Castor Oil Dehydration Kinetics

F. Seniha Guner

Istanbul Technical University, Chemical Engineering Department, 80626 Maslak - Istanbul, Turkey

ABSTRACT: The dehydration reaction kinetics of castor oil was investigated with sodium bisulfate–sodium bisulfite mixture (SB–SB) or *p*-toluenesulfonic acid as catalyst. Reactions were carried out at 210, 220, and 230°C, and a kinetic model was determined for each case. The reactions with SB–SB catalyst at 210 and 220°C and with *p*-toluenesulfonic acid at 210°C followed second-order kinetics. A first-order rate equation showed the best fit to the experimental data for the reaction with SB–SB at 230°C. *p*-Toluenesulfonic acid-catalyzed reactions at 220 and 230°C were also first-order reactions. Additionally, some mathematical equations were derived between iodine value, refractive index, viscosity, and reaction time.

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KEY WORDS: Castor oil, dehydrated castor oil, kinetics.

Castor oil is a versatile material because of its high ricinoleic acid content (1). The oil can be used directly in the manufacture of nondrying alkyd resins and, additionally, it serves as a plasticizer in nitrocellulose, urethane, and alkyd systems (2). However, large amounts of this oil are converted to dehydrated castor oil (DCO) derivatives that can be used as a conjugated oil substitute (3–6). DCO gives good flexibility, rapid drying, excellent color retention, and water resistance to protective coatings (7). In the manufacture of DCO, castor oil is subjected to catalytic dehydration. Many catalysts are reported for dehydration of castor oil, the most widely used being sulfuric acid, sodium bisulfate, and acid-activated clays (8–14). An additional way to produce DCO is to split the secondary esters of castor oil (15–18). Our laboratory has studied the kinetics of splitting secondary esters of castor oil with fatty acids (19). The splitting mixtures of the secondary esters of castor oil were evaluated in the preparation of synthetic drying oils. For this purpose, the mixed fatty acids of linseed, sunflower, and *Ecballium elaterium* seed oils were used in the esterification reaction (19). A splitting mixture was also employed in the preparation of an oil-modified alkyd type resin (20).

In the catalytic dehydration process, the choice of catalyst is important because the reaction conditions and quality of the resulting product are mainly dependent on the catalyst. For instance, sulfonic acid and phosphoric acid result in a product with high conjugated diene content. However, these products show poor drying characteristics (21).

Because conjugated double bonds are formed during dehydration, polymerization is likely to take place. To prevent such polymerization, an antipolymerization agent should be used together with the catalyst. In this regard, when sodium bisulfate catalyst is used, sodium bisulfite is offered as an antipolymerization agent (21). It is reported that DCO obtained with sodium bisulfate–sodium bisulfite mixture (SB–SB) is light-colored, of low viscosity, and has high levels of conjugated diene. Aluminum and zinc powders are also reported as antipolymerization agents (21).

In spite of a large number of studies on castor oil dehydration, the reaction has not been investigated for reaction kinetics. In the present study, the reaction kinetics of dehydration of castor oil were investigated with SB–SB mixture as catalyst. Because sulfonic acid-type substances were largely used in previous dehydration studies, *p*-toluenesulfonic acid (PTSA) was included in this study for a comparison. Reactions were carried out at 210, 220, and 230°C, and a kinetic model was determined for each case.

EXPERIMENTAL PROCEDURES

Materials. Commercially purchased castor oil was used. The main characteristics of the oil were: refractive index (RI) (n_D^{25}), 1.4767; acid value, 2.97; saponification value, 177; hydroxyl value (HV), 164.4; iodine value (IV), 90.6. Other reagents were analytical-grade Merck products (Darmstadt, Germany).

