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The Molecular Structure in Monolayers of Saturated Triglycerides on Water as Related to Three-Dimensional Polymorphic Forms¹

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The condensed monolayers of saturated triglycerides on water were found to be in the solid state and analogous in cross-sectional area and melting point to the three-dimensional α -forms. Complete melting of the condensed monolayers resulted in transformation to a fluid expanded state rather than to the more stable polymorphic β - or β' -forms. However, under certain specific conditions the solid monolayers were unstable and possessed some of the properties characteristic of a mesomorphic tilted form. The monolayers of saturated mixed triglycerides were found to be similar to those of simple triglycerides. The significance of the results is discussed in relation to the tuning-fork and chair structure of triglycerides.

Introduction

The molecular structure in the polymorphic forms of triglycerides has been investigated by means of X-ray diffraction and monomolecular films.³⁻⁶ Angles of tilt and cross-sectional areas have been calculated from the X-ray long spacings of the unit cells and density data. In the β -form of saturated triglycerides the hydrocarbon chains are tilted at an angle of approximately 65° with respect to the planes formed by the end methyl groups. In the β' - and α -forms the angles are 75° and 90° , respectively. Clarkson and Malkin⁵ have proposed the tuning-fork structure for triglyceride molecules on the basis that this structure matches more closely the long spacing data and does not possess the mechanical strain of a structure in which the three chains are aligned side by side. Although the existence of a tuning fork structure in monolayers has been questioned by Adam,⁷ the data of Dervichian⁶ indicate that certain three-dimensional polymorphic forms of triglycerides occur as stable or unstable states in the monolayers.

The relationship of the molecular structure in mono- and multimolecular films to three-dimensional states has produced conflicting theoretical viewpoints from many workers.^{6,8-10} In making correlations of this type one must assume that a density in three dimensions approximates the density of the film, since the absolute densities of the latter have never been measured. Such correlations also are questionable on the basis of differences in molecular interactions, which involve molecular multiplicity and alignment in the three-dimensional unit cells and the possibility of hydration in the case of monolayers.

This study was undertaken to clarify, if possible, the relationship of the molecular structure in monolayers of triglycerides to three-dimensional states. Tristearin and a series of saturated mixed triglycerides were used to obtain the monolayer data. Tristearin was selected as a typical simple triglyceride because accurate X-ray, density, and dilatometric data are available for each of the polymorphic forms that exist in three dimensions.

Experimental

Tristearin.—A sample of tristearin was prepared by the direct esterification of glycerol with stearyl chloride in quinoline-chloroform solution according to the method of Sidhu and Daubert.¹¹

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(3) C. E. Clarkson and T. Malkin, *J. Chem. Soc.*, 666 (1934).

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(9) W. D. Harkins and E. Boyd, *J. Phys. Chem.*, **45**, 20 (1941).

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The melting point and X-ray spacings given in Table I conformed to the results reported by Filer, *et al.*¹²

The density of the β -form was determined by the pycnometer method. Powdered crystals were used to displace a saturated solution of tristearin in acetone-free methanol in a 25-ml. pycnometer. The densities of saturated solutions were determined for the elimination of solubility error. All weighings were corrected for air buoyancy and the volumes were corrected for glass expansion. The density at 20° was 1.022 g./ml. The densities of the α -, β' -, and liquid forms given in Table I were calculated from dilatometric data reported by Bailey and Singleton.¹³

TABLE I

MELTING POINTS, DENSITIES, AND MOLECULAR DIMENSIONS OF TRISTEARIN

	M.p., °C.	Density, g./ml. 20°	Long spacing, Å.	Cross-sectional area, Å. ²	
Tristearin	β	72.0	1.022	45.1	64.2
	β'	64.0	0.986	46.8	64.1
	α	54.0	0.976	50.6	59.9 (59.7)
Liquid tristearin	β		0.905 ^{23°}	45.1	72.5
	β'		.905 ^{23°}	46.8	69.9
	α		.905 ^{23°}	50.6	64.6

The average cross-sectional areas in Ångstrom units of the polymorphic forms were calculated from the density and X-ray long spacing data. Another calculation was made for the cross-sectional area of the α -form from its single side spacing of 4.14 Å. by assuming that the structure of this form is hexagonal. The calculation gave a value of 19.9 Å.² per chain or 59.7 Å.² per molecule, which is almost identical with the value of 59.9 Å.² calculated from the density and long spacing. Theoretical areas per molecule of tristearin in hypothetical polymorphic liquid forms also were calculated from the X-ray data and the extrapolated density of the liquid. These calculations are justifiable in part on the basis that crystal nuclei are known to exist at temperatures slightly above the melting point. The results of these calculations are given in Table I.

