the total error would not exceed ±0.4% in values calculated for ΔH°_{298} by the third-law method. The maximum probable error in temperature measurement is ±2°, which corresponds to a ±0.2% error in ΔH°_{298} values. The total uncertainty in ΔH°_{298} calculation resulting from experimental errors is then ±0.6%.

The uncertainties in values for the free-energy functions arise from errors of ±10% in vibrational frequencies and ±0.05 A. in bond distances. Thus the free-energy function may be in error by ±1.2%. Considering the small contribution made by dimerization corrections, the third-law heats of sublimation should be correct within ±2%. Considering all estimated errors, the selected sublimation energies for the cobalt dihalides are: CoF_2 78 ± 1.5, $CoCl_2$ 54 ± 1, $CoBr_2$ 52 ± 1, and CoI_2 46 ± 2 kcal. per mole.

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NOMENCLATURE

A = area of orifice, sq. cm.
a_1, a_2 = area of effusion orifices, sq. cm.
D = torsion constant, dyne-cm./deg.
f_1, f_2 = force correction factor
K = Clausing factor for orifice
M = molecular weight

P_K = vapor pressure, mm. of Hg
P_T = vapor pressure of sample, dynes/sq. cm.
q_1, q_2 = momentum arm lengths, cm.
t = time, seconds
T = temperature, ° K.
ΔW = weight loss, grams
θ = angular displacement, deg.

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Thermal Behavior of Some Resin Acid Esters

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The isomerization of the methyl esters of three of the four conjugated dienoic resin acids of pine gum in the presence and absence of base, as well as in the presence of added carboxylic acid, was examined.

THE THERMAL isomerization of levopimaric, palustric, and neoabietic acids and esters was investigated some time ago by Lawrence and coworkers (3). The isomerization of levopimaric, palustric, neoabietic, and abietic acids at 200° C. has recently been found to result in the formation of an equilibrium mixture of 81% abietic, 14% palustric, and 5% neoabietic acids (3). The isomerization of methyl abietate at 200° C. proceeded at the same rate as the acid and gave the same final distribution of abietate, palustrate, and neoabietate (2). Disproportionation was extensive in the case of the ester as compared to the acid (2). The addition of base very strikingly inhibited both isomerization and disproportionation. The temperature of 200° C. was selected for study, in that it is about 25° C. higher than the melting point of the highest melting of the four conjugated dienoic acids. Thus measurements are not complicated by lengthy "heat up" or melting periods at the beginning of each run. For comparison, the esters were then also run at 200° C.

It thus became of interest to investigate the thermal isomerization, in the presence and absence of added base, of the methyl esters of the other three conjugated dienoic resin acids found in pine gum. This was of special importance in view of the demonstrated inhibitory effect of small traces of base, accumulated during the preparation of the ester, upon the isomerization of methyl abietate (2).

The results are summarized in terms of half lives in Table I.

Table I. Half Lives of Conjugated Dienoic Resin Acids, Esters, and Esters in Presence of Base at 200° C.

	Half Lives, Min.		
	Acid (3)	Ester	Ester + 5 mole % KOH
Levopimaric	15	15	2.5 hr.
Palustric	40	84	50 days
Abietic	75	70 (2)	200 days (2)
Neoabietic	120	134 hr.	200 days

The rate of isomerization of the esters is in about the same order as the corresponding acids. Surprisingly, methyl levopimarate and methyl abietate isomerize at about the same rate as the free acids, whereas methyl palustrate isomerizes somewhat more slowly and methyl neoabietate very much more slowly than the corresponding acids. In the presence of base, again the same order of reactivities is approximately maintained.

Methyl palustrate and methyl neoabietate were isomerized in the presence of an equimolar amount of dehydroabietic acid. In both cases, the rate of isomerization was essentially the same as that of the corresponding free palustric and neoabietic acids. This would support the notion of an acid-catalyzed mechanism in the isomerization reaction.

Methyl levopimarate in the presence of 5 mole % of potassium hydroxide at 200° C. does not isomerize nor disproportionate to any appreciable extent. However, a new and unusual series of base-catalyzed rearrangements takes place, resulting in cleavage of rings A and B (4).

Methyl levopimarate in the presence of ethanolic hydrochloric acid gives about the same equilibrium distribution of abietate (94.5%), palustrate (2.9%), and neoabietate (2.6%) as is observed for methyl abietate (2), and all four conjugated dienoic acids (3).

EXPERIMENTAL

All ultraviolet spectra and optical rotations were run in 95% ethanol. The esters were sealed in Carius tubes and evacuated, and the air was replaced with nitrogen, evacuated, sealed, and immersed in a constant temperature oil bath held at 200° ± 0.5° C. Tubes from a given set were removed at intervals and analyzed by gas-liquid chromatography (3).

Isomerization of Resin Acid Methyl Esters at 200° C. Esters were prepared by using a distilled ether (2) solution of diazomethane prepared from Diazald.