For the determination of fatty acid composition, fatty acid methyl esters of castor oil were subjected to capillary gas-chromatographic analysis with a Hewlett-Packard 6890 (Palo Alto, CA), fitted with a flame-ionization detector, under the following conditions: column, HB 5 30 m × 320 µm × 0.25 µm, 5% diphenyl, 95% dimethyl polysiloxane; injection temperature, 240°C; oven temperature program, 60°C for 10 min, 60–275°C (6°C/min), 275°C for 30 min; flame-ionization detector temperature, 250°C. The main fatty acid composition of castor oil was 1.2% palmitic, 1% stearic, 4.4% oleic, 5.5% linoleic, 87.9% ricinoleic acid.

Experimental setup. Dehydration reactions were carried out in a four-necked flask, equipped with a stirrer, a thermometer, an inert gas inlet tube, and an inclined air condenser.

Dehydration of castor oil. Castor oil was placed into the reaction flask and heated to the reaction temperature. Catalyst

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was added to the reaction flask. The stirring rate was adjusted to 200 rpm, and nitrogen was passed over the surface of the oil at a rate of 200 mL/min to provide an inert atmosphere and to remove water. Samples of oil were taken at appropriate intervals and cooled immediately by immersion into cold water. HV (22), IV (23), viscosity (V) (22), and RI (22) of the samples were determined.

RESULTS AND DISCUSSION

The change of HV with time for the dehydration reaction is shown in Figure 1. Constant HV of 26.7, 15.6 and 16.9, in the reaction with PTSA, are reached after 40 min at 210 and 220°C, and after 25 min at 230°C, respectively. However, for SB–SB, the constant HV of 31.8, 31.1, and 22.9 are obtained after 120 min at 210°C and 90 min at 220 and 230°C, respectively. From these results, it is obvious that PTSA is more effective than SB–SB as a dehydration catalyst because the elapsed time for about the same magnitude of HV is shorter than for SB–SB. However, PTSA gives a dark-colored product. This is most probably due to the high acidic strength of PTSA compared to sodium bisulfite.

To understand the effect of catalyst on the conjugation, samples were analyzed for their conjugated diene contents. For this purpose, ultraviolet absorption at 235 nm was measured on a Beckman model DB-GT spectrophotometer (Fullerton, CA) (24). As seen in Table 1, the final percentages of conjugation with both catalysts at all three temperatures were similar.

TABLE 1
Some Properties of the Dehydration Reaction Mixtures at Optimal Reaction Times

Catalyst used in the reaction	Reaction temperature (°C)	Reaction time (min)	Hydroxyl value	Conjugated dienoic acid (%)[a]
SB–SB	210	120	31.8	19.49
	220	90	31.1	19.46
	230	90	22.9	20.71
PTSA	210	40	26.7	17.78
	220	40	15.6	20.93
	230	25	16.9	23.76

[a]Determined according to Reference 24; SB–SB, sodium bisulfate–sodium bisulfite mixture; PTSA, *p*-toluenesulfonic acid.

The rate of dehydration was constructed from experimental data by considering the disappearance of hydroxyl groups. The integral method was used to correlate the experimental data. The first-order rate equation showed the best fit to the experimental data for the reaction with SB–SB at 230°C. PTSA-catalyzed reactions at 220 and 230°C were also first-order reactions. The results are shown in Figure 2. The reactions with SB–SB catalyst at 210 and 220°C and with PTSA at 210°C followed second-order kinetics (Fig. 3).

From the slopes of the straight lines, the rate constants were calculated, and the results are presented in Table 2. The activation energies given in the same table were determined from the slopes of the lines obtained by plotting ln k against 1/T. Comparing rate constants belonging to the same ordered reactions, it can be seen that PTSA is a more effective catalyst than the SB–SB mixture. This is undoubtedly because PTSA is a stronger acid compared to SB–SB.

