*Synthesis and Physical Properties of Normal Higher Primary Alcohols. IV. Thermal and X-Ray Studies on the Polymorphism of the Alcohols of Even Carbon Numbers from Dodecanol to Tetratriacontanol**

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Since X-ray study on a series of normal paraffins was reported by Müller[1], several investigations have been made on the transition phenomenon of many long-chain compounds including acids[2-5], esters[3,6], bromides[7], and alcohols[8]. In these compounds, phase change is known to occur just below their freezing points accompanying the changes in a number of physical properties such as crystal structure, thermal property, and dipole moment in polar compounds. Recently nuclear magnetic resonance studies were also reported[9]. The α phase, which appears at the high temperature side, has been found to possess molecular freedom, the molecule being assumed to rotate about the long axis because of the characteristics of symmetrical crystal structure and high dielectric constant in this phase.

Although Hoffman et al.[10] recently summarized the results of the several investigations mainly on paraffins and bromides, some problems seemed to remain to be solved. The results on the higher alcohols appearing in the literature seemed to be somewhat ambiguous and the data for the alcohols with odd carbon atoms and with more than eighteen carbon atoms are too scanty to permit generalization of the series. On the other hand, the transition phenomenon has been known to be affected by the presence of extremely small amounts of impurities as well as variations in the technique of measurements and in thermal histories of the materials. Therefore it was felt to be important to examine the phenomenon with a series of pure compounds under conditions as comparable as possible. In view of these facts, the author has undertaken a study of synthesis and physical properties of normal higher alcohols with more than ten carbon atoms in order to establish the existence of transition in each member and its dependency on chain length. The reports on the synthesis have been published[11] and in this paper investigation of thermal analyses and X-ray studies on the alcohols of even carbon atoms from dodecanol to tetratricontanol are reported.

Nomenclature of the Phases.—*α-Form.*—This form obtained on crystallization from the melt is somewhat transparent and on further cooling changes to the more opaque β or γ form at the transition point. X-Ray analysis indicates that the hydrocarbon chain is vertical to the plane of the end groups and the dielectric constant is higher than those of the β or γ or liquid phase. It has also been known that this form is unstable and gradually transforms into a more stable γ form on standing.

β-Form. — This form, in which the hydrocarbon chain is vertical to the plane of the end groups, appears below the transition point mainly in odd members and in shorter members of the even alcohols. In the latter case, gradual transformation from β to γ form is known to exist in some of the members.

γ-Form.—This form, in which the hydrocarbon chain inclines to the plane, appears below the transition point only in even compounds and is stable at low temperature.

The correspondence of the present nomenclature to those adopted by other workers is as follows.

* This study has been carried out at the Department of Physics, Faculty of Science, Kyoto University, as a part of the cooperative research on "Synthesis and Physical Properties of Long Chain Compounds".

1) A. Müller, *Proc. Roy. Soc.*, **A138**, 514 (1932).
2) W. E. Garner and A. M. King, *J. Chem. Soc.*, **1929**, 1849.
3) J. D. Meyer and R. E. Reid, *J. Am. Chem. Soc.*, **55**, 1574 (1933).
4) F. Francis et al., *Proc. Roy. Soc.*, **A128**, 214 (1930); ibid., **A158**, 691 (1937).
5) E. Stenhagen and E. Sydow, *Arkiv. Kemi.*, **6**, 309 (1953).
6) W. O. Baker and C. P. Smyth, *J. Am. Chem. Soc.*, **60**, 1229 (1938).
7) R. W. Crowe and C. P. Smyth, ibid., **72**, 1098 (1950).
8) a) J. W. C. Phyllips and S. Munford., ibid., **55**, 1747 (1933). b) K. Higasi and M. Kubo, *Pap. Inst. Phys. Chem. Res.*, **36**, 286 (1939). c) J. D. Hoffman and C. P. Smyth, *J. Am. Chem. Soc.*, **71**, 431 (1949). d) Y. Kakiuchi and T. Sakurai, *J. Phys. Soc. Japan*, **4**, 365 (1949). e) Y. Kakiuchi, T. Sakurai and T. Suzuki, ibid., **5**, 369 (1950). f) D. G. Kolp and E. S. Lutton, *J. Am. Chem. Soc.*, **73**, 5593 (1951). g) K. Asai, *J. Phys. Soc. Japan*, **14**, 1084 (1959).
9) a) E. R. Andrew, *J. Chem. Phys.*, **18**, 607 (1950). b) S. Kojima and O. Ogawa, *J. Phys. Soc. Japan*, **8**, 283 (1953).
10) J. D. Hoffman and B. F. Decker, *J. Phys. Chem.*, **57**, 520 (1953).
11) A. Watanabe, This Bulletin, **32**, 1295 (1959); A. Watanabe, ibid., **33**, 531 (1960); A. Watanabe, ibid., **34**, 398 (1961).

