

to an ionic reaction, may take the form

$$k_{\infty} = Z_0 e^{-E_0/RT} \quad (12)$$

Use of k_{∞} and E_0 should be most nearly comparable with a reaction between uncharged gas molecules, if calculation of the collision frequency is to take the simplest form. This frequency, Z_0 , in terms of moles, liters and minutes, is given by

$$Z_0 = \frac{60N}{1000} \sigma^2 \left[\frac{8\pi RT}{\mu} \right]^{1/2} \quad (13)$$

where σ is the average collision diameter and μ is the reduced molecular weight, taken in this case to equal $19 \times 121/140$.

On combining equations (12) and (13) there is obtained

$$\log \sigma = 1/2 \log k_{\infty} - 13.92 + E_0/2730 \quad (14)$$

Table IV gives $\log k_{\infty}$ (equation (5), using $(r_A + r_B) = 1.79 \text{ \AA.}$) and the corresponding values of σ . It is evident that there is reasonable agreement with the collision theory in its simplest form.

TABLE IV

COLLISION DIAMETERS FOR $D = \infty, 25^\circ$		
% Dioxane	$\log k_{\infty}$	$\sigma, \text{ \AA.}$
0	0.65	3.72
10	.63	2.09
20	.65	1.66
30	.64	1.25

Similar calculations were made by Amis and LaMer¹² for the reaction of brom phenol blue and hydroxyl ion, and similar results were obtained.

Summary

The rate of reaction of potassium ethyl xanthate

in dilute acetic acid-sodium acetate buffers has been measured, at five temperatures from 15 to 35°, in dioxane-water mixtures from 0 to 60% dioxane. The effect of added dioxane, or changed dielectric constant, on the over-all reaction, has been shown to be small. Also, in agreement with previous work, the effect of low concentrations of inert salt has been found negligibly small.

The possible mechanism of the reaction has been discussed, and the formation of a critical complex by bimolecular reaction of xanthate and hydrogen ions has been proposed as most probable. Since the ionization constant of acetic acid in dioxane-water mixtures is known, it was possible to calculate the bimolecular rate constants for the postulated rate determining step.

The variation of rate constants with dielectric constant was found to follow the predictions of electrostatic theory (the Christiansen-Scatchard equation) over the range found usable in other cases ($D = 80$ to 50), and reasonable values for the radius of the critical complex or $(r_A + r_B)$ were obtained.

The experimental energy, free energy and entropy of activation have been calculated, and the electrostatic contribution to these quantities has been evaluated. Constancy of the values calculated for $D = \infty$ has been found satisfactory.

It has been shown that reasonably good agreement with the simple collision theory is obtained when rate constants and activation energies extrapolated to $D = \infty$ are used in the calculations.

It is believed that these factors support the suggested reaction mechanism.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Molecular Freedom and Proton Transfer in Solid Long-Chain Amines¹

BY JOHN D. HOFFMAN AND CHARLES P. SMYTH

In the course of investigations of solid long-chain alcohols^{1a} a direct current conductivity effect probably attributable to proton transfer² was found almost uniquely associated with the solid rotator state, often called the " α phase." The term "rotator" was not meant to imply actual dynamic rotation of all the molecules, but merely their possession of sufficient energy of rotational vibration to permit of frequent passage over restricting potential barriers. The effect also appeared to a smaller extent below the transition point. No such phenomenon appeared in long-chain bromides,³ ketones⁴ or esters.⁵ It was

(1) This research was carried out with the support of the Office of Naval Research.

(1a) Hoffman and Smyth, *THIS JOURNAL*, **71**, 431 (1949).

(2) Stearn and Eyring, *J. Chem. Phys.*, **5**, 113 (1937); Bernal and Fowler, *ibid.*, **1**, 515 (1933).

(3) Hoffman and Smyth, to be published.

(4) Müller, *Proc. Roy. Soc. (London)*, **A158**, 403 (1937).

(5) Baker and Smyth, *THIS JOURNAL*, **60**, 122 (1938).

thus thought advisable to look for proton transfer and transitions in the amines. If the molecules rotated about their long axes, direct current proton transfer conductivity giving rise to Maxwell-Wagner polarization would be expected to appear.

Purification of Substances

The samples of *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl and *n*-octadecyl amines obtained from the Paragon Chemical Company were purified by a single vacuum distillation.

