product was taken up in benzene, and the benzene evaporated. Distillation of the residue gave a first fraction which was discarded and a second fraction, b. p. 132–150° (0.4 mm.) weighing 11.13 g. This oil was heated with 1.00 g. of palladium-on-charcoal catalyst[27] at 320–360° for two hours during which time 1513 cc. (N. T. P.) of hydrogen (67.5%) was evolved. The material was distilled, and the distillate dissolved in petroleum ether and chromatographed on alumina. The least strongly adsorbed material was discarded (small amount of naphthalene), and the balance of the product with the exception of some very strongly absorbed material recovered. Crystallization from methanol gave 2.80 g. of colorless crystals, m. p. 44.7–46.6°. The pure sample used for ultraviolet absorption spectrum measurements had m. p. 45.7–48.0°.

Anal.[28] Calcd. for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.5; H, 6.6.

2-*o*-Tolylnaphthalene did not form complexes with picric acid or 2,4,7-trinitrofluorenone[29] when solutions of the two components were mixed in the usual manner. A concentrated solution of the hydrocarbon and *s*-trinitrobenzene in alcohol gave a first crop of *s*-trinitrobenzene. The mother liquor precipitated bright yellow crystals, m. p. 101.2–102.5°, which were shown by analysis to contain one mole of the hydrocarbon to two moles of the nitro compound.

Anal.[29] Calcd. for $C_{29}H_{20}N_6O_{12}$: N, 13.04. Found: N, 13.1.

Acknowledgments.—The authors wish to acknowledge the helpful suggestions of Drs. J. J. McGovern and E. Solomon and the loan of the former's instrument for checking purposes. Thanks are due Lois Pierce and Ruth Borgman, who determined the spectra.

Summary

Steric hindrance effects are discussed in connection with the spectra of 1,1′-, 1,2′- and 2,2′-dinaphthyl, 1- and 2-phenylnaphthalene, diphenyl and various derivatives of some of these compounds. Short wave length peaks are detected in the region 205 to 212 mμ for compounds containing two aromatic ring systems conjugated without steric hindrance. These bands and the longer wave length bands appear to converge toward each other when the coplanarity of the systems is hindered by introduction of interfering groups.

All spectra were determined to 206 mμ on a Beckman spectrophotometer; two spectra were measured to 202 mμ. The simple methods for attaining this limit, as well as increased resolution, are described.

PITTSBURGH, PENNSYLVANIA RECEIVED MAY 29, 1947

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(28) Microanalysis by Arlington Laboratories, Fairfax, Virginia.

(29) Orchin and Woolfolk, THIS JOURNAL, **68**, 1727 (1946).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Kinetics of Neutralization of Nitroethane with Ammonia and Methylamines

BY RALPH G. PEARSON

The rates of neutralization of the simple nitroparaffins with hydroxyl ion and other charged bases have been measured by several investigators.[1] The reaction is a slow process conveniently

$$R_1R_2CHNO_2 + B^- \longrightarrow R_1R_2CNO_2^- + BH \quad (1)$$

measured at 0° in water solution. This paper reports the rates of neutralization of nitroethane with ammonia, methyl-, dimethyl- and trimethylamine in aqueous solution at 0 and 5.2°. The reactions were followed by the change in conductance as the ions were formed

$$CH_3CH_2NO_2 + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} CH_3CHNO_2^- + BH^+ \quad (2)$$

where B stands for the neutral base and BH$^+$ for the conjugate acid.