Present paper	Kolp, Lutton	Smyth et al.
α	Alpha	α
β	Sub-alpha	β_1
γ	Beta	β_2

Experimental

Purity of the Materials.—The alcohols used in this study were all prepared by the lithium aluminum hydride reduction of the corresponding fatty acids or their ethyl esters, the acids above octadecanoic being synthesized from the commercially available lower acids which were initially purified by fractional distillation followed by recrystallization. Since it is difficult to purify the compounds in high purity or to obtain a reliable method to establish their purity when the carbon chain is considerably long, the present efforts were made especially toward the purification of the alcohols above tetracosanol.

As is generally known, elemental analysis data which were presented in previous papers[11], are poor criterions for judging the purity of the compounds with more than about eighteen carbon atoms. It was found, however, in the present study that the transition point rather than the melting point proved to be reliable because repetition of the purification process resulted in the raising or disappearance of the transition points though the melting point did not vary noticeably. Table I gives the melting, freezing and transition points of pure and mixed alcohols.

X-Ray examinations also revealed the interesting facts that the presence of as much as 0.5% of hexadecanol in octadecanol resulted in the apparance of β spacing while only γ spacing was found in octadecanol assumed to be pure. Similar states were found in higher members. Fig. 1 shows this phenomenon clearly.

The purification of the final products were carried out extensively by means of high-vacuum distillation followed by recrystallization until the melting points, transition points and X-ray spacings became constant.

The facts that the melting points and transition points of the alcohols obtained fell on smooth curves (Fig. 8) and the X-ray spacings of the alcohols above hexadecanol gave only γ form, indicate the high purity of the materials.

Time-heating Curves. — The melting points and transition points were determined by thermal analysis. A small drop of the molten substance was put on a junction of thermocouple which is made of copper and constantan of about 0.01 mm. in diameter and it was inserted into a doubly air-jacketed tube placed in a water bath.

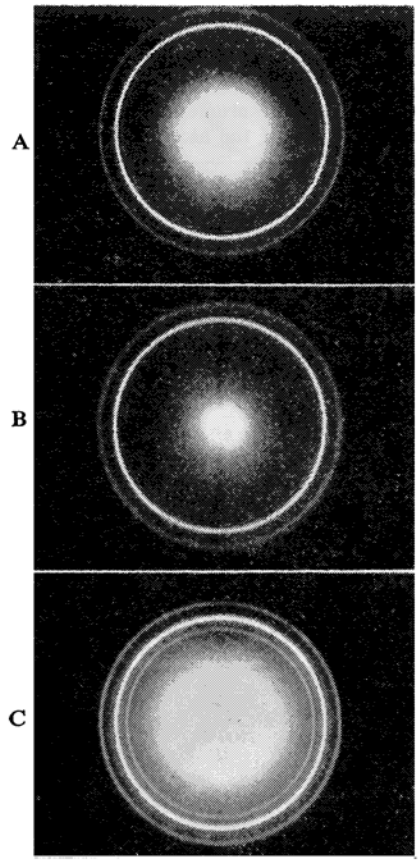

Fig. 1. X-Ray diffraction patterns of pure and mixed alcohols.
A Pure $C_{18}H_{37}OH$
B $C_{18}H_{37}OH$ containing 0.5%$C_{16}H_{33}OH$
C $C_{22}H_{45}OH$ containing 1% $C_{24}H_{49}OH$