To follow the reaction course with easy measurable properties, some additional work was carried out. For this purpose, the relations of HV, IV, V, and RI with time and with one another were derived by applying the least-square curve fitting method. The best fits for the experimental data were decided by considering the coefficients of determination (r^2). The decrease in hydroxyl groups during the reaction resulted in changes in the other properties. For instance, while the hydroxyls decrease, IV and RI increase. The obtained

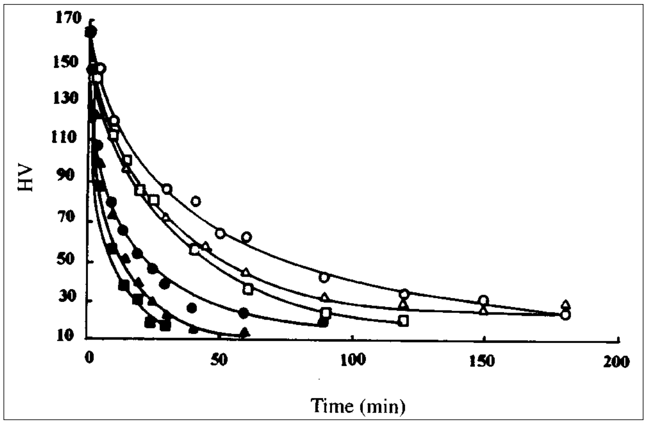

FIG. 1. The change of hydroxyl value (HV) for the dehydration reaction of castor oil: ○, with SB–SB at 210°C; △, with SB–SB at 220°C; □, with SB–SB at 230°C; ●, with PTSA at 210°C; ▲, with PTSA at 220°C; ■, with PTSA at 230°C. SB–SB, sodium bisulfate–sodium bisulfite mixture; PTSA, *p*-toluene sulfonic acid.

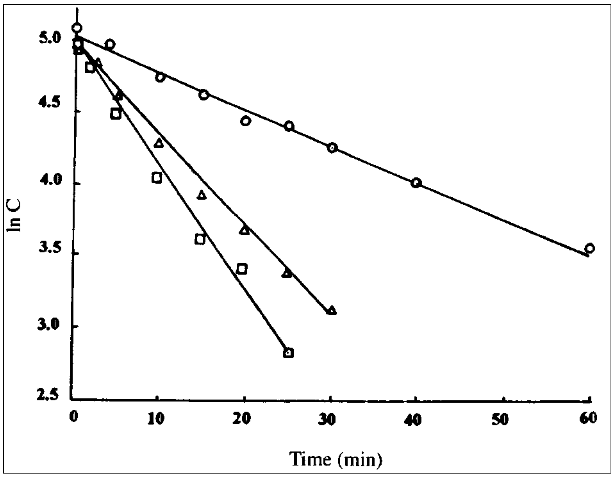

FIG. 2. Rate of dehydration reaction of castor oil: ○, with SB–SB at 230°C, r^2 (coefficient of determination) = 0.9899; △, with PTSA at 220°C, r^2 = 0.9881; □, with PTSA at 230°C, r^2 = 0.9899. See Figure 1 for abbreviations.

TABLE 2
Rate Constants and Activation Energies for the Dehydration of Castor Oil

Catalyst used in the reaction	Rate constant, k^a $(\text{min})^{-1}$			Activation energy, E, kcal/mole
	210°C	220°C	230°C	
SB–SB	2.09×10^{-4}	2.88×10^{-4}	2.53×10^{-2}	15.1
PTSA	6.46×10^{-4}	6.41×10^{-2}	8.57×10^{-2}	14.3

[a]Units of the rate constants for SB–SB-catalyzed reactions at 210 and 220°C and for PTSA-catalyzed reaction at 210°C are $(\text{wt}\%)^{-1}$ $(\text{min})^{-1}$. See Table 1 for abbreviations.

