ror in the points near the transition, as indicated by their spread, is not much smaller in magnitude than the change described.

No positive indication of any latent heat of transition in the magnetic field was found. An irregularity in the data in a field of 500 gausses might be attributed to this source, but since it does not appear again at higher fields, the possibility diminishes that it is evidence of a latent heat.

Investigations of tin[4] and thallium[5] bear out the validity of Rutgers' formula for predicting the discontinuity of specific heat of soft superconductors, for which the magnetic field which first penetrates the body of the material also restores the resistance. Studies of metals for which penetration begins at a much lower field than that required to restore resistance have also been made. Mendelssohn and Moore[9] observed that the heat capacity of an alloy of lead and thallium does not show such a large jump as that predicted on the basis of the field needed to restore resistance. Their measurements were not precise enough to indicate whether a smaller discontinuity existed. Shubnikov and Chotkevitch[8] made a similar observation on an alloy of lead and bismuth. Keesom and Desirant[6] observed that the change in heat capacity of tantalum at its transition temperature corresponds to a much lower critical field slope than is indicated by the depression of the temperature of the calorimetrically observed transition in a magnetic field. They found that the calculated $\mathrm{d}H/\mathrm{d}T$ corresponds nearly to the threshold field which first penetrates the specimen, while the temperature of the anomaly is more nearly that at which resistance is restored by a given magnetic field.

The powdered columbium nitride used in these measurements has a behavior similar to tantalum in that the lowering of the transition temperature in magnetic field cannot be predicted from the magnitude of the anomaly. Unfortunately, the strength of magnetic field necessary to penetrate CbN has not been measured as a function of temperature, so that it is not possible to compare the slope of this function with that calculated from the calorimetric data by Rutgers' equation.

Because of the resemblance of the thermal properties of CbN to those of alloys and of tantalum, the possibility was considered that some hysteresis phenomenon might cause a difference in the heat capacity observed when the sample is cooled through the transition in the presence of a magnetic field from that observed when the field is applied only below the transition temperature. The data of July 9 were taken with this in mind. No difference is observable in the heat capacity measurements using the different procedure.

In view of the lack of data on the penetration of columbium nitride and the restoration of its resistance by magnetic fields, it is not possible to say whether this compound may behave in other ways like a hard superconductor or an alloy. In any attempt to account for its observed behavior it is reasonable to question whether this behavior is due to the lack of stoichiometric proportions in the sample of the compound used here, or to the small size and irregular shape of the particles, or whether the observed behavior is characteristic of the pure compound in bulk.

Summary

The heat capacity of columbium nitride has been determined in the temperature range from 11 to 21°K. An anomaly of 0.023 cal. mole^{-1} occurs at 15°K., and may be associated with the transition to superconductivity. The effect of magnetic fields of 250, 500, 750 and 1000 gausses is very small both on the magnitude of the heat capacity and the change in temperature of the anomaly. No latent heat of transition was observed.

NEW HAVEN, CONN. RECEIVED MARCH 8, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

Kinetics of the Decomposition of Ethyl Xanthic Acid

BY ALFRED CHATENEVER AND CECIL V. KING

The rate of decomposition of various xanthic acids was first studied in detail by V. Halban and Kirsch,[1] who tried to correlate the rates with dielectric constant and other properties of the solvents used. Later V. Halban and Hecht[2] studied the decomposition rates of potassium methyl and ethyl xanthates in aqueous hydrochloric acid at 0°. They found that these xanthic acids are not fully ionized, and assumed the reaction to be a unimolecular decomposition of the undissociated acid, though recognizing this to be kinetically identical with a bimolecular reaction between hydrogen and xanthate ions.

The decomposition of ethyl xanthic acid in dilute aqueous buffers has been studied by King and Dublon.[3] It was shown that there is little or no salt effect on the rate in acetic acid–sodium acetate buffers of low ionic strength, since primary and secondary effects cancel; in aniline–anilinium ion buffers, on the other hand, there is a large primary salt effect.

The rate of decomposition of various xanthic acids in non-aqueous solvents has been studied in

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(1) V. Halban and Kirsch, *Z. physik. Chem.*, **82**, 325 (1913).

(2) V. Halban and Hecht, *Z. Elektrochem.*, **24**, 65 (1918).

(3) King and Dublon, THIS JOURNAL, **54**, 2177 (1932).

this Laboratory by F. M. Lewis.[4] Free ethyl xanthic acid is quite stable in anhydrous benzene, and the catalytic effect of added substances is roughly proportional to their strength as bases.