Since a higher heating rate was found to be advantageous for good determination of the temperature, the measurements were carried out at the rate of about 2.0°C per minute, readings being taken every 10 sec. Each compound was run at least five times and the reproduciblity of the data was good. Probable errors of the temperatures determined on heating were estimated as being 0.1 to 0.3°C depending on the sharpness of the inflexion points and on the errors on calibration of

Table I. Weight percentage of lower compounds

		0	0.5	1	3	97	99	99.5	100
C_{16}—C_{18}	M.p.	57.3—58.1	57.1—58.0	56.7—57.6	55.7—56.6	48.1—49.7	48.2—49.3	48.1—49.1	48.3—49.3
	F.p.	57.0—56.9	56.8—56.6	56.5—56.4	56.7—56.5	48.0—47.8	48.3—48.1	48.4—48.2	48.4—48.2
	T.p.	51.3—51.1	49.0—48.9	48.6—48.5	47.0—46.7	37.8—37.6	39.2—39.0	40.9—40.8	41.8—41.7
C_{22}—C_{24}	M.p.	74.0—75.0	73.8—75.0	73.8—75.0	73.7—74.6	69.2—69.8	69.5—70.0	69.5—70.1	69.5—70.2
	F.p.	74.3—74.1	74.0—73.8	73.8—73.6	73.6—73.3	69.0—68.8	69.2—69.0	69.8—69.6	69.6—69.4
	T.p.	69.5—69.2	67.9—67.7	66.9—66.6	66.1—65.9	58.6—58.4	60.5—60.2	61.0—60.7	61.7—61.4

The temperature was measured by capillary method and uncorrected.
The heating or cooling speed was 1°C per minute.

the thermocouple, but those of cooling were about 1°C because the high temperature forms tended to supercool before the transitions, as may be seen in Fig. 4.

X-Ray Pattern Measurements.—It is known that the crystal spacings of the alcohols so far investigated here consist of β and or γ modifications in their low temperature forms and α modification in their high temperature form. The three modifications indicate different long spacing depending on different angles of inclination of hydrocarbon chains with respect to the planes of end groups. The most inclined γ form shows the shortest spacing. The short spacing also indicates a greater value in α and β forms because the molecules are more loosely packed in these forms than in the γ form. The data of all the compounds were reported in a previous paper[12] and are represented graphically here (Fig. 2). In the present investigation emphasis was laid on changes of spacings under various conditions especially on the correlations with thermal analyses using the same materials. The X-ray photographs were all taken using Cu-K radiation at 40 KV. and 20 ma. Camera distances and exposure times were varied depending on the chain lengths of the compounds.

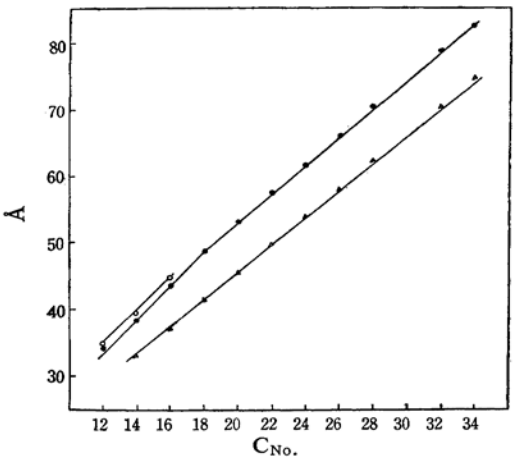

Fig. 2. Long spacings of *n*-higher alcohols.