Methyl levopimarate was recrystallized from methanol; $[\alpha]_D^{25}$ -263° (c 2.0); ultraviolet max. 272 mμ (ϵ 6000); m.p. 59-61° [lit. (1) $[\alpha]_D^{25}$ -269° (c 2.0 in 95% EtOH); ultraviolet 272 mμ (ϵ 5690); m.p. 62-64.5° C.]. The isomerization of the methyl ester proceeded at about the same rate as the free acid (3). The final equilibrium distribution of esters was abietate (81.3%), palustrate (14.0%), and neoabietate (4.7%), based on only the yields of these esters. There was no change in the quilibrium distribution of these three esters after 504 hours (21 days). Disproportionation occurred simultaneously with isomerization. At the end of 1 day, the methyl dehydroabietate yield was 10%; after 21 days it was 23%. The yield of total esters other than levopimarate, palustrate, neoabietate, and abietate at the end of 1 day was 18.5%; after 21 days it was 48.2%. No rearrangement to ring cleavage products was observed (4).

Methyl palustrate was crystallized from methanol; m.p. 22-25° C., ultraviolet max. 265 mμ (ϵ 8630) [lit (1) m.p. 24-27° C., ultraviolet max. 265 mμ (ϵ 8530)]. Methyl palustrate isomerized somewhat more slowly than the free acid (3). The final equilibrium distribution of methyl abietate (78.9%), palustrate (14.9%), and neoabietate (6.2%) was reached in about 3 hours with no appreciable change up to 24 hours. No disproportionation was observed up to 24 hours. When somewhat impure samples of methyl palustrate were used, the rate fluctuated between runs and some disproportionation was observed. The methyl palustrate was freshly prepared before each run and was demonstrated by gas-liquid chromatographic analysis to be free from methyl dehydroabietate. No rearrangement to ring cleavage products was observed (4).

Methyl neoabietate was recrystallized from methanol; m.p. 62-64°; $[\alpha]_D^{25}$ +158.3° (c 1.0); ultraviolet max. 251 mμ (ϵ 24,100) [lit. (1) m.p. 61.5-62° C.; $[\alpha]_D^{25}$ + 148° (c 2 in 95% EtOH); ultraviolet max. 251 mμ (ϵ 24,460)]. The isomerization of methyl neoabietate is very slow, the slowest of all the esters and slower than any of the free acids (3) including neoabietic acid. After 35 days, the distribution of esters was still changing and had reached the values of methyl abietate (61.1%), neoabietate (25.3%), and palustrate (13.6%). No disproportionation was observed to take place in 35 days and no rearrangement to ring cleavage products was observed (4).

In Presence of 5 Mole % Potassium Hydroxide at 200° C. A mixture of the ester and 5 mole % of potassium hydroxide was prepared in methanol and charged to Carius tubes, the solvent was removed under vacuum, and the tubes were sealed as usual (1) and heated at 200° C.

Methyl Palustrate. The isomerization occurred much more slowly than in the absence of added base. After 15 days, the ratio of products was still changing and the values of the esters were methyl abietate (15.2%), neoabietate (0.0%), palustrate (74.5%), and dehydroabietate (10.3%). No formation of ring cleavage products occurred (4).

Methyl Neoabietate. The isomerization occurred very slowly. The rate was considerably less than in the absence of added base. After 49 days, the ratio of products was still changing and the values of the three esters were methyl abietate (10.3%), palustrate (1.7%), and neoabietate (88.0%). At the end of this time, the values observed were $[\alpha]_D^{25}$ +120.7° (c 1.0) and ultraviolet max. 251 mμ (ϵ 20,800). No disproportionation or formation of ring cleavage rearrangement products (4) was observed in 49 days.

In Presence of Dehydroabietic Acid at 200° C. A 1 to 1 molar mixture of the methyl ester of the resin acid and dehydroabietic acid was prepared in ether solution. Equal portions were charged to the reaction tubes, the solvent was removed under reduced pressure, and the tubes were sealed in the usual manner (3) and heated at 200° C.

Methyl Palustrate. The rate of isomerization was about the same as that of palustric acid (3). The equilibrium distribution of esters was reached in about 2 hours [methyl abietate (79.2%), palustrate (14.9%), neoabietiate (5.9%)] and was unchanged at the end of 26 hours. No disproportionation was observed through 26 hours.

Methyl Neoabietate. The rate of the isomerization was about the same as that of neoabietic acid (3). The distribution of esters at the end of 24 hours was methyl abietate (77.0%), palustrate (15.7%), and neoabietate (7.3%). No disproportionation occurred through 24 hours.

Isomerization of Methyl Levopimarate in 0.5N Ethanolic Hydrochloric Acid. A 1% solution of methyl levopimarate in 0.5N ethanolic hydrochloric acid was prepared and allowed to stand at 25° C. Aliquots were removed periodically and poured into water. The precipitated resin acid ester mixture was immediately extracted with ether (quantitatively), washed with water, and dried, the ether removed under reduced pressure, and the residue analyzed by gas-liquid chromatography (3). The isomerization reached an equilibrium distribution of resin acids of methyl abietate (94.5%), palustrate (2.9%), neoabietate (2.6%) (neglecting methyl dehydroabietate present) after about 7 days and remained unchanged through 21 days. Methyl dehydroabietate was formed to the extent of 6.5% after 21 days.

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