TABLE I

Amine	M. p., °C.	F. p., °C.	n_D
<i>n</i> -Octyl	0.0		
<i>n</i> -Dodecyl	27.5	28 ⁶ 28.32 ⁷	1.4377 (30°)
<i>n</i> -Tetradecyl	37.6	37 ⁶ 38.19 ⁷	1.4382 (40°)
<i>n</i> -Hexadecyl	45.6	46.77 ⁷	1.4389 (50°)
<i>n</i> -Octadecyl	52.2	53.06 ⁷	

(6) "International Critical Tables."

(7) Ralston, Hoerr, Pool and Harwood, *J. Org. Chem.*, **9**, 102 (1944).

n-Octylamine, also from Paragon, was distilled at atmospheric pressure, b. p. 179°. Carbon dioxide, which forms the carbamates, was carefully excluded in the distillations and handling. The melting points of the purified compounds are given in the second column of Table I with literature values for comparison. Refractive indices for the D sodium line are given in the last column.

Experimental Results

The experimental method used to make dielectric constant-temperature runs at 0.5, 5.0 and 50 kc. has been described previously.^{1a} In addition to the usual precautions regarding moisture entering the dielectric cell, a tube containing Ascarite was attached to the air vent on the cell to prevent contamination by carbon dioxide. The dielectric constants for the amines studied are given in Table II as a function of temperature. Only the cooling curves are given since the warming curves were very similar. The melting points were higher than the freezing points by 0.2 to 1.3°. The dielectric data are plotted in Figs. 1-5. *n*-Dodecylamine was cooled from 100 to 0° as rapidly as possible in the dielectric cell, and the dielectric constant at 0.5, 5.0 and 50 kc. plotted as a

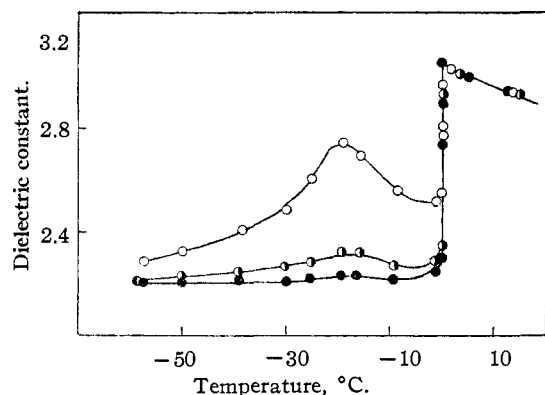


Fig. 1.—Temperature dependence of dielectric constant of *n*-octylamine. Hollow circles represent values at 0.5 kc., half-filled circles values at 5.0 kc., and filled circles values at 50 kc.

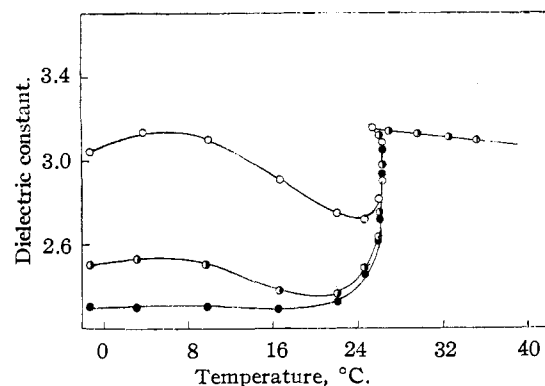


Fig. 2.—Temperature dependence of dielectric constant of *n*-dodecylamine. Hollow circles represent values at 0.5 kc., half-filled circles values at 5.0 kc., and filled circles values at 50 kc.

TABLE II
DIELECTRIC CONSTANTS OF AMINES MEASURED WITH FALLING TEMPERATURE

<i>t</i> , °C.	ϵ'		
	0.5	5 kc.	50
Octylamine			
12.3	3.90	3.90	3.90
2.0	..	4.05	4.05
0.2	4.13
- 0.3	..	3.90	3.90
- 0.4	..	3.55	3.53
- 0.4	..	2.70	2.70
- 0.4	3.10	2.65	2.60
- 1.3	3.05	2.58	2.50
- 8.8	3.12	2.55	2.45
-15.7	3.40	2.63	2.47
-18.7	3.48	2.63	2.47
-26.0	3.20	2.56	2.43
-29.7	2.95	2.52	2.42
-38.7	2.80	2.48	2.42
-49.7	2.63	2.44	2.41
-61.7	2.55	2.41	2.40