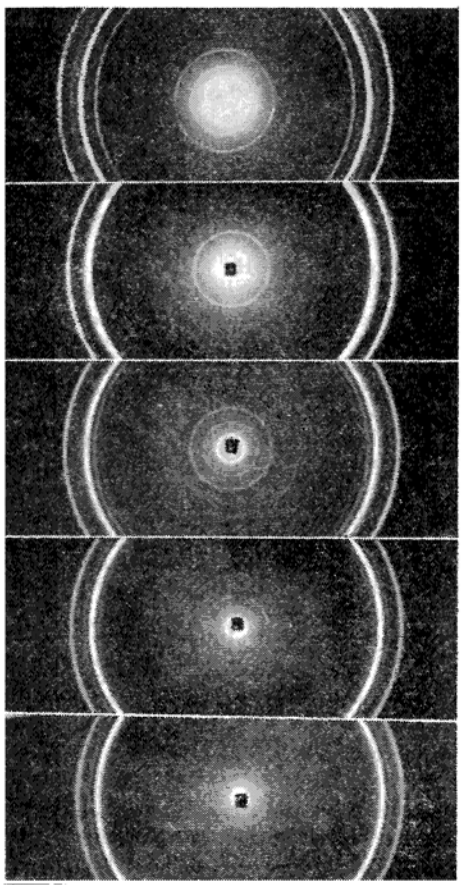

Fig. 3. Representative X-ray diffraction patterns of alcohols. The patterns in discending order are from C_{12}, C_{16}, C_{18}, C_{24}, C_{28} alcohols.

Patterns such as Fig. 3 were taken by the method of sampling as follows. The melted samples were mounted on aluminum rings with about 1.2 mm. diameter and 0.8 mm. width and then solidified in the air. The beam was irradiated perpendicularly to the plane of the sample.

An effective method for the detection of α or β form in γ form was found to be the measurement of the short spacing rather than that of the long spacing. To prepare specimens for these measurements the melted materials were drawn into thin-walled capillary tubes of about 0.2 mm. diameter. The rapidly cooled specimens were obtained by plunging the capillary tube containing the melt into an ice bath. On taking a photograph the capillary tubes were rotated during exposure. An electrically heated brass furnace in which the capillary tube was inserted was used, if necessary. Accuracy of the temperatures measured by means of a copper-constantan thermocouple was within 0.5°C.

Results and Discussion

The transition temperatures on cooling which were obtained by visual observation have been presented in earlier paper[11], but in this method it was experienced to be difficult to

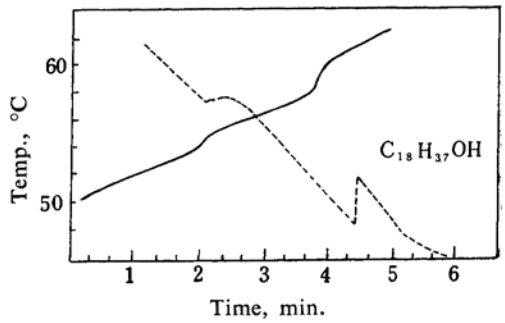

Fig. 4. Time-temperature curves for octadecanol.

12) a) K. Tanaka, T. Seto and T. Hayashida, *Bull. Inst. Chem. Res. Kyoto. Univ.*, 35, 123 (1957). b) K. Tanaka, T. Seto and A. Watanabe and T. Hayashida, ibid., 37, 281 (1959).

identify the transition point on heating. By the present study more reliable and detailed results could be obtained.

Rotational Transition.—Typical thermograms obtained for octadecanol are given in Fig. 4. Phase transitions, which occur at 54.5°C on heating and at 52.5°C on cooling, are shown by the break in the curves, latent heat absorption or evolution being indicated. Evidently the transition is of the first order and reversible. The previous X-ray diffraction patterns[12] and dipole moment measurements[13] indicated that the transition is rotational. For the alcohols from tetradecanol to hexacosanol similar thermograms were obtained as those presented above in contrast with the results of Phillips and other workers[8a,f] who reported the transitions only on cooling in most of these alcohols. However, the present results were very reproducible even when the thermal histories of the samples had been varied and, furthermore, the data were consistent with those obtained by the previous X-ray patterns[12].*.

Although the present thermal studies for tetradecanol and hexadecanol could not reveal three formes, the previous X-ray studies[12] indicated that these compounds are trimorphic in the solid state and the low temperature forms which consisted of β and γ forms, transform them into high temperature form (α) at the different temperatures, the lower temperatures being the β to α transition point; the alcohols above hexadecanol showed the simple γ to α transitions.

The break in the heating curve of hexacosanol was barely detectable and the interval between the melting and transition points is narrow (1.2°C) (Fig. 5). The behaviors of the alcohols above hexacosanol differ markedly from those of the lower members of the series. The curves for octacosanol and dotriacontanol showed that the transitions on heation are missing while those on cooling are still present. However, both transitions were found to disappear at tetratriacontanol. These results are consistent with those by the present X-ray data, according to which in two shorter members (C_{28}, C_{32}) the γ form persisted up to the melting points and in the last member (C_{34}) only the γ form appeared at the temperature just below its freezing point.