TABLE 3
Relations for the Changes of Iodine Value, Refractive Index, and Viscosity with Time[a]

Property	Temperature (°C)	Equation for[a] SB–SB catalyst	Coefficient of determination, r^2	PTSA catalyst	Coefficient of determination, r^2
Iodine value	210	$IV = -0.0031\ t^2 + 0.7354t + 94.25$	0.9870	$IV = 9.9783\ \ln(t) + 84.709$	0.9715
	220	$IV = -0.0026\ t^2 + 0.681t + 100.61$	0.8714	$1/IV = -0.001\ \ln(t) + 0.0114$	0.9899
	230	$IV = -0.0161\ t^2 + 1.6515t + 92.437$	0.9860	$1/IV = -0.01\ \ln(t) + 0.0111$	0.9958
Refractive index, n_D^{25}	210	$RI = -2 \times 10^{-7}\ t^2 + 6 \times 10^{-5}\ t + 1.477$	0.9870	$RI = 0.0009\ \ln(t) + 1.4776$	0.9737
	220	$RI = 10^{-7}\ t^2 - 3 \times 10^{-5}\ t + 0.6769$	0.9200	$RI = 0.0012\ \ln(t) + 1.4773$	0.9903
	230	$1/RI^2 = 7 \times 10^{-7}\ t^2 - 8 \times 10^{-5}\ t + 0.4585$	0.9918	$1/RI = -0.0006\ \ln(t) + 0.6768$	0.9731
Viscosity, St, 25°C	210	$V = 0.003\ t^2 - 0.0695\ t + 5.9906$	0.9476	$1/V^2 = -7 \times 10^{-6}\ t^2 + 0.001\ t + 0.0227$	0.9434
	220	$V = 8 \times 10^{-5}\ t^2 - 0.018\ t + 3.1089$	0.7581	$V = 0.0015\ t^2 - 0.1472t + 6.6487$	0.9884
	230	$1/V^2 = -4 \times 10^{-5}\ t^2 + 0.0055\ t + 0.0044$	0.9646	$V = 0.0037\ t^2 - 0.2344t + 6.2105$	0.9879

[a]Legends: t, time (min); IV, iodine value; RI, refractive index; V, viscosity; SB–SB, sodium bisulfate–sodium bisulfite; PTSA, *p*-toluenesulfonic acid.

relations are given in Tables 3 and 4, together with the corresponding r^2.

Table 5 shows that the HV with PTSA is lower compared to that obtained with SB–SB at the same temperature after the same time period. However, the product is more viscous. These results indicate that thermal polymerization is more likely to occur in the presence of PTSA due to the high content of double bonds formed through dehydration. Thus, both PTSA and SB–SB can be used as the dehydration catalyst but, if a light-colored and low-viscosity product is required, SB–SB is preferred.

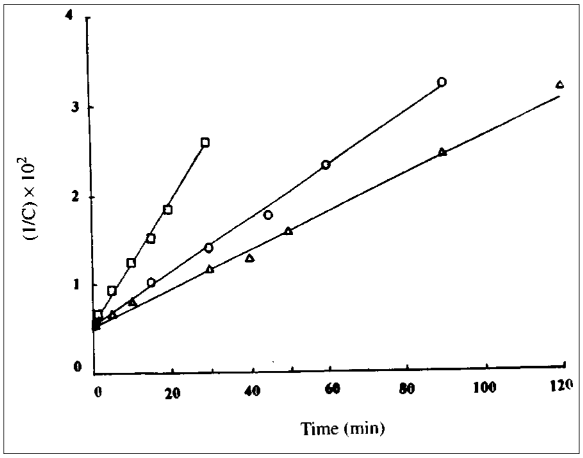

FIG. 3. Rate of dehydration reaction of castor oil: △, with SB–SB at 210°C, r^2 (coefficient of determination) = 0.9928; ○, with SB–SB at 220°C, r^2 = 0.9963; □, with PTSA at 210°C, r^2 = 0.9977. See Figure 1 for abbreviations.