Dodecylamine (Cooling)

35.0	..	3.10	..
32.4	..	3.12	..
29.5	..	3.13	..
26.7	..	3.14	..
26.0	..	3.12	..
26.2	..	3.10	3.09
26.3	3.10	2.97	2.94
26.0	2.92	2.74	2.74
25.8	2.82	2.63	2.63
24.5	2.72	2.48	2.47
21.9	2.74	2.36	2.32
16.7	2.91	2.38	2.28
9.6	3.10	2.50	2.30
3.1	3.14	2.53	2.29
- 1.4	3.04	2.50	2.29

Tetradecylamine (Cooling)

39.4	..	2.90	..
36.3	..	2.94	..
36.8	2.78	2.81	2.82
36.9	2.60	2.57	2.54
36.8	2.39	2.41	2.41
36.4	2.32	2.32	2.32
35.4	2.30	2.28	2.28
32.4	2.24	2.24	2.24
28.5	2.23	2.23	2.23

Hexadecylamine (5 kc.) Octadecylamine (5 kc.)

55.2	2.71	58.2	2.64
45.3	2.75	53.2	2.67
45.4	2.53	50.6	2.66
45.3	2.40	51.8	2.60
44.2	2.32	51.8	2.55
42.3	2.29	51.7	2.46
34.4	2.25	51.5	2.40
28.4	2.25	49.8	2.33
19.7	2.24	43.7	2.30
		38.3	2.30
		35.5	2.29
		25.4	2.27

function of time as shown in Fig. 5. No values are given for the loss factor since they were negligibly small except for *n*-octylamine and *n*-dodecylamine in the region below the freezing point where direct current conductance was observed. The omitted curve for *n*-hexadecylamine is similar to those in Figures 3 and 4.

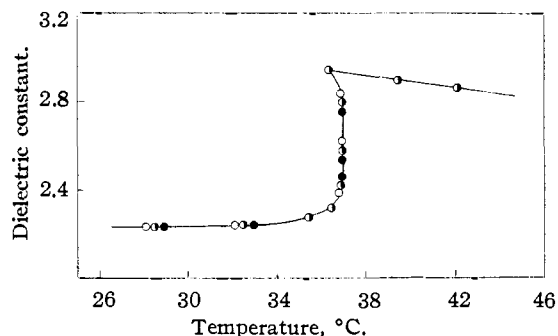


Fig. 3.—Temperature dependence of dielectric constant of *n*-tetradecylamine. Hollow circles represent values at 0.5 kc., half-filled circles values at 5.0 kc., and filled circles values at 50 kc.

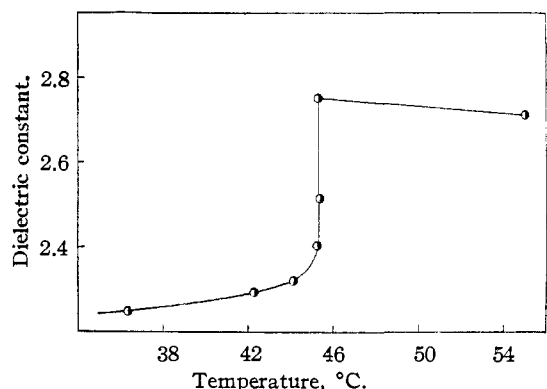


Fig. 4.—Temperature dependence of dielectric constant of *n*-hexadecylamine at 5.0 kc.

Discussion of Results

No transitions in the solid are evident in any of the compounds studied, and all of the materials appear to freeze predominantly into the stable non-rotator form. Thus the large direct current conductivity effect originally sought in this research cannot appear in full force since no α phase producing sheets of rotating $-\text{NH}_2$ groups appears. Proton transfer demands molecular rotation and a convenient path such as a sheet of $-\text{NH}_2$ or $-\text{OH}$ groups.^{1a,2} A small conductivity effect appears in the two shorter amines even though few of the molecules are rotating. The effect is thus analogous to the conductivity observed in *n*-tetradecyl, *n*-octadecyl and *n*-docosyl alcohol below the transition point. The conductance is manifested as Maxwell-Wagner polarization as shown in Figs. 1, 2 and 5. The dispersion should not be confused with anomalous dispersion, since, at low frequency, the dielectric constant exceeds the extrap-

