time t , respectively. Since the value of K in the first order reaction depends only on units of time, equation 7 can be written as

$$Kt = 2.303 \log \frac{(S-X_0)}{(S-X)}$$

or

$$\log (S-X) = \frac{-Kt}{2.303} + \log (S-X_0) \quad [8]$$

In plotting $\log (S-X)$ against time for different temps of decomposition, values for X and t were taken from Table II while value of S was taken as 200.0 for all samples. The straight line nature of the plots indicated that the reaction was of the first order.

With m as the slope of the plotted lines, K , the rate constant is calculated from the relation $m = \frac{-K}{2.303}$

Table V gives the calculated rate constants at different temps. On plotting values of $\log K$ against $1/T$, a straight line was obtained from the slope of which the activation energy E was found to be 56.4 kcal Grummit and Flemming (22) and Smith (23) obtained the values of 44.5 kcal and 44.2 kcal as activation energies for the thermal decomposition of acetylated castor oil and methyl acetyl ricinoleate, respectively.

Optical Activity of Estolides. Castor oil has an optical rotation of about 4. Theoretically, dehydrated castor oil should show a much lower rotation. Bolley (25), however, observed dehydrated castor oil to be optically active, its specific rotation being about 5. This was attributed to the estolides present in the dehydrated oil. Priester (24) also observed that the estolides had a high optical activity. Bolley (25) further found that acetylated castor oil had an optical rotation of 25–26 which is five to six times that of castor oil.

In the present work, it was found that during estolide formation, higher the degree of estolide formation, higher was the optical activity. In fact, plots of A.V.'s against optical rotations of all the samples irrespective of the temp of estolide formation, were found to lie on a straight line (Figure 2). The optical rotation is thus a measure of the extent of estolide formation. At the maximum estolide formation obtained, the optical rotation was 25.5 (not shown in Figure 2) similar to the value obtained by Bolley (25) for

TABLE V
Values of m , K , $\log K$ and $1/T$ at Different Temps of Estolide Decomposition

Temp °C	$m \times 10^3$	$K \times 10^3$	$\log K$	$1/T \times 10^3$
257	- 0.585	1.34	-2.8703	1.887
270	- 2.203	5.09	-2.2930	1.842
280	- 5.509	12.69	-1.8966	1.808
290	-11.73	27.02	-1.5684	1.776
307.5	-59.32	136.7	-0.8645	1.723

Units of K are min^{-1}

acetylated castor oil. Therefore, acylation at the hydroxyl group, whether by acetic acid or by a much higher mol wt acid, seems to enhance the optical rotation to the same extent.

Optical rotations of different samples obtained during estolide decomposition have been given in Table II. These when plotted against A.V. of the samples were also found to have linear relationship (Figure 2). However, this line is shifted at an angle to the left of the line relating to optical rotations and A.V. during estolide formation. The two curves almost meet at low A.V.'s. This is explained by the fact that the end product of estolide formation was the starting material for decomposition studies.

The increasing deviation of the two lines with increasing A.V.'s is obviously due to the different types of products being present at identical A.V.'s. A decomposed product having a certain A.V. has less asymmetry than a product having the same A.V. obtained during polyesterification.