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TABLE 4
Relations for the Changes of Iodine Value, Refractive Index, and Viscosity During the Dehydration of Castor Oil[a]

Reaction temperature (°C)	Equation for[a]			
	SB–SB catalyst	Coefficient of determination, r^2	PTSA catalyst	Coefficient of determination, r^2
210	$IV = 11748\ RI - 17262$	0.9819	$IV = 10892\ RI - 16010$	0.9816
	$IV = 1.1277\ V^2 - 21.273\ V + 181.49$	0.9923	$IV = -6.008\ V^2 + 47.579\ V + 30.271$	0.9265
	$IV = -0.3478\ HV + 147.06$	0.9077	$1/IV^2 = 5 \times 10^{-7}\ HV + 5 \times 10^{-5}$	0.9804
	$RI = 0.0002\ V^2 - 0.0029\ V + 1.4869$	0.9749	$RI = -0.0006\ V^2 + 0.0048\ V + 1.4723$	0.8632
	$1/RI = 10^{-5}\ HV + 0.675$	0.9831	$1/RI = 10^{-5}\ HV + 0.6748$	0.9745
	$V = 8 \times 10^{-5}\ HV^2 - 0.014\ HV + 1.9895$	0.9854	$V = -0.0001\ HV^2 - 0.0338\ HV + 3.6476$	0.9384
220	$IV = 12260\ RI - 18013$	0.9820	$IV = 9050.5\ RI - 13281$	0.9459
	$IV = 5.1445\ V^2 - 55.412 + 235.73$	0.9427	$IV = -0.7159\ V^2 - 5.2845\ V + 156.33$	0.9663
	$IV = -0.3532\ HV + 149.16$	0.9804	$1/IV^2 = 4 \times 10^{-7}\ HV + 5 \times 10^{-5}$	0.9920
	$RI = 0.0004\ V^2 - 0.0045\ V + 1.4885$	0.9200	$RI = -0.0002\ V^2 + 0.0007\ V + 1.4816$	0.8961
	$1/RI = 10^{-5}\ HV + 0.675$	0.9968	$1/RI = 10^{-5}\ HV + 0.6747$	0.9828
	$V = 0.0003\ HV^2 - 0.0185\ HV + 2.54$	0.9987	$V = -0.0002\ HV^2 - 0.054\ HV + 2.4594$	0.9953
230	$IV = 11857\ RI - 17417$	0.9859	$IV = 9360.4\ RI - 13737$	0.9557
	$IV = 0.5756\ V^2 - 14.915\ V + 163.87$	0.9641	$IV = -0.6238\ V^2 - 6.3037\ V + 155.39$	0.9827
	$IV = -0.3703\ HV + 154.01$	0.9738	$1/IV^2 = 5 \times 10^{-7}\ HV + 5 \times 10^{-5}$	0.9907
	$RI = 0.0002\ V^2 - 0.0027\ V + 1.4857$	0.8992	$RI = -0.0001\ V^2 + 0.0003\ V + 1.4836$	0.9559
	$1/RI = 10^{-5}\ HV + 0.675$	0.9920	$1/RI = 2 \times 10^{-5}\ HV + 0.6746$	0.9818
	$V = 0.0002\ HV^2 - 0.0084\ HV + 2.2735$	0.9745	$V = -0.0001\ HV^2 - 0.0517\ HV + 1.7264$	0.9883

[a] Legends: HV, hydroxyl value; IV, iodine value; RI, refractive index (n_D^{25}); V, viscosity (St, 25°C); SB–SB, sodium bisulfate–sodium bisulfite; PTSA, *p*-toluenesulfonic acid.

TABLE 5
Some Properties of the Dehydration Reaction Mixtures[a]

Reaction temperature (°C)	Reaction time (min)	Catalyst used in the reaction	Properties		
			Hydroxyl value	Iodine value	Viscosity (St, 25°C)
210	60	SB–SB	62.4	125.6	3.1
		PTSA	22.1	124.9`	4.5
220	60	SB–SB	43.5	136.2	2.4
		PTSA`	14.3	134.5	3.2
230	60	SB–SB	46.8	134.5	2.4
		PTSA	19.2	130.3	2.6

[a] See Table 1 for abbreviations.

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