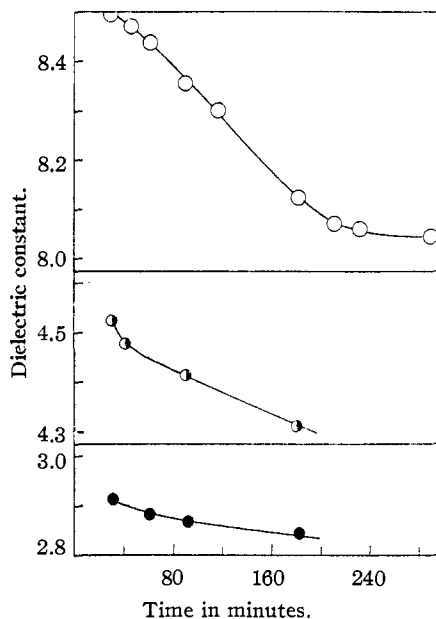


Fig. 5.—Dependence of dielectric constant of *n*-dodecylamine at 0° on time. Sample was cooled rapidly from 100 to 0° . Hollow circles represent values at 0.5 kc., half-filled circles values at 5.0 kc., and filled circles values at 50 kc.

olated liquid value (Fig. 5) and the loss factor, ϵ'' , was observed to exceed $(\epsilon_0 - \epsilon_\infty)/2$, where ϵ_0 is the static dielectric constant and ϵ_∞ , the so-called optical dielectric constant. It is thus clear that, as in the alcohols, the high dielectric constant is not due to orientation polarization. When $\epsilon'' \geq \epsilon'$ and when two phases of different conductivity are present, large dielectric constants exceeding those possible by orientation polarization are commonly observed.^{1a} In *n*-octylamine and *n*-dodecylamine the high conductivity observed for some distance below the freezing point makes $\epsilon'' \geq \epsilon'$, and causes the dielectric constant to be abnormally high, suggesting the possible coexistence of two phases with proton transfer occurring in one of them. In Fig. 5 it is shown that the dielectric constant of *n*-dodecylamine at 0° at low frequency drops with time, just as was found for *n*-octadecyl alcohol. This indicates that a slow change of condition perhaps, a trace of vertical phase transforming to tilted, often called a β_1 - β_2 transition, is taking place, wherein molecules capable of molecular freedom and proton transfer are reorienting into more stable positions in the lattice. It should be emphasized that the combination of proton transfer and Maxwell-Wagner effect greatly magnifies the effect of what is undoubtedly a rather small amount of molecular freedom in the solid state.

The pronounced maximum in the low frequency dielectric constant which occurs at about 20° below the freezing point in *n*-octylamine and *n*-dodecylamine has no analog in the alcohols. The maximum would seem to suggest a second order transition, but this view must be regarded with

caution. It has been shown that the observed dielectric constant due to Maxwell-Wagner effect depends on the ratios of the conductivities of the two phases.^{1a,8} It is much more likely that the ratio of the conductivities of the two phases varies in such a way as to produce a maximum of the type shown in Figs. 1 and 2.

Molecular freedom in the solid state may have several origins. Impurities may cause the formation of small amounts of liquid with corresponding molecular freedom. Premelting⁹ has been attributed by Oldham and Ubbelohde to the effect of a network of cooperative flaws which breaks up a crystal into a mosaic producing a sort of unsharp melting and molecular freedom. The flaws may stem from impurities or thermal fluctuations. Premelting is generally considered to be operative only near the melting point. Another cause of molecular freedom in the solid state is the rotation of a molecule from one equilibrium position to another due to cooperative loosening of the lattice. The term "prerotation" has been used to describe this effect below the transition point.¹⁰ This effect will also occur if no transition point is present. Operationally, prerotation differs from premelting in that it covers a much wider temperature range, and its onset is more gradual. Prerotation will be used henceforth in this paper to describe the occasional rotation or reorientation of molecules in a solid at any temperature, probably due to cooperative loosening of the lattice. Finally, molecular freedom may result in a solid from the presence of a stable or unstable rotator phase, or a substance which contains a portion of such a rotator phase. A rotator phase will yield a liquid-like dielectric constant.