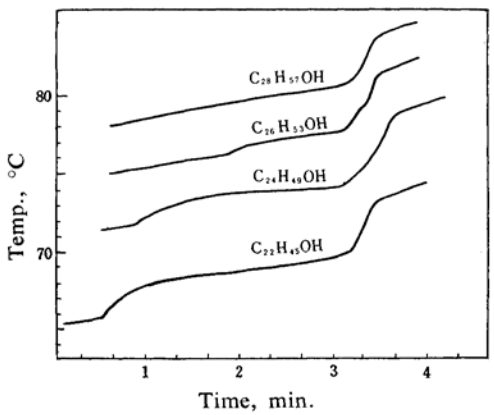

Fig. 5. Time-temperature curves for C_{22}, C_{24}, C_{26}, C_{28} alcohols.

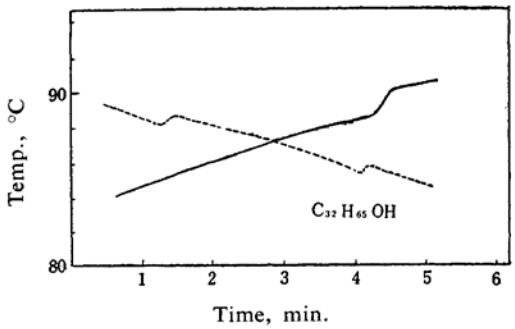

Fig. 6. Time-temperature curves for dotricontanol.

Concerning the existence of transition in dodecanol some disagreements can be found in the literature[8ac,9ab,12a,14-16]. In the present study, non-existence of the transition was verified by the method such as thermal analysis using rapidly or slowly cooling technique, or X-ray pattern measurements made just below the freezing point with an exposure time of 15 min., and dielectric constant measurements

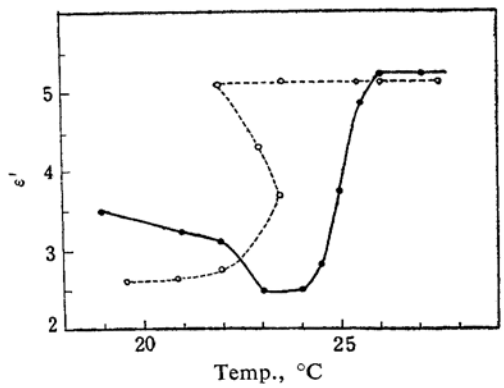

Fig. 7. Temperature dependence of the dielectric constant of dodecanol at 0.5 KC.
● Heating ○ Cooling

13) K. Asai, E. Yoda and S. Yamanaka, *J. Phys. Soc. Japan*, **10**, 634 (1955).

* Some disagreements will be found between the previous and present results. The former must be revised in view of the use of purer materials and more accurate techniques in measurements in the present study.

14) J. D. Bernal, *Nature*, **129**, 870 (1932).
15) E. Ott, *Z. physik. Chem.*, **193**, 218 (1944).
16) E. Frosch, *Ann. Physik*, **42**, 254 (1942).

at 0.5 (Fig. 7) and 5 KC. in which the results agreed with those of Smyth.

In Table II the data obtained by thermal analyses are given together with those obtained from the literature. The corresponding diagram is shown in Fig. 8.

TABLE II

Alcohol	Carbon No.	M. p. °C	Transition points, °C	
			Heating	Cooling
Dodcyl	12	24.0	—	—(21.6)Ph.
Tetradecyl	14	38.0	36.2	33.5(35.0)Ph. (34.4)S.
Hexadecyl	16	49.5	45.7	43.0(45.0)Ph. (43.2)S. (43.8)K.
Octadecyl	18	58.5	54.5	52.5(53.6)Ph. (53.4)S. (54.7)K.
Eicosyl	20	65.0	63.5	58.2
Docosyl	22	70.5	67.6	63.5(64.5)S.
Tetracosyl	24	75.5	72.8	71.5
Hexacosyl	26	79.3	78.1	73.5
Octacosyl	28	82.5	—	77.5
Dotriacontyl	32	88.5	—	86.2
Tetratriacontyl	34	91.0	—	—

Ph.; Phillips and Munford (Thermal analyses).
S.; Smyth et al. (Dielectric measurements).
K.; Kolp and Lutton (Thermal analyses).