The work was undertaken both to obtain fundamental data on the kinetics of ionization of neutral molecules in a solvent of high dielectric constant and to see how the rates for the various amines correlate with their base strengths. The increased basicity of methylamine and dimethylamine compared with ammonia and the sharp decrease in base strength for trimethylamine have been the subject of several papers.[2]

Experimental

Preparation of Materials.—Commerical Solvents nitroethane was dried with magnesium sulfate, refluxed with urea, dried with phosphorus pentoxide and fractionated through a 10-plate column. Small middle portions boiling within a 0.1° range were taken for use. The organic amines were obtained from Eastman Kodak Co. white label hydrochlorides or amines converted to hydrochlorides. The salts were recrystallized from water and the amines freed by adding measured amounts of sodium hydroxide and distilling in all glass carbon dioxide-free apparatus into conductivity water. For methylamine and dimethylamine, one-third of the amount of sodium hydroxide needed was added and the distillate discarded, another one-third of sodium hydroxide was added and the distillate collected. For trimethylamine the distillate from the first one-third equivalent of sodium hydroxide was collected. Ammonia was obtained by distilling C. P. ammonia into conductivity water. Solutions were made up 0.05 to 0.10 molar as determined by titration and stored in a carbon dioxide-free apparatus connected to a buret. Solutions of nitroethane were made up by direct weighing, adding conductivity water and storing in a cold room until used.

Apparatus.—Conductances were measured with a modified Jones–Josephs bridge[3] using an oscilloscope for a null point indicator. This combination of direct reading

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(1) (a) Pedersen, *Kgl. Danske Videnskab. Selskab., Math-fys. Medd.*, **12**, No. 1 (1932); (b) Junell, Dissertation, Upsala, 1935; (c) Maron and La Mer, THIS JOURNAL, **60**, 2588 (1938).

(2) (a) Wynne-Jones and Everett, *Proc. Roy. Soc.* (*London*), **A177**, 499 (1941); (b) Brown, THIS JOURNAL, **67**, 374, 378 (1945).

(3) Dike, *Rev. Sci. Inst.*, **2**, 379 (1931).

bridge and rapid visual indicator greatly simplified the following of the resistance with time. A Washburn type cell for medium conductivities was used. Time was followed with a calibrated stop watch. Temperature control was obtained by using ice-water mixtures in a large Dewar flask at 0° and a solid-liquid benzene slush at 5°. With manual stirring temperature could be maintained constant to ± 0.02° during a run using the benzene freezing mixture. Low humidity, however, was essential for good results.

General Procedure.—The quantity of base needed to react with 10 cc. of nitroethane was run into a flask, stoppered and cooled to the reaction temperature. The separately cooled nitroethane solution was added with a pipet and the stop watch started during the course of the addition. After mixing, a sample was drawn into the conductance cell, placed in the bath and vigorously stirred for two or three minutes before readings were begun. The times required for sufficient readings ran from fifteen minutes to an hour. The cell contents and bath were placed in a cold room for a day or two and the equilibrium value of the resistance read after bringing back to the reaction temperature. Wrapping the entire system in aluminum foil greatly aided in preserving the benzene-bath.

Calculations.—The kinetics are complicated by the simultaneous reactions of nitroethane with the amine and hydroxyl ion and by the reversal of reaction (2).

$$CH_3CH_2NO_2 + OH^- \xrightarrow{k_3} CH_3CHNO_2^- + H_2O \quad (3)$$

However, the rate constant, k_3, for hydroxyl ion is known.[1c] Also we have sufficient data on the acid ionization constant of $C_2H_5NO_2$,[4] and the basic ionization constants of the amines[2a,5] to get the equilibrium constant for (2). We have

$$K_1 = \frac{k_1}{k_2} = \frac{K_aK_b}{K_w} \quad (4)$$

Since K_a for $C_2H_5NO_2$ is 2.67×10^{-9} at 0°, K_w for water is 1.14×10^{-15} at 0°,[6] and K_b for the amines runs from 10^{-5} to 5×10^{-4} we see that $k_1 > k_2$ by a factor of 30 to 1000 and that we can neglect the reverse reaction provided we do not carry the measurements too far.