Force-area data for the monolayers were obtained using the apparatus described in a previous publication¹¹ except petroleum ether was used as the solvent for spreading the films. The petroleum ether was washed with sulfuric acid, dried, and distilled from zinc and sodium hydroxide.

The monolayer of tristearin at 23.0° (Fig. 1) was a condensed solid with a limiting area of 59.7 Å.². The pressure at equilibrium rose on a nonlinear curve from approximately 70 to 60 Å.². The initial pressures, however, were unstable and higher than shown in Fig. 1. The solid monolayer at 60 Å.² resisted further compression and the pressure at 58.6 Å.² was 52.5 dynes/cm. At this point the film was beginning to crumple as shown by visible ridge lines in a small amount of talc dusted on the surface. Further slight reductions in area produced larger ridge lines until finally the monolayer collapsed at 58.4 Å.². The compressibility expressed as the reciprocal slope of the isotherm was 0.027 cm.³/dyne. At 56° the monolayer expanded and occupied 120 Å.² per molecule at negligible pressure.

Saturated Mixed Triglycerides.—The preparation, polymorphic behavior, and X-ray data for the saturated mixed triglyc-

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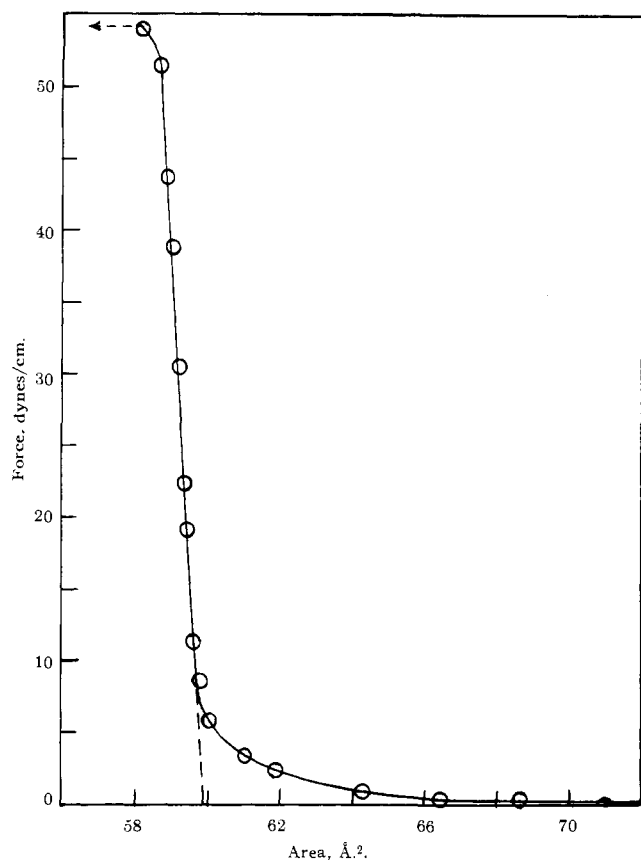


Fig. 1.—Force-area curve for tristearin at 23°.

erides have been reported previously.^{11,15,16} The force-area data for these compounds are given in Fig. 2-5 and Table II.

TABLE II

MONOLAYER DATA FOR THE CONDENSED AND EXPANDED STATES OF SATURATED MIXED TRIGLYCERIDES

Temp., °C.	—Condensed state—			—Expanded state—		
	Limiting area, Å. ²	Col-lapse area, Å. ²	Col-lapse press., dynes/cm.	Limiting area, Å. ²	Col-lapse area, Å. ²	Col-lapse press., dynes/cm.
18-16-12 ^a	10.2	60.0	58.6	30.8		
	23.2	61.3	59.8	30.8		
	31.2	65.7	61.3	26.2		
18-12-16	10.2	60.7	58.9	38.0		
	22.0	61.3	59.9	37.3		
	31.0	65.4	61.2	30.8		
18-10-14	9.4	61.0	59.0	28.3		
	23.2	66.0	62.0	19.2	117	95.0
	31.2				129	91.4
18-12-10	9.4	62.0	59.8	23.8		
	23.2				123	79.5
	30.6				132	88.2
18-10-12	8.6	62.5	60.0	25.1		
	22.9				130	87.4
	30.6				132	88.0

^a This designation represents the hydrocarbon chain length of the ester groups.