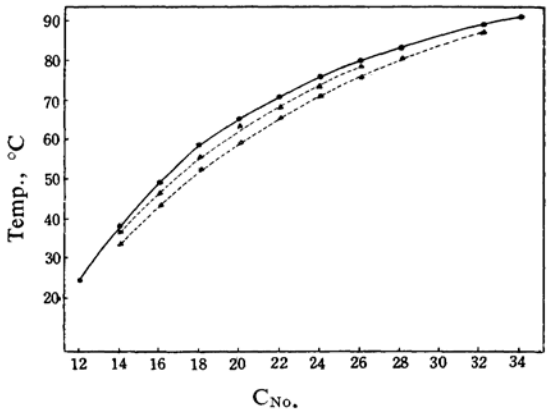

Fig. 8. Melting and transition points of *n*-higher alcohols.
● Melting point
▲ Transition point (heating)
△ Transition point (cooling)

It appears to be interesting that variations in properties of the α forms were observed as the chain length of the compounds increased. In the previous and present studies the following observations have been obtained.

I) Opacities of α forms increase in visual inspections.

II) Inflexions at the transition points become smaller (Fig. 5).

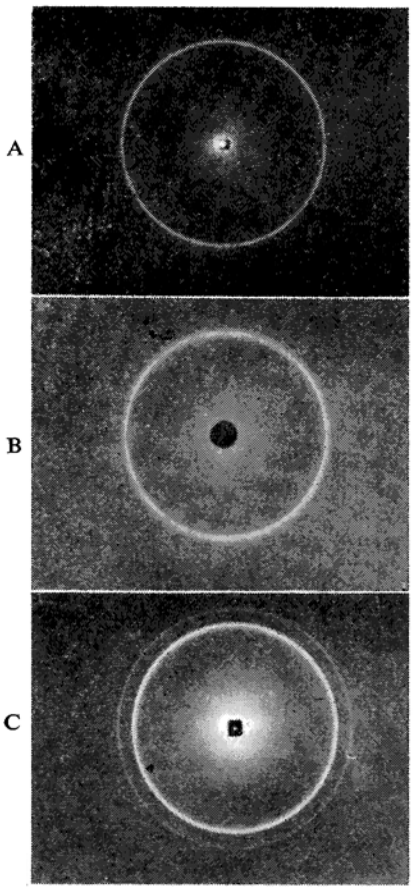

Fig. 9. X-Ray diffraction patterns of the α forms. The photographs were taken after the samples had been standing at the temperatures just below their freezing points for 2 hr.
A $C_{16}H_{33}OH$ C $C_{14}H_{29}OH$
B $C_{26}H_{53}OH$

III) Side spacings of α forms split into two lines (Fig. 9).

IV) In α forms inclination of the hydrocarbon chain to the plane of the ends increases (Fig. 2).

These facts would suggest that deviations in configurations or molecular motions from the typical rotational state may increase as the chain lengthens. Although it is necessary for complete interpretations of the data to await to obtain further data, a possible surmise is that molecular vibration around the axis, rather than rotation, may be caused in such longer compounds.

β to γ Transformation*.—It was reported by Smyth et al.[8c] to explain their result by dielectric constant measurements that in octadecanol and other alcohols rotational transition

* According to Hoffman, the term transformation will be used here to denote phase changes such as β to γ or α to γ which occur spontaneously on storage.

appeared when the sample was heated immediately after it was cooled from the melt while the transition failed to appear on heating the stored sample. Their argument suggests that the β form obtained on cooling may transform into the α form but the transformation of this β form into the γ form which has occurred during the storage, may make it difficult for the transition to take place. The latter X-ray investigation made by Kolp and Lutton[8f] seemed to substantiate this fact although there appeared to remain some doubts in their thermal analysis. As described above, however, the present thermal studies showed that heating transitions invariably appeared in the materials which had been prepared under various conditions such as rapid cooling, slow cooling, or prolonged storage and X-ray data also revealed the existence of γ to α transitions.