In the present case, impurities and premelting may be ruled out as the cause of the molecular freedom in the lattice 20° below the freezing point in the two shorter amines, so the effect must be due to prerotation or the presence of a small amount of a rotator phase which is unstable. Inasmuch as prerotation is an equilibrium phenomenon, it would appear, in view of the drop in dielectric constant with time observed in *n*-dodecylamine, that the major part of the molecular freedom may be due to the presence of a small amount of unstable rotator phase. The longer amines show a definite decrease of dielectric constant with temperature far below the freezing point with no Maxwell-Wagner effect. This is characteristic of prerotation. The decrease of conductivity in the longer amines may be ascribed, in part, to the fact that fewer dipoles are present per cc. and, in part, to a lower cooling rate used in the measurements.

The amines differ from the corresponding alcohols in that they have no rotational transitions in the solid in the range studied. This may be connected with the fact that hydrogen-bonding in the

amines is weaker than in alcohols or acids. The differing degree of hydrogen-bonding may be seen by comparison of the boiling points of the eight-carbon acid, alcohol and amine. *n*-Octanoic acid boils at 237°, *n*-octyl alcohol at 195°, and *n*-octylamine at 179°. An unassociated long-chain molecule will generally exhibit rotation about the long axis, as manifested by solid transitions, if it is at least eighteen to twenty-four carbon atoms long. Thus, *n*-docosyl bromide and *n*-docosane show monotropic transitions, while *n*-octadecyl bromide and *n*-hexadecane do not. Since hydrogen-bonding will change the effective chain length, we might expect the compounds with the strongest hydrogen-bonding (*e. g.*, acid dimers) to have transitions at shorter formula weight chain length than weakly bonded substances. In accordance with this, acids show transitions when the chain length is eleven carbons,¹¹ and alcohols at thirteen carbons,¹¹ while amines do not show transitions at eighteen or shorter. Thus, the eleven-carbon acid dimer, which has an effective chain length of about twenty-four atoms behaves like a hydrocarbon of that length. It should be pointed out that, in addition to increasing the effective length of a molecule, hydrogen-bonding may stabilize the tilted form, which does not rotate, and thus alter the chain length at which transitions are observed. It is likely that a solid rotator state will be found in amines of twenty-two to twenty-six carbon atoms in length.

The evidence for proton transfer rests mainly on the appearance of direct current conductivity accompanied by strong Maxwell-Wagner polarization below the freezing point in *n*-octylamine and *n*-dodecylamine, and the similarity of this phenomenon to that found below the transition points in the alcohols. The dielectric constant showed time dependence in these materials, which strengthened the correlation with the alcohols. Since molecular rotation is a requirement for proton transfer, some molecular freedom was indicated. It has been pointed out that the failure of any rotational transitions to appear in the amines may be due to the different degree of hydrogen bonding in the amines as compared to the alcohols. Prerotation was observed in the higher members of the series.

Summary

The dielectric constants of *n*-octyl, *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl, and *n*-octadecyl amines have been investigated in the vicinity of the melting point. No solid phase corresponding to all the molecules rotating about their long axes was detected, so that the large apparent direct current conductivity due to proton transfer associated with the rotator state could not be investigated. In *n*-octylamine and *n*-dodecylamine the dielectric data indicated the presence of a small conductivity in the solid state attributable to proton transfer. The dielectric data for the longer mem-

(8) Frosch, *Ann. Physik*, **42**, 254 (1942).

(9) Oldham and Ubbelohde, *Proc. Roy. Soc. (London)*, **A176**, 50 (1940).

(10) Smyth, *Trans. Faraday Soc.*, **42A**, 175 (1946).

(11) Meyer and Reid, *This Journal*, **56**, 1574 (1933).

bers indicate some molecular freedom below the freezing point, but no Maxwell-Wagner polarization due to conductivity was encountered in the cases of the three longer molecules. The dielectric

properties of the alcohols and amines have been compared, and tentative reasons advanced for the absence of the rotator state in the amines.

PRINCETON, NEW JERSEY RECEIVED MARCH 29, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

A Synthesis of Vinylcyclopropane¹

BY ROSS VAN VOLKENBURGH, K. W. GREENLEE, J. M. DERFER AND C. E. BOORD

The hydrocarbon vinylcyclopropane is interesting from both the synthetic and theoretical points of view. In 1922, Demjanov and Dojarenko² prepared it by exhaustive methylation of the amine obtained from the oxime of methyl cyclopropyl ketone, and they stated that this hydrocarbon could not be prepared by the dehydration of methylcyclopropylcarbinol. It has sometimes been assumed that vinylcyclopropane is "incapable of existence."³ Recently there has been speculation concerning the possible utility of the hydrocarbon in the manufacture of synthetic rubber.⁴ In the present work methylcyclopropylcarbinol was successfully dehydrated to vinylcyclopropane, and some of the hydrocarbon's properties were observed.