The rate expression then becomes

$$d[C_2H_4NO_2^-]/dt = k_1[C_2H_5NO_2][B] + k_3[C_2H_5NO_2][OH^-] \quad (5)$$

Now if we assume that the equilibrium

$$B + H_2O \rightleftharpoons BH^+ + OH^- \quad (6)$$

is always maintained, we can write

$$[OH^-] = K_b[B]/[BH^+] \quad (7)$$

where we now substitute for the activities the molar concentrations and use the thermodynamic equilibrium constant as we shall do throughout. The rate expression then becomes

$$\frac{dx}{dt} = k_1(a - x)^2 + k_3K_b\frac{(a - x)^2}{x} \quad (8)$$

where $x = [C_2H_4NO_2^-] = [BH^+]$, $a = [C_2H_5NO_2]_0 = [B]_0$, and $(a - x) = [C_2H_5NO_2] \doteq [B]$. Equation (8) can be integrated by the use of partial fractions giving

$$t = c + \frac{k_3K_b}{(ak_1 + k_3K_b)^2}\ln\frac{(a - x)}{(k_1x + k_3K_b)} + \frac{1}{(ak_1 + k_3K_b)}\frac{a}{(a - x)} \quad (9)$$

The use of the integration constant, c, eliminates the necessity of matching the start of the reaction with the zero of time.

Assuming that equivalent conductances do not change over the range of ionic concentration encountered in an experiment, it is possible to write (9) in terms of the measured resistance R. It is necessary to allow for the conductance of the hydroxyl ion which is appreciable only during the early part of a run. Thus we have

$$\frac{z}{R} = \Lambda_{OH^-}K_b\frac{(a - x)}{x} \times (\Lambda_{BH^+} + \Lambda_{C_2H_4NO_2^-})x \quad (10)$$

where z is a constant for the cell and the Λ's refer to the equivalent ionic conductances. This can be converted to

$$\frac{z}{R} = \frac{z(a - x)}{R_0x} + \frac{zx}{R_ca} \quad (11)$$

where R_0 is a quantity estimated from values of K_b, measured conductances of sodium hydroxide solutions in the cell used for the kinetic studies, and the transference numbers of Na^+ and OH^-. R_c is a value of the equilibrium resistance corrected for the incompleteness of reaction (2). If we let R_e be the measured value of the equilibrium resistance, then R_c differs from R_c by a factor of $K_1^{1/2}/(K_1^{1/2} + 1)$. Solving for x in (11)

$$x = \frac{aR_c}{R}\left(1/2 + R/2R_0 + 1/2\sqrt{1 + \frac{R^2}{R_0^2} + \frac{2R}{R_0} - \frac{4R^2}{R_0R_c}}\right) = \frac{aR_c'}{R} \quad (12)$$

Actually the values of R_c' calculated from (12) differ by only a few per cent. from the constant value R_c. Equation (9) now becomes

$$t = c + \frac{k_3K}{(ak_1 + k_3K_b)^2}\ln\frac{(R - R_c')}{\left(k_1R_c' + \frac{k_3K_b}{a}R\right)} + \frac{1}{(ak_1 + k_3K_b)}\frac{R}{(R - R_c')} \quad (13)$$

We have from (13) that t is a function of the resistance and several constants of which only k_1 is unknown. For the three organic amines the log term is only a small correction factor and a good estimate of k_1 can be made by plotting t against $R/(R - R_c')$ and setting the slope equal to $1/(ak_1 + k_3K_b)$. Placing this value of k_1 in the log term it is possible to solve (10) algebraically using pairs of t and R readings and get a better value of k_1. For methylamine and dimethylamine the k_1 values calculated for pairs selected at random usually agree to 1 or 2%. For trimethylamine and ammonia k_1 show a systematic decrease as the reaction proceeds. For ammonia the log term is

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[4] Turnbull and Maron, THIS JOURNAL, 65, 212 (1943).

[5] Everett and Wynne-Jones, *Proc. Roy. Soc.* (*London*), **A169**, 190 (1938).

[6] Harned and Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943.