The isotherms for the condensed state show that a slight pressure usually was recorded when the area was reduced to 70 Å.². A layer of talc dusted on the surface at this point was immobile. At the low temperatures decompression of these monolayers always followed the extrapolation and not the initial nonlinear rise. At times the nonlinear portions of the curves disappeared, especially when the water surface contained traces of a sample

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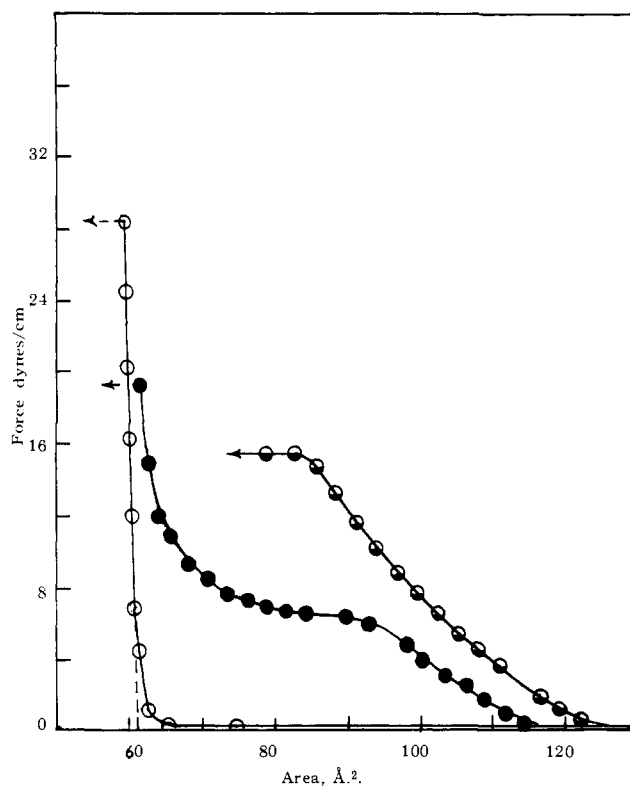


Fig. 2.—Force-area curves for 1-stearyl-2-myristyl-3-caprylglycerol: ○, 9.4°; ●, 23.2°; ◐, 31.2°.

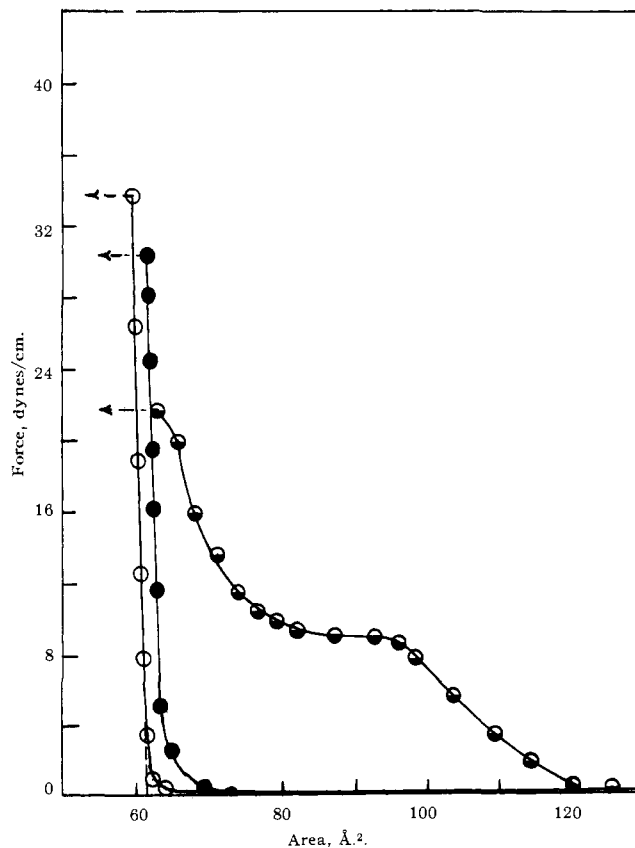


Fig. 3.—Force-area curves for 1-palmityl-2-myristyl-3-laurylglycerol: ○, 12.8°; ●, 22.5°; ◐, 30.8°.

from a previous determination. These hysteresis effects were to a certain extent variable with temperature and observed only in solid condensed monolayers at temperatures below the melting points. The magnitude was approximately several dynes/cm. with a unit change in area.