Apart from the facts described above, examination with β to γ transformation seemed to be so interesting that more detailed X-ray studies were undertaken. The results of the experiments with tetradecanol and hexadecanol indicated that this transformation took place as evidenced by the increasing intensity of the γ spacings. They appeared to be very gradual, occurring over a wide temperature range. For example, after being kept at 42°C for 24 hr. a sample of hexadecanol showed nearly equal amounts of β and γ forms in their low temperature form which had consisted of about $2/3\beta$ and $1/3\gamma$ forms before the heating. Both compounds indicated no transformation on storage at about 25°C for 24 hr. It was also found that the low temperature forms of these alcohols contained more γ forms when they were cooled slowly from the melt as compared with when they were cooled rapidly. This may be partly due to the β to γ transformations which occurred during the cooling and partly due to the α to γ transformations which will be discussed in the next section.

Because of the absence of the β form in alcohols above hexadecanol, this transformation can not be considered in these compounds. It may be concluded that the β to γ transformation exists only in tetradecanol and hexadecanol but it is so slow as to provide no appreciable effects on rotational transitions in qualitative measurements.

α to γ Transformation.—This transformation, as well as β to γ transformation, was reported by Smyth, Kolp and other workers[8ef]. Recently Asai[13] demonstrated the stability of the α form in octadecanol in his dielectric constant measurements. In the present X-ray investigations the behaviors of α forms in the series were examined by careful control of the temperatures of the samples. It was found that the high temperature form of tetradecanol consists of α and γ forms, the former being the less stable. The data were obtained by holding the compound at the temperature just below its freezing point for about 2 hr., indicating that about 2/3 of the initially existing α form was transformed into the γ form (Fig. 9). In hexadecanol evidence of a smilar behavior was found at the temperature 1°C above its transition point, but at the temperature 1°C below its freezing point the observed spacing indicated only the α form. This α form proved to be stable so that no transformation could be observed within a few hours (Fig. 9). The α forms appearing in the alcohols above hexadecanol showed a considerable stability over the entire region of the temperatures. The relationship described above is illustrated diagrammatically in Fig. 10. It

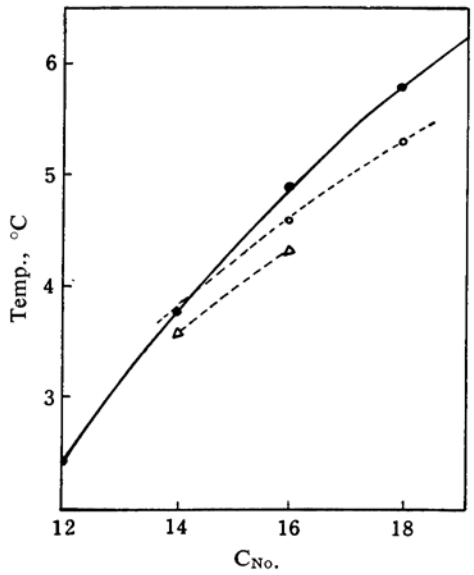

Fig. 10.

● Melting point
○ γ to α transition point
△ β to α transition point

will be apparent that γ to α transition points are higher than β to α transition points and that the α form is unstable only when it coexists with the γ form but once γ to α transformations have taken place the resulting α form is stable.

It is expected that the α form obtained only on cooling may be somewhat unstable. However, the X-ray examinations show that the α form in dotriacontanol is stable at least within about 2 hr.

Summary

1. Determination of the melting points and transition points of the even carbon numbered alcohols from C_{12} to C_{34} was made by thermal analysis. The transition points of the alcohols above C_{18}, except C_{22}, have never been reported.

2. The reversible transition sets in at C_{14} and terminates at C_{26}. The transition of C_{28} and C_{32} is irreversible, appearing only on cooling and both transitions disappear at C_{34}. Probably the pure sample of dodecanol may indicate no transition in any methods of measurements.

3. Properties of the α forms gradually change with increasing chain lengths.

4. The β to γ and α to γ transformations were examined by X-ray pattern measurements and the results were discussed.

5. Transition points and X-ray spacings may be reliable criteria of purity of higher alcohols, and probably of some other long chain compounds.

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