In the present work the decomposition rate was studied with potassium ethyl xanthate in dilute acetic acid–sodium acetate buffers, with added dioxane from 0 to 60% by volume, at temperatures from 15 to 35°. The purpose of the work was to obtain the energy and other thermodynamic quantities of activation, to attempt to learn more about the mechanism of the reaction, and to test the applicability of the theories dealing with electrostatic effects on ionic reaction rates.

Experimental

In all the experiments reported here small weighed samples of solid potassium ethyl xanthate were dissolved in 60 ml. of solution containing 0.0848 *M* acetic acid and 0.0106 *M* sodium acetate. Rates were measured by following the evolution of carbon disulfide in an apparatus similar to that used previously.[3] Ground caps with mercury seals and no lubrication were used on the flasks, and a solenoid release mechanism served to drop glass capsules containing the xanthate. Measurements were made at 15, 20, 25, 30 and 35°, and the thermostat temperature was maintained constant to ±0.02°. The thermometer used was compared, at each temperature, with one calibrated at the Bureau of Standards.

Potassium ethyl xanthate was prepared by recrystallizing a commercial sample from alcohol until an aqueous solution of the dried salt was neutral to litmus. A sample synthesized in the laboratory gave identical rates.

Acetic Acid.—Sodium acetate buffers were made by partial neutralization of an appropriate solution of the acid with carbonate-free sodium hydroxide (standardized with potassium acid phthalate). The mixture was then diluted to volume with water or dioxane and water.

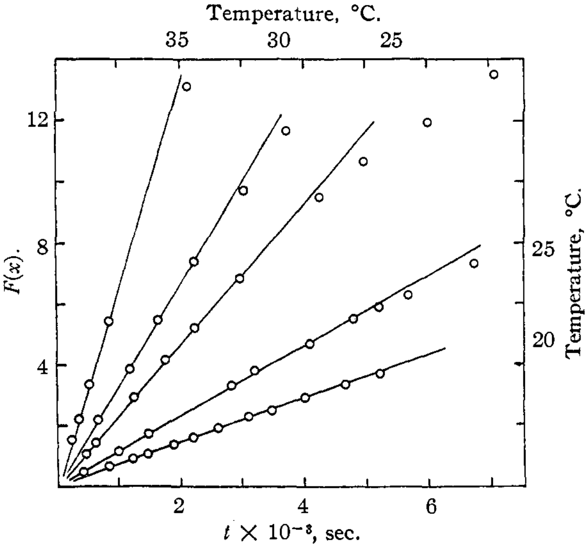
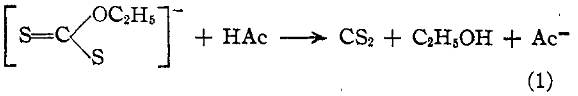


Fig. 1.—Time *vs.* $F(x) = (a + c) \log a/a - x - (b + c) \log b/b - x$; solvent 30% dioxane by volume.

Dioxane (**dioxane-1,4**) was purified by refluxing a commercial product with sodium until a fresh surface of the metal remained untarnished for several hours; a portion was then distilled just prior to use. The boiling point was 101.2°, in agreement with the data of Kraus and Vingee.[5] Some determinations were made using dioxane prepared by the more exacting method of Harned and Morrison,[6] with no appreciable difference in rate. Solutions were made with 10, 20, 30, 40, 50 and 60 ml. of dioxane per 100 ml. of solution, and weight per cent. values were obtained by interpolation using densities in the literature.[7]

Specific Rate Constants.—In acetic acid buffers the over-all reaction is essentially



$$\left[S{=}C\begin{matrix}OC_2H_5\\ S\end{matrix}\right]^- + HAc \longrightarrow CS_2 + C_2H_5OH + Ac^- \quad (1)$$

and the rate equation derived previously[3] may be written

$$k(\text{expt.}) = kK_0 = \frac{2.3}{(b - a)t}\left[(a + c) \log \frac{a}{a - x} - (b + c) \log \frac{b}{b - x}\right] \quad (2)$$

In this equation *a*, *b* and *c* are the initial molar concentrations of xanthate ion, acetic acid and acetate ion, respectively; $a - x$ and $b - x$ are values at the time *t* (in minutes), and the value of K_0 depends on the mechanism of the reaction (see below). The quantity in brackets (called $F(x)$ in Fig. 1) was plotted *vs.* time for each experiment and *k*(expt.) was evaluated from the slope. Typical plots are shown in Fig. 1, and while it is seen that there is some deviation as the reaction progresses, the linear relation is satisfactory over about 70% of the reaction.