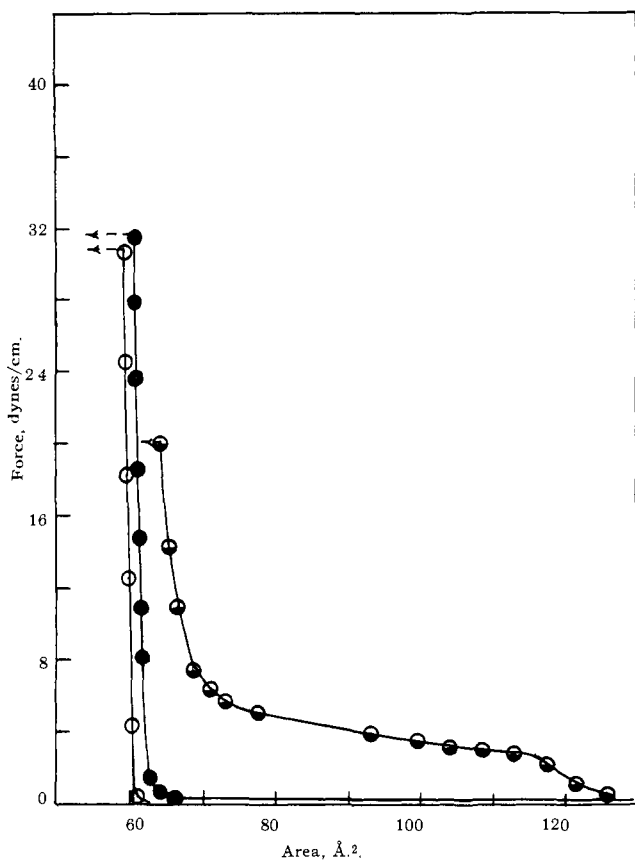


Fig. 4.—Force-area curves for 1-stearyl-2-myristyl-3-lauryl-glycerol: O, 10.2°; ●, 23.2°; ◐, 31.2.

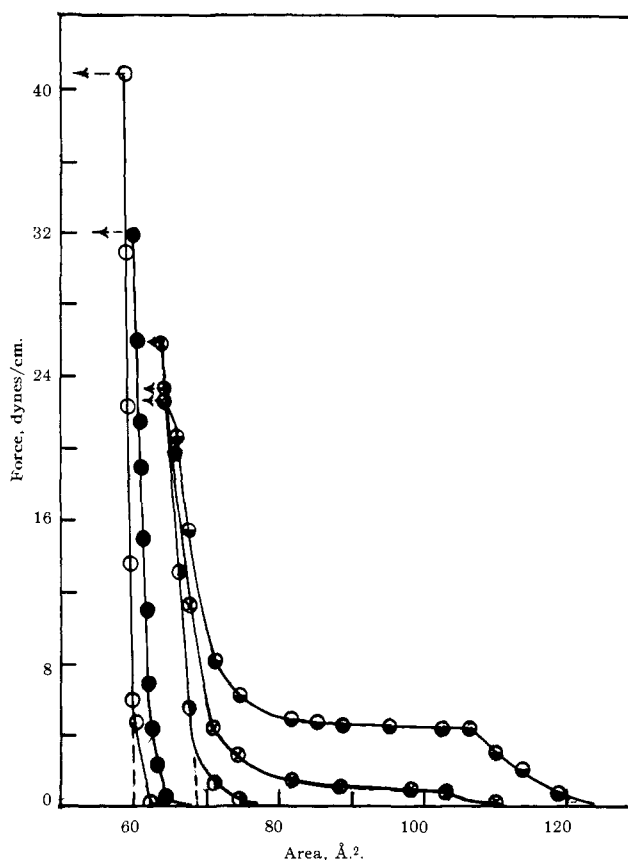


Fig. 5.—Force-area curves for 1-stearyl-2-lauryl-3-myristyl-glycerol: O, 11.2°; ●, 22.5°; ◐, 29.2°; ⊗, 29.8°; ◑, 32.5°.