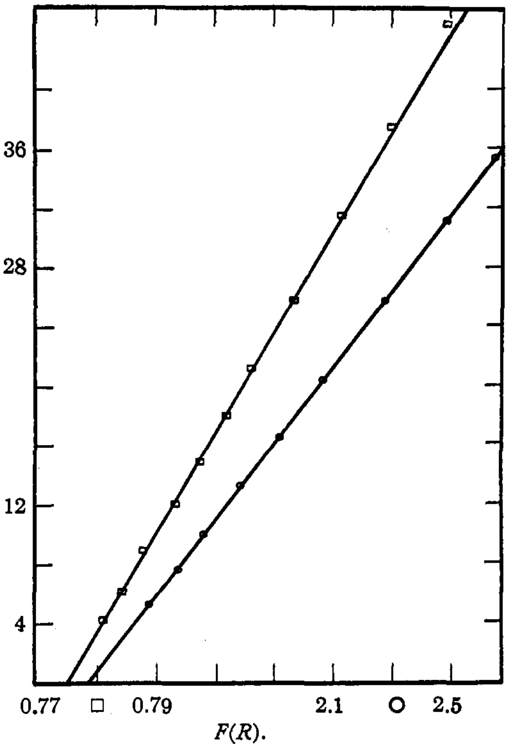

Fig. 1.—□, 0.0212 *M* ammonia, 0°, slope = 585; ○, 0.0258 *M* methylamine, 0°, slope = 28.2.

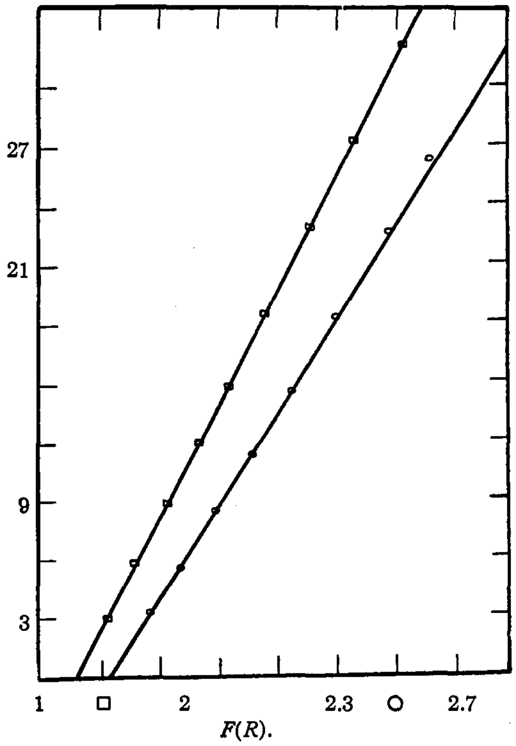

Fig. 2.—□, 0.0252 *M* dimethylamine, 0°, slope = 12.30; ○, 0.0333 *M* trimethylamine, 0°, slope = 14.35.

quite important, and it is necessary to try several values of k_1 until the calculated values agree with the starting one.

Another method of analyzing the data is to write (10) as

$$t = c + \frac{1}{ak_1 + k_3K_b} F(R) \qquad (14)$$

where

$$F(R) = \frac{k_3K_b}{(ak_1 + k_3K_b)} \ln \frac{R - R'_e}{(k_1R'_e + (k_3K_bR/a))} + \frac{R}{(R - R'_e)} \qquad (15)$$

and use the estimated value of k_1 to solve for $F(R)$. Then plotting t against $F(R)$ should give a straight line with a slope from which k_1 can be found. Figures 1 and 2 show the results obtained in this way with the four bases in typical runs. The values of the rate constants from the best values of the slopes agree with the one used to get $F(R)$. The falling off of the rate constant for ammonia and trimethylamine is clearly evident. The extent of reaction in the measured portions for various runs was approximately from 10 to 25% for ammonia, from 20 to 40% for trimethylamine, and from 25 to 75% for methylamine and dimethylamine. Table I is a tabulation of the rate constants k_1 obtained at 0 and 5.2°. The units of