Up to 30% dioxane the precision of *k*(expt.) is about ±3%. At higher dioxane concentrations the solubility of carbon disulfide increases, the pressure rise in each experiment becomes less, and the possible error in *k* becomes as high as ±10% in 60% dioxane. The concentration of potassium xanthate varied from one experiment to another, averaging about 0.009 *M*. Limitations of the apparatus made it difficult to use higher concentrations in order to increase the pressure rise in the apparatus.

The rate constants are summarized in Table I, each value being the average from two or more experiments. The dielectric constants *D* were interpolated from large plots of the data of Åkerlöf and Short.[8] The columns headed K_0 and *k* will be referred to later.

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(4) Lewis, Dissertation, New York University, 1947.

(5) Kraus and Vingee, THIS JOURNAL, **56**, 511 (1934).

(6) Harned and Morrison, *Am. J. Sci.*, **33**, 161 (1937).

(7) Hovorka, Schaefer and Dreisbach, THIS JOURNAL, **58**, 2264 (1936); Harned and Calmon, *ibid.*, **60**, 334 (1938).

(8) Åkerlöf and Short, *ibid.*, **58**, 1241 (1936).

Several experiments were carried out with the addition of 0.025 *M* and 0.05 *M* sodium chloride to the solutions. Only at the highest dioxane concentrations was the effect on the rate greater than 3%, and it may be concluded that the constants given in Table I are essentially valid for zero ionic strength.

TABLE I

THE RATE CONSTANTS IN DIOXANE-WATER MIXTURES

t, °C.	Volume % dioxane	D	k (expt.) × 10^3 min.$^{-1}$	log $K_0 + 8$	log k
15.00	0	82.3	1.39	3.24	1.90[a]
	10	73.0	1.33	2.99	2.13
	20	63.7	1.29	2.70	2.41
	30	54.5	1.34	2.35	2.77
	40	45.5	1.37	1.95	3.19
	50	36.4	1.23	1.42	3.74
	60	27.7	1.14	0.73	4.33
20.00	0	80.4	2.29	3.24	2.12
	10	71.2	2.24	3.00	2.35
	20	62.1	2.31	2.70	2.66
	30	53.0	2.22	2.36	2.99
25.00	0	78.6	4.17	3.24	2.38
	10	69.5	4.17	3.00	2.62
	20	60.5	4.04	2.70	2.90
	30	51.7	4.31	2.36	3.27
	40	42.9	4.56	1.95	3.71
	50	34.4	4.56	1.42	4.24
	60	26.2	3.80	0.72	4.86
30.00	0	76.7	6.59	3.24	2.58
	10	67.7	6.25	2.99	2.80
	20	58.9	6.33	2.70	3.10
	30	60.3	6.61	2.36	3.46
35.00	0	74.9	10.9	3.24	2.80
	10	66.1	11.5	2.98	3.08
	20	57.5	12.4	2.69	3.40
	30	49.0	12.4	2.35	3.75
	40	40.6	11.5	1.93	4.13
	50	32.5	12.1	1.40	4.69
	60	24.7	11.2	0.69	5.36

[a] k in (moles/liter)$^{-1}$ (min.).$^{-1}$

Analysis of Results.—As seen in Table I, the addition of dioxane, changing the dielectric constant as much as from 82 to 28, has very little effect on the observed rate or on values of k (expt.). While the variation at each temperature is outside the precision of individual experiments, it is probably within the over-all experimental error, at least to 50% dioxane. The small effect of changing the solvent is not unexpected if activity coefficients involved in the rate expression cancel, although the dielectric constant effect on a reaction between an ion and a neutral molecule is probably usually somewhat greater.

Average values of k(expt.) at each temperature, up to 40% dioxane, may be expressed with a maximum deviation of about 5% by the equation

$$\log k(\text{expt.}) = 11.56 - 19{,}050/2.3RT \qquad (3)$$

where 11.56 is the Arrhenius frequency factor and 19,050 cal. is the activation energy.

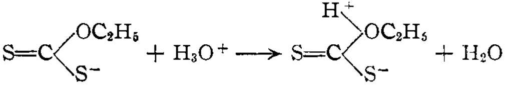
Mechanism of Reaction.—While the stoichiometric reaction is closely approximated by equation (1), it is evident that the rate-determining step is not between xanthate ion and molecular acetic acid, which would not be in accord with the rate equation (2). As postulated by V. Halban, the reaction could be a unimolecular decomposition of undissociated xanthic acid or a bimolecular reaction with hydrogen ion. In the first case K_0 of equation (2) would be the equilibrium constant of the reaction

$$X^- + HAc \rightleftarrows HX + Ac^-$$

where X^- indicates the xanthate ion; then $K_0 = K_{HAc}/K_{HX}$, the ratio of the two ionization constants.