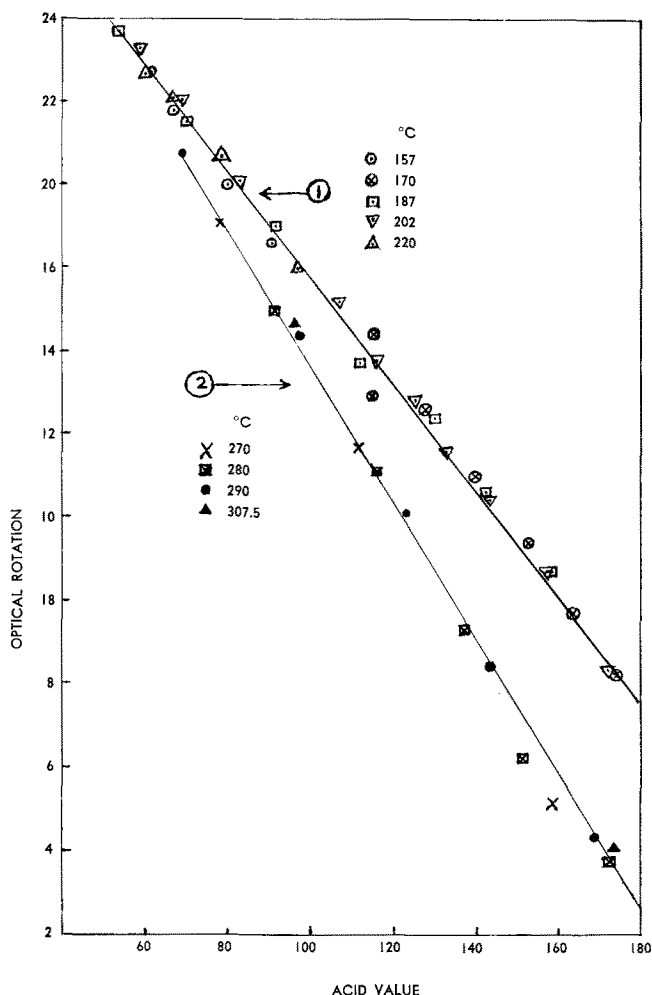


Fig. 2. Relationship between A.V. and optical rotation during 1) estolide formation and 2) estolide decomposition.

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Deuterium Tracer Studies of the Mechanism of Homogeneous Catalytic Hydrogenation of Sorbic Acid with Pentacyanocobaltate II¹

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Abstract

Exchange of deuterium and hydrogen during homogeneous catalytic reduction of sorbic acid with pentacyanocobaltate II has been investigated three ways: isotopic exchange between D₂ and H₂O, H₂-D₂O exchange, and D₂-anhydrous methanol exchange. In contrast to experiments with heterogeneous catalysts, where complete exchange and equilibration occur readily, mass spectrometric analysis of the gas phase above the pentacyanocobaltate II shows slow, incomplete exchange during the course of reduction of either catalyst alone or catalyst and substrate.

Mass spectra of methyl hexenoates from the deuterium exchange experiments have been examined. The fragmentation patterns of the esters reduced in the presence of D₂O were compared with those reduced in H₂O and with authentic 2-, 3-, and 4-hexenoates. Little or no exchange occurred with the hydrogen of valeric acid in the presence of pentacyanocobaltate deuteride ion [DCo(CN₅)]³⁻ and deuterium oxide. Experimental results indicate that either the hydrogen or deuterium that adds to the double bond originates predominantly from the solvent. It appears that the hydrogen atoms on the δ-carbon atoms in both 2- and 3-hexenoates exchange with deuterium during reduction in heavy water solutions.

Introduction

RECENT WORK IN THIS LABORATORY has confirmed that sorbate is selectively hydrogenated by pentacyanocobaltate II and has demonstrated that in aqueous and methanolic solutions 2-hexenoate is produced in 82 and 96% yield, respectively (14). In this reduction it was not known whether the hydrogen in reduced sorbate came from the hydrogen in the gas phase or in the water phase; such a question

could be answered by labelling the hydrogen in question. By using a solvent labeled isotopically, its role in the reaction could be investigated.

Since the original experiments described by Iguchi (10), several others have published on this subject. Many of the earlier reports were concerned with the structure of the catalyst (1,2,7,9). Nuclear magnetic resonance studies have shown the presence of a hydrido complex ion [HCo^{III}(CN)₅]³⁻ in reduced aqueous pentacyanocobaltate solutions (7). Visible and ultraviolet studies indicate that [Co(CN)₅]³⁻ reacts reversibly with H₂ to form the hydrido complex ion (11). Furthermore, the aging process involves the homolytic scission of water to yield hydrido and hydroxo complex ions (4,11).

In 1953, Ogg (16) reported that when an acidified pentacyanocobaltate II solution liberated hydrogen in the presence of D₂, hydrogen deuteride was formed. Formation of HD was considered due to the presence of "nascent" hydrogen and cobalt species thought not to be active catalytically. When [Co(CN)₅]³⁻ was prepared in D₂O from anhydrous salts, no proton resonance appeared in the high field region even after H₂ had been passed through the solution for 1 hr. Since resonance is found when solutions in H₂O are prepared under nitrogen, these observations can only be interpreted to mean that the [HCo(CN)₅]³⁻ ion must be formed by interaction of pentacyanocobaltate II ions with water (7). Mills, Weller, and

TABLE I
Effect of Pentacyanocobaltate II^a Concentration and Anions in Aqueous Solutions on Deuterium Absorption

Co. concn mM/liter	Anion	Observed D ₂ absorbed mM	D ₂ absorbed %
74.8	Acetate	25.31	67.67
81.7	Acetate	26.31	64.47
86.8	Acetate	29.12	67.07
149.2	Acetate	48.26	64.68
84.8	Chloride	32.22	75.97
86.4	Chloride	32.27	74.70
152.8	Chloride	56.58	74.05

¹ Presented at the AOCS meeting, Minneapolis, 1963.

² A laboratory of the No. Utiliz. Res. and Dev. Div., ARS, USDA.

^a Ratio of CN ions to Co ions was 6:1; 25C.