TABLE I

KINETICS OF B + $C_2H_5NO_2$

Temp., °C.	Base	Concentration moles/liter	k_1 liters/mole-minute
0	Ammonia	0.0212	0.057
0	Ammonia	.0218	.057
0	Ammonia	.0650	.047
5.2	Ammonia	.0206	.097
5.2	Ammonia	.0218	.097
5.2	Ammonia	.0650	.079
0	Methylamine	.0214	.86
0	Methylamine	.0258	.84
0	Methylamine	.0325	.85
0	Methylamine	.0440	.78
5.2	Methylamine	.0258	1.47
5.2	Methylamine	.0325	1.45
5.2	Methylamine	.0416	1.41
0	Dimethylamine	.0173	2.60
0	Dimethylamine	.0232	2.50
0	Dimethylamine	.0249	2.67
0	Dimethylamine	.0359	2.60
0	Dimethylamine	.0430	2.54
0	Dimethylamine	.0510	2.44
5.2	Dimethylamine	.0228	4.50
5.2	Dimethylamine	.0252	4.60
5.2	Dimethylamine	.0458	4.42
0	Trimethylamine	.0320	2.04
0	Trimethylamine	.0333	2.08
0	Trimethylamine	.0448	2.04
5.2	Trimethylamine	.0198	3.68
5.2	Trimethylamine	.0314	3.64
5.2	Trimethylamine	.0448	3.60
0	Hydroxyl ion		39.1
5.2	Hydroxyl ion		59.5

all rate constants are liters/mole-minute. The corresponding data for hydroxyl ion have been included for comparison using the results of Maron and LaMer.[1c]

From the relationship indicated in (4) we can calculate k_2 also, the rate constant for the recombination of the ions. Unfortunately the constants k_1 are seen to be not quite independent of concentration, decreasing somewhat in solutions more concentrated than 0.04 molar. Neglecting the results for these more concentrated solutions where the interionic effects will be greatest, we can calculate the values of k_2 for the range 0.02 to 0.04 molar which will be at least comparable for the several bases. From the variation of k_1 with temperature the activation energy, E_{act}, can be found. Also using the transition state theory of reaction velocity[7]

$$k = \frac{RT}{Nh} e^{\Delta S^{\neq}/R}\, e^{-\Delta H^{\neq}/RT} \qquad (16)$$

and

$$E_{\text{act}} = \Delta H^{\neq} + RT$$

we can calculate the heats and entropies of activation for the reaction (2). Then the corresponding quantities for the reverse reaction can be obtained from

$$\Delta H^0 = \Delta H_1^{\neq} - \Delta H_2^{\neq} \qquad (17)$$

and

$$\Delta S^0 = \Delta S_1^{\neq} - \Delta S_2^{\neq} \qquad (18)$$

where the subscripts 1 and 2 refer to the forward and reverse processes. The standard state is unit activity though actually we are neglecting the difference between activity and concentration for reactants, products and activated complex alike. Table II summarizes all of this information calculated at 0°. The source of the thermodynamic data is from references (2a), (4) and (5). Since the data on nitroethane do not go down to 0°, it was assumed that $\Delta C_p^0 = -40$ cal./degree for the ionization of nitroethane in computing ΔH^0 and ΔS^0 at 0° from the data at 10 and 25°. According to Pitzer[8] this is a reasonable value for the heat capacity change in the ionization of a weak acid if the change in entropy is negative. The correction involved is small and will not affect the relative values for the four bases.