This mechanism does not appear plausible for two reasons: since molecular xanthic acid is stable in aprotic solvents, there is no reason why it should decompose spontaneously in water; such decomposition would have to be pseudo-unimolecular, actually reaction with some basic component of the solution, as water or acetate ion, and this has not been detected.

The rate-determining step must then be a bimolecular reaction with hydrogen ion, but this could not be the rapid equilibrium reaction which maintains a very small concentration of undissociated xanthic acid. It is probably an attack on the oxygen bridge in the xanthate molecule, as suggested by Lewis[4]


(4)

critical complex

In this case K_0 in equation (2) is the ionization constant of acetic acid, at zero ionic strength in each solvent and at each temperature; and k is the constant for the bimolecular, rate-determining step.

Evaluation and Analysis of the Rate Constant *k*.—Since accurate values of K_0 for the ionization of acetic acid in the solutions used are available, it is possible to evaluate $k = k(\text{expt.})/K_0$ on the assumption that the mechanism is correct. The ionization constant of acetic acid has been measured in dioxane–water mixtures over a wide temperature range by Harned and Kazanjian,[9] and Harned and Fallon[10] have shown that accurate interpolation is possible. Values of log K_0 and log k are given in Table I for each experimental condition.

The rate constants for a reaction between two ions are related with dielectric constant, ionic strength and size of the interacting ions by the Christiansen–Scatchard equation.[11] In the absence of salt effects this equation becomes

$$\log k = \log k_\infty - \frac{Z_A Z_B \epsilon^2 N}{2.3DRT}\frac{1}{r_A + r_B} \qquad (5)$$

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[9] Harned and Kazanjian, THIS JOURNAL, **58**, 1912 (1936).

[10] Harned and Fallon, *ibid.*, **61**, 2377 (1939).

[11] Scatchard, *ibid.*, **52**, 52 (1930); *Chem. Revs.*, **10**, 229 (1932).

In this expression k_∞ refers to the rate constant extrapolated to infinite dielectric constant ($D = \infty$), where coulombic forces between ions should vanish. A plot of log k *vs.* $1/D$ at constant temperature should give a straight line from whose slope the sum of the radii of the interacting ions ($r_A + r_B$), or the radius of the critical complex, may be calculated. Figure 2 gives such a plot for the five temperatures used. Values of ($r_A + r_B$) obtained from the slopes of the linear portions of these curves vary between 1.77 and 1.81 Å., with an average of 1.79 Å. Points at lower dielectric constants deviate from the linear relation, as has often been found in similar cases.[12,13,14]

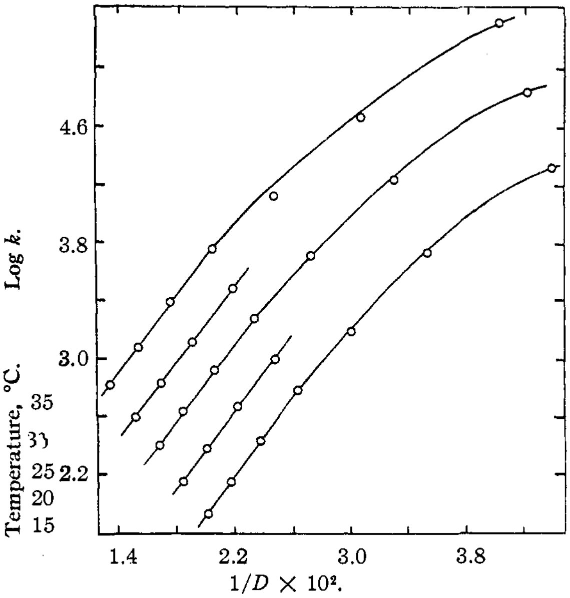

Fig. 2.—Log k *vs.* reciprocal of dielectric constant. Subtract 0.02 from abscissa values for 30°, 0.04 for 25°, etc.

The Arrhenius frequency factor (log A) and activation energy (E) were calculated by the method of least squares and are given in Table II. The equations implied fit the data of Table I with a maximum deviation of 0.05 log unit and an average deviation of <0.02 log unit. The "maximum error" of E is then about ±400 calories, the "probable error" about ±250 cal. There is no indication of variation of E with temperature over this short range.