The methylcyclopropylcarbinol was prepared by reduction of methyl cyclopropyl ketone; four different methods were tried. Catalytic hydrogenation gave the desired carbinol along with a nearly equal amount of the close-boiling 2-pentanol. Reduction by sodium and ammonium sulfate in liquid ammonia gave ring-opening products exclusively. The Meerwein-Ponndorf method gave the desired carbinol in low yield along with large amounts of condensation products. The only method which gave methylcyclopropylcarbinol exclusively and in high yield was reduction with lithium aluminum hydride.

The dehydration of methylcyclopropylcarbinol was accomplished by refluxing it with a catalytic amount of sulfuric acid, giving 39% yield of vinylcyclopropane with 0.8° boiling range (Fig. 1). The dehydration was extremely slow, apparently because of the influence of the cyclopropane ring adjacent to the carbinol group; this may explain

the failure of previous workers to observe it. The structure of the hydrocarbon was proved by an ozonolysis experiment from which both formaldehyde and cyclopropanecarboxaldehyde were identified. The physical properties listed in Table I were determined on a sample of vinylcyclopropane, estimated from a time-temperature freezing curve to be 96 ± 2 mole % pure.

Evidence for conjugation between the double bond and the cyclopropane ring of vinylcyclopropane

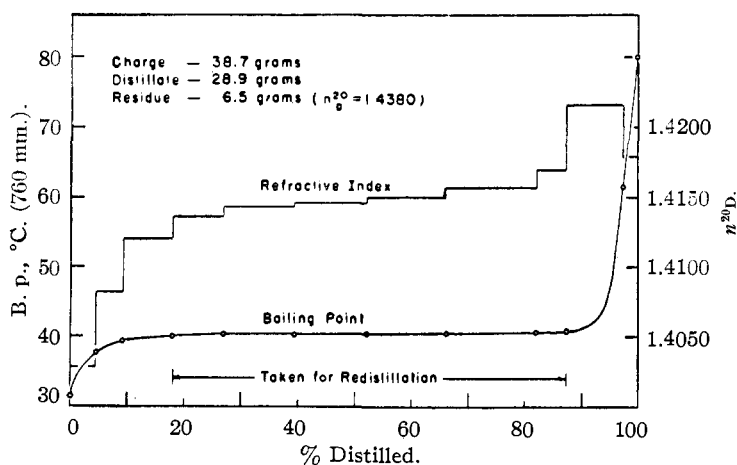


Fig. 1.—Distillation of crude vinylcyclopropane.

pane is seen in the boiling point which is 4.5° higher than that of ethylcyclopropane; by contrast, the double bond produces a 7.8° lowering when the related 2-methylbutane is converted to 3-methyl-1-butene. Similarly, the refractive index of vinylcyclopropane shows an elevation of 0.0264 (at 20°) which approaches the elevation of 0.0332 exhibited by 2-methyl-1,3-butadiene.

TABLE I

	VINYL-CYCLOPROPANE	
	This work	Literature ²
F. p., °C.	-112.6
B. p., °C. (760 mm.)	40.41	40.0 to 40.2 (755 mm.)
<i>d</i> ²⁰ ₄	0.7160	0.723 at 18°
<i>n</i> ²⁰ _D	1.4156	1.4172 at 15°

A small portion of the hydrocarbon was hydrogenated over Raney nickel. The product, insufficient for purification by distillation, was identi-

(1) This paper forms part of the dissertation submitted in 1949 by Ross Van Volkenburgh to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. It was presented before the Organic Division at the 116th meeting of the American Chemical Society. The investigation was sponsored by the American Petroleum Institute Research Project 45 in cooperation with The Ohio State University Research Foundation.

(2) Demjanov and Dojarenko, *Ber.*, **55B**, 2718 (1922).

(3) Whitmore, "Organic Chemistry," D. Van Nostrand Company, Inc., New York, N. Y., 1937, p. 632.

(4) Jones, *Chem. Eng. News*, **27**, No. 7, 454 (1949).