TABLE II

EQUILIBRIA $B + C_2H_5NO_2 \rightleftarrows BH^+ + C_2H_4NO_2^-$ AT 0°

Base	K_1	ΔH°, kcal.	ΔS°, E. U.	$\Delta H_1^{\neq}$, kcal.	$\Delta S_1^{\neq}$, E. U.
Ammonia	29.8	−10.0	−32.4	14.9	−17.9
Methylamine	836	−10.5	−27.9	15.0	−12.0
Dimethylamine	951	− 8.9	−21.5	15.9	− 6.6
Trimethylamine	60.4	− 5.4	−14.1	15.8	− 7.3
Hydroxyl ion	2.35×10^6	−12.2	−18.3	12.1	−15.5

Kinetics of $BH^+ + C_2H_4NO_2^-$ at 0°

Acid	k_2, liters-mole-min.	$\Delta H_2^{\neq}$, kcal.	$\Delta S_2^{\neq}$, E. U.
Ammonium ion	1.91×10^{-3}	24.9	+14.5
Methylammonium ion	1.02×10^{-3}	25.5	+15.9
Dimethylammonium ion	2.74×10^{-3}	24.8	+14.9
Trimethylammonium ion	3.44×10^{-2}	21.1	+ 6.8
Water	1.66×10^{-5}	24.3	+ 3.0

Discussion

It is evident that there is no linearity between the rates of neutralization and the base strengths of the amines, dimethylamine and particularly trimethylamine, reacting more rapidly than their basicities would warrant. This is in accord with previous observations that substitutions close to the center of reaction destroy any linear free energy relationships between rates and equilibria.[9] It is interesting also to compare the values of k_2 determined in these experiments with those calculated from an equation due to Junell,[1b] who measured the rates of combination of a number of neutral acids with the anion of nitroethane. Junell found that k_2 would be calculated from K_a, the acid ionization constant by the equation

$$\log k_2 = 1.54 + 0.37 \log K_a \qquad (18)$$

Taking K_a for the ammonium ions as K_w/K_b, we find for k_2 6.6×10^{-3}, 1.95×10^{-3}, 1.90×10^{-3} and 5.2×10^{-3} for NH_4^+, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$ and $(CH_3)_3NH^+$, respectively. We see from Table II that NH_4^+ and $CH_3NH_3^+$ react more slowly and $(CH_3)_2NH_2^+$ and $(CH_3)_3NH^+$ react more rapidly. In fact, the reason for the low basicity of trimethylamine, judging from this one reaction, is the abnormally high rate of conversion of the ion to the neutral base.

The heats of activation for the forward reaction appear to be normal for bimolecular reactions in solution. The entropies of activation, while fairly large and negative, compare with that for the hydroxyl ion reaction. For the reverse process $\Delta H^{\neq}$ is high, in agreement again with the hydroxyl ion reaction. The trimethylammonium ion has a conspicuously low heat of activation. The entropies of activation for the reverse reaction are large and positive. The interpretation of this in terms of the transition state theory is as follows: if we identify the entropy decrease in ionization with the electrostriction of the solvent or the binding of solvent molecules around the ions, the activated complex is solvated more than the neutral reactants but less than the product ions. Hence there is a loosening of structure in going from the ions to the complex and $\Delta S_2^{\neq}$ is positive. The desolvation of the ions accounts for the high energy barrier in forming the complex. Trimethylammonium ion does not appear to be as strongly solvated then as the other ions. This would be expected in view of the hydrophobic nature of the

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(7) Glasstone, Laidler and Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, Chapt. IV.

(8) Pitzer, THIS JOURNAL, 59, 2365 (1937).

(9) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, Chapt. VII.

methyl groups compared with the hydrogen atoms that they displace.

Summary

1. The second order rate constants for the reaction of nitroethane with ammonia, methyl-, dimethyl- and trimethylamine in water at 0 and 5.2° are reported.

2. The values of the rate constants at 0° are calculated from equilibrium data for the reaction of ammonium ion, methyl-, dimethyl- and trimethylammonium ions with the anion of nitroethane.

3. The heats and entropies of activation for the above reactions are computed.

4. The interpretation of the data indicates that the activated complex is not as strongly solvated as the product ions but more solvated than the reactants.

5. The decreased base strength of trimethylamine appears to be due to the decreased solvation energy and hence increased reactivity of the trimethylammonium ion.