At 23° the limiting area of completely condensed monolayers ranged from 60 to 66 Å.² and the compressibilities from 0.033 to 0.075 cm.³/dyne. At higher temperatures in the vicinity of the melting points the "limiting areas" approached 70 Å.² and the mean compressibility increased to 0.1–0.3 cm.³/dyne.

At low temperature these monolayers collapsed at 58.5–60.0 Å.² and at a lower pressure than did tristearin. At the higher temperatures most of these monolayers were in the expanded state. The approximate temperatures at which the monolayers expanded are given in Table III in comparison to the melting points of the α -forms.

TABLE III

TEMPERATURES OF EXPANSION FOR THE CONDENSED MONOLAYERS OF SATURATED MIXED TRIGLYCERIDES AS COMPARED TO THE MELTING POINTS OF THE α -FORMS

	Monolayer expansion at °C.	M.p., α -forms, °C
18-16-12	31-33	33.4
18-12-16	31-33	32.0
18-14-12	Between 23.2 and 31.2	27.5
18-12-14	29	28.8
18-14-10	Between 10 and 23	21.5
18-10-14	Between 10 and 23	22.3
18-12-10	Slightly <9.4	14.5
18-10-12	Slightly <8.6	14.0

The data for the expanded monolayers show that these films can be condensed if the temperature is not too far above the melting point. A layer of talc dusted on the surface again became immobile at 70 Å.². Further compression decreased the area, but the monolayers were not very stable and collapsed at relatively low pressures. Hysteresis effects were absent in these condensed monolayers. At temperatures well above the melting points the expanded monolayers collapsed to form oil lenses of equal spreading pressure.

The precision of the monolayer data depends on the accuracy of weighing, torsion wire calibration, pipet calibration and delivery, the amount and cleanliness of the water in the tray of the balance, and the temperature. The variation in C.S.A. between independent determinations was approximately ± 0.25 Å.².

Discussion of Results

The monolayers of saturated mixed triglycerides were found to be similar to those of simple triglycerides and to each other except for variations in the stability, compressibility, and limiting area of the solid condensed state with temperature and molecular weight. An increased molecular weight and/or a lower temperature results in stabilities, compressibilities, and limiting areas, which are characteristic of tristearin. The tendency for the limiting areas to approach 59.7 Å.² at low temperature shows that variation in the limiting area from 60 to 66 Å.² is merely a function of variation in kinetic activity. It is not unreasonable to expect marked changes in limiting area with temperature or molecular weight because the α -forms have a relatively high coefficient of expansion. Bailey and Singleton¹³ have found a relatively abrupt contraction for the α -form of tristearin well below the melting point and the dilatometric curve was nonlinear. The area of 59.7 Å.² is in excellent agreement with the cross-sectional areas calculated for the α -form of tristearin in three dimensions.

The stability of the monolayers in the condensed state was not a simple function of the average chain length per molecule but in some cases depended on the variation in chain length within a given molecule. The triglycerides 18-14-10 and 16-14-12 (Fig. 2 and 3) have the same average chain length but their monolayers were in different states at 23°, the former being expanded and the latter condensed. The condensed monolayers of triglycerides are more stable if the three hydrocarbon chains are more equal in length. The difference in compressibility and stability indicates that the shorter hydrophobic chains of the molecules could be partially submerged in the aqueous substrate. The stability of positional isomers such as 18-14-12

and 18-12-14 (Fig. 4 and 5) and 18-12-10 and 18-10-12 (Table II) were about equal with the transformations of state occurring at about the same temperature.

The solid condensed monolayers, which existed at 70 \AA^2 , resemble in certain respects the mesomorphic monolayers of fatty acids and monoglycerides.^{6,14} However, the monolayers are stable in this state only at 70 \AA^2 and within a narrow temperature range, which is just below the complete melting point.⁶ At lower temperatures the monolayers are easily compressed, unstable, and exhibit hysteresis. Hysteresis indicates the presence of states or forms which are not in equilibrium. These properties and the uniformity of the area at 70 \AA^2 are not commensurate with those of fatty acids and monoglycerides, which have an extremely high stability, a relatively low compressibility, low viscosity, and variable limiting areas.⁹ It is interesting to note that the area of 70 \AA^2 corresponds with the theoretical cross-sectional area of 69.9 \AA^2 calculated for liquid crystals of tristearin in a β' -form. The absence of hydroxyl groups could account for the instability and rigidity of the films at this point.