TABLE II

EXPERIMENTAL ENERGY, FREE ENERGY AND ENTROPY OF ACTIVATION

Dioxane, %	log A	E	ΔF^*, 25°	ΔS^*, 25°
0	15.83	18380	16640	3.76
10	16.60	19100	16310	7.28
20	17.31	19670	15930	10.56
30	17.73	19750	15420	12.45
40	17.72	19150	14820	12.41
50	17.08	17530	14100	9.48
60	20.22	20960	13250	23.86

The free energy and entropy of activation were calculated using the equations[15]

$$\Delta F^* = 2.3RT\ (\log RT/Nh - \log k) \qquad (6)$$

$$\Delta S^* = 2.3R\ (\log A - \log eRT/Nh) \qquad (7)$$

These values are given in Table II.[16] Since log A, E, ΔF^* and ΔS^* vary considerably with dielectric constant, they cannot be compared directly with similar quantities for a reaction in an ideal (gaseous) state. It was suggested by Svirbely and Warner[17] that rate constants obtained in mixed, iso-dielectric media (as temperature is varied), would be more nearly comparable to rate constants for ideal gas reactions. While this method frees ΔS^* from electrostatic effects, it still leaves log A, E and ΔF^* as variables with dielectric constant.

Probably a more satisfactory treatment is to calculate log k_∞, E_0, ΔF_0^* and ΔS_0^*, values of these quantities at infinite dielectric constant. Following the suggestion of LaMer,[18] equation (5) may be written as

$$\Delta F^* = \Delta F_0^* + \Delta F_D^* \qquad (8)$$

Analogous equations for energy and entropy are $E = E_0 - E_D$ and $\Delta S^* = \Delta S_0^* - \Delta S_D^*$. The dielectric contributions are given by

$$\Delta F_D^* = \frac{Z_A Z_B \epsilon^2 N}{D(r_A + r_B)} \qquad (9)$$

$$E_D = \Delta F_D^* + T\ \Delta S_D^* + RT \qquad (10)$$

$$\Delta S_D^* = \frac{\Delta F_D^*}{D} \cdot \frac{\partial D}{\partial T} \qquad (11)$$

The values of E_0, ΔF_0^* and ΔS_0^* should be independent of solution composition in the range of validity of equation (5), and ΔS_0^* should be the same as ΔS^* obtained from isodielectric media.

These quantities are given in Table III up to 30% dioxane, and are seen to be constant within the experimental error. The calculation is useless when $D < 50$, since equation (5) is not valid, as shown by Fig. 2.

TABLE III

ACTIVATION ENERGY AND ENTROPY AT $D = \infty$, 25°

% Dioxane	ΔF_0^*	E_0	ΔS_0^*
0	19000	16840	−7.4
10	18970	17180	−6.1
20	19000	17310	−5.7
30	19010	17000	−7.0

Comparison with the Collision Theory.—The fundamental collision theory equation, applied

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[12] Amis and LaMer, THIS JOURNAL, **61**, 905 (1939).

[13] Davis and LaMer, *J. Chem. Phys.*, **10**, 585 (1942).

[14] King and Josephs, THIS JOURNAL, **66**, 767 (1944).

[15] Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 195–199.

[16] The Arrhenius or experimental energy of activation is designated as E and differs by RT from the internal energy of activation ΔE^*.

[17] Svirbely and Warner, THIS JOURNAL, **57**, 1883 (1935); Warner, *Ann. N. Y. Acad. Sci.*, **39**, 345 (1940).

[18] LaMer, *J. Franklin Inst.*, **225**, 709 (1938).

to an ionic reaction, may take the form

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

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

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

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

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

$$\log \sigma = {}^1/_2 \log k_\infty - 13.92 + E_0/2730 \qquad (14)$$

Table IV gives log k_∞ (equation (5), using $(r_A + r_B) = 1.79$ Å.) 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°

% Dioxane	log k_∞	σ, Å.
0	0.65	3.72
10	.63	2.09
20	.65	1.66
30	.64	1.25

Similar calculations were made by Amis and LaMer[12] 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.

NEW YORK, N. Y. RECEIVED JUNE 11, 1949

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Molecular Freedom and Proton Transfer in Solid Long-Chain Amines[1]

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 transfer[2] 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] ketones[4] or esters.[5] It was 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
n-Octyl	0.0		
n-Dodecyl	27.5	28[6] 28.32[7]	1.4377 (30°)
n-Tetradecyl	37.6	37[6] 38.19[7]	1.4382 (40°)
n-Hexadecyl	45.6	46.77[7]	1.4389 (50°)
n-Octadecyl	52.2	53.06[7]	

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[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).

[6] "International Critical Tables."

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