EVANSTON, ILLINOIS RECEIVED FEBRUARY 24, 1947

CONTRIBUTION FROM THE ARMOUR RESEARCH FOUNDATION OF THE ILLINOIS INSTITUTE OF TECHNOLOGY]

Crystallization of p,p'-DDT from Binary Melts

BY VICTOR GILPIN,[1] WALTER McCRONE, ANNETTE SMEDAL AND HELEN GRANT

Introduction

Little work has been reported in recent years on the linear crystallization velocity (C.V.) of supercooled melts of organic compounds. Undoubtedly, part of this lack of interest has been due to the belief that C.V. measurements have no physical significance, because the problem of conducting the heat of crystallization away from the solid-liquid interface has made true temperature measurements difficult.[2,3] This difficulty has arisen in two ways. In the first place, the majority of investigators have been interested in the maximum C.V.; as Michel[4] has shown, this quantity is of value as a criterion of purity, but, due to the rapid movement of the crystal front, the temperature recorded is that of the thermostat, not that of the interface. In the second place, most previous workers employed capillary tubes of several millimeters bore; the crystal front accordingly had only a small portion of its surface exposed to the thermostat.

It is believed that the method recently developed for microscopic quantitative analysis of p,p'-DDT[5] avoids both these difficulties, and permits the measurement of true equilibrium temperatures over a limited range. The method employs thin films of the melt (less than 0.1 mm.) which have a correspondingly larger fraction of the interface in contact with the thermostat. Measurements are made on the lower temperature branch of the C.V. *vs.* temperature curve, in which region the rates are relatively slow, and where, moreover, rate measurements are uncomplicated by the transition in the reverse direction. It should be possible to attempt theoretical interpretation of data obtained in this way. The aim of the present and future work is to provide such data.

No claim of originality is made for the method of measuring such rates under the microscope. Dreyer[6] appears to have been the first to measure the C.V. on microscope slides.

Experimental Results

Effect of Temperature.—The technique described previously for o,p-DDT/p,p'-DDT mixtures[5] was used to establish C.V. *vs.* temperature curves for various mixtures of p,p'-DDT with 1,3,5-triphenylbenzene (TPB) and with 5-methyl-2-isopropylphenol (thymol). Figure 1 shows the general form of such curves. To avoid crowding, some experimental curves were omitted. In agreement with much earlier work on binary melts[7] the scatter of experimental points becomes considerable for p,p'-DDT mixtures containing more than about twenty-five weight per cent. of a second component. Thymol results are indicated in the smoothed curves of Fig. 2, in the rate *vs.* composition form used previously,[5] because a rate *vs.* temperature plot leads to undue crowding here. A similar increase in C.V. on addition of certain types of impurities was first noted by Dreyer.[8]

In Fig. 4 of the previous publication,[5] the Arrhenius lines were drawn through the raw experimental data. Because of the scatter of experimental points, it is now believed that a better representation of the true trend of the Arrhenius lines is achieved by using smoothed data from the C.V. *vs.* temperature curves. In Fig. 3, the best line was drawn through the smoothed data for pure p,p'-DDT, and the other lines were drawn parallel (except for thymol). The same procedure was used in constructing the graph for TPB mixtures (Fig. 4). Only one point of the one per cent. thymol line has been included, and several thymol

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(1) Present address: School of Chemistry & Physics, Pennsylvania State College, State College, Pa.

(2a) Tammann, "Kristallisieren and Schmelzen," Leipzig, 1903; (2b) Frenkel, "Kinetic Theory of Liquids," Oxford University Press, London, 1947.

(3) Luyet, *Biodynamica*, No. **48**, 28 (1939).

(4) Michel, *Bull. soc. chim. Belg.*, **48**, 105 (1939).

(5) McCrone, Smedal and Gilpin, *Ind. Eng. Chem., Anal. Ed.*, **18**, 578 (1946).

(6) Dreyer, quoted in (1).

(7) Bogojawlensky, *Z. physik. Chem.*, **27**, 585 (1898).

(8) Dreyer, *ibid.*, **48**, 467 (1940).