Polymorphic transformation to higher melting forms did not occur in any of the monolayers, which remained fluid above the melting points and expanded to approximately 120 \AA^2 . The excellent agreement between the melting points of the three-dimensional α -forms and the temperatures at which the condensed monolayers expanded to 120 \AA^2 (Table III) is good evidence that the intermolecular forces in the condensed monolayer are similar to those in the α -form. If the temperature was not too far above the melting point, additional pressure condensed the expanded monolayers. An approximate calculation for dT/dP from the Clapeyron equation and an estimated heat of fusion shows that it should be possible to solidify the α -form of a triglyceride several degrees above its melting point (T_m) under a pressure of 20 dyne/cm. Although the curves do not represent a complete set of isothermals, several of them indicate that the temperature range from T_m to T_{cc} (temperature of critical crystallization) is approximately 5° . Above T_{cc} it was impossible to obtain a condensed monolayer and collapse resulted

in a constant pressure, the monolayer being fluid and in equilibrium with an oil lens. The absence of a stable β -form in the monolayers may be ascribed to the fact that this form requires a tuning-fork or chair arrangement of the chains with alternate molecular packing. Intra- and intermolecular packing of this nature would not be expected to occur in monolayers on water.

This investigation supports the generally accepted theory that the α -form is the only stable form in the condensed monolayers of triglycerides and confirms the presence of a second form, which is unstable under pressure and could be related to the β' -form.

The results also lead to the conclusion that the hydrocarbon chains of triglyceride molecules in the α -form are aligned in the same direction. The construction of a molecular model of a saturated triglyceride shows very little mechanical strain for such a structure. It is significant that the β - or β' -forms are always obtained by crystallization from a polar solvent in which the solute molecules have an unlimited degree of freedom with respect to each other. In the case of the pure compounds, rapid crystallization at low temperature of a completely liquid melt almost always produces the α - or β' -forms, whereas gradual cooling, which promotes a slow rate of crystal growth, usually yields the β -form. β -Forming compounds are very prone to supercooling and even though their crystal nuclei persist to some extent in a melt at temperatures slightly above the melting point, rapid cooling of such a melt usually results in a mixture of forms. When a large volume of liquefied tristearin is allowed to cool slowly to room temperature, there is considerable surface and internal eruption, which is visible evidence for inter- and intramolecular rearrangement during crystallization. This phenomenon is not observed in β' or α crystallizations, which as a rule occur with very little supercooling. Apparently the molecular structure of the liquid, α -, and β' -forms differs radically from that of the β -form. In view of these facts, X-ray data, and the results of this investigation it seems quite logical in theory to visualize a tuning-fork or chair structure for the β -form as opposed to coalignment of the chains in the α - and β' -forms.

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The Unstable Species and the Isotope Effect in the Pyrolysis of Diborane in a Shock Tube¹

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The pyrolysis of diborane has been examined using a chemical shock tube as a reactor. Additional evidence for the existence of hexaborane-12 and heptaborane-11 and -13 has been obtained. The presence of a large net normal isotope effect in the formation of tetraborane and hexaborane and a net inverse isotope effect in the formation of pentaborane-9 are observed. A mechanism, consisting of a series of competitive reactions and equilibria in which tetraborane is the precursor of pentaborane-11 and hexaborane but not of pentaborane-9, is shown to be compatible with the observed isotope effect. Data obtained by examining the pyrolysis of various mixtures of boron hydrides are also consistent with the mechanism.

Introduction

It has long been known that the boron hydrides are unstable with respect to heat² and their pyrolysis reactions have been the subject of considerable research in the past. The various studies have been sum-

marized by Morey and Hill³ and Lipscomb⁴ and consequently will not be repeated in detail here. Briefly, however, kinetic studies⁵ and work on the various isotopic exchange reactions⁶ indicate that the initial two steps in the pyrolysis of diborane are the rapid borane equilibrium followed by a rate-determining at-

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