of this fraction consists of a mixture of sterols about 56% of which occur in the free state. Measurements of unsaturation of the sterol fraction by per acids show the presence of an unsaturated sterol with at least two double bonds in addition to the isomeric sitosterols and dihydrositosterol. Determination of unsaturation on sterols by iodine values was found to be unreliable.

The non-sterol fraction of the unsaponifiable material required 2.91% available oxygen. Preliminary work on this fraction indicates the presence of polyene hydrocarbons as well as an alcohol.

MINNEAPOLIS, MINN. RECEIVED DECEMBER 16, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heats of Activation of the Related Reactions Involved when *l*-Bromosuccinic Acid is Treated with Chloride Ion

BY A. R. OLSON AND F. A. LONG

In a previous article[1] we reported on an experimental determination of the mechanism of reactions that involve substitution on a carbon atom. We showed that, for the reactions which we studied, every substitution on the carbon atom was accompanied by a configurational inversion of the molecule. A quantitative proof of this inversion was obtained from the results for the reaction which occurs at 50° between *l*-bromosuccinic acid and chloride ion. However, in order to study the kinetics of this reaction quantitatively it was necessary to study the rates of all the other reactions which can take place in an acidified solution of *l*-bromosuccinic acid and chloride ion. Thus it was necessary to know the rate of decomposition of both *l*-bromo- and *l*-chlorosuccinic acids and the rates of reaction of these two optically active substances with both bromide ions and chloride ions. The previous article contained the results for the rate constants that were obtained for these six reactions at 50°.

The present paper deals with an extension of these studies to other temperatures in order to determine the heats of activation and the collision factors for these related reactions.

Experimental

The preparation of the materials and the methods of investigation were the same as in the previous article. The temperatures are all accurate to within ±0.05°. In obtaining the concentrations at the various temperatures the expansion of the solvent has been taken into account.

For all the rate constants, the unit of time is the minute, but for the collision factors that are given in the various Arrhenius equations, the unit of time is the second.

Experimental Results

1. The Decomposition of *l*-Bromosuccinic Acid, $COOHCH_2CHBrCOOH \xrightarrow{k_1} COOHCH{=}CHCOOH + H^+ + Br^-$.—This reaction was followed by titration of the produced bromide ion with silver nitrate, using chromate indicator. Before titrating the excess acid, the solutions were chilled with ice to minimize the error due to production of further bromide ion through lactone formation, etc. This titration, of course, corresponds to the total amount of fumaric acid and malic acid formed. However, at these high hydrogen-ion concentrations, the amount of malic acid that is produced is small.

Samples for analysis were withdrawn from each run at four different times, the last sample being taken when about four-fifths of the original *l*-bromosuccinic acid had disappeared. Assuming a unimolecular reaction, the result from the bromide ion titration for each sample allows a value for the specific rate constant to be calculated. That the observed rate was indeed unimolecular may be seen from the deviations tabulated in Table I, which lists the results for this reaction at the various temperatures. For all these, the initial concentration of *l*-bromosuccinic acid was 0.180 molar.

The calculated rate constants that are given in the last column of Table I have been obtained from the expression

$$k_1 = 0.755 \times 10^{10} e^{-24,010/RT} \qquad (1)$$

The agreement between the calculated and observed rate constants indicates that the heat of

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[1] Olson and Long, THIS JOURNAL, **56**, 1294 (1934).

TABLE I

INITIAL *l*-BROMOSUCCINIC ACID = 0.180 *M*

Temp., °C.	Molar concn. of $HClO_4$	No. of runs	Av. dev. in % of indiv. k_1's	Average $k_1 \times 10^4$	Calcd. $k_1 \times 10^4$
50	2.000	3	1	0.257[a]	0.255
62	2.000	3	2.5	0.977	0.973
75	2.000	4	1	3.75	3.74
88	1.024	2	2.5	13.9	
88	1.967	3	1.5	12.5	12.5
88	2.941	1	1.5	12.0	

[a] For the work given in our previous paper the precaution of chilling the samples was not taken and so the results obtained for k_1 were too high. However, since the fumaric acid reaction contributes only a very minor correction to the other reactions, the change in the value of this rate constant makes no change in any of the conclusions of that paper.

activation is correct to ±100 cal. This value for the heat of activation, 24,010 cal., is 400 cal. less than that reported for this reaction by Zawidzki and Wyzcalkowska[2] and 2600 cal. less than the value reported by Ölander.[3] These latter values were obtained under different experimental conditions, and are therefore not strictly comparable with our results. This point will be reverted to later.

2. The Decomposition of *l*-Chlorosuccinic Acid in Two Molar Perchloric Acid Solution, $COOHCH_2CHClCOOH \xrightarrow{k_3} COOHCH{=}CH\text{-}COOH + H^+ + Cl^-$.—The procedure for this reaction was identical with that of the preceding section. The results of the investigations, for an initial concentration of 0.180 *M* *l*-chlorosuccinic acid, are summarized in Table II.

TABLE II

INITIAL *l*-CHLOROSUCCINIC ACID = 0.180 *M*

Temp., °C.	Molar concn. of $HClO_4$	No. of runs	Av. dev. in % of indiv. k_3's	Average $k_3 \times 10^4$	Calcd. $k_3 \times 10^4$
50	2.000	2	0.5	0.0763	0.0760
62	2.000	2	0.5	0.293	0.294
75	2.000	4	2	1.15	1.14
88	1.024	1	0.5	2.89	
88	1.965	3	1	4.02	4.04
88	2.951	2	1	5.05	

As in the preceding section, the results for a definite hydrogen ion concentration can again be summarized by an Arrhenius equation, which for this reaction is

$$k_3 = 0.313 \times 10^{10} e^{-24,220/RT} \qquad (2)$$

The agreement between the observed rate constant, and those calculated from this equation indicates that the heat of activation is correct to ±80 cal.

In the sections to follow we have made the assumption that the rates for the decompositions of these substituted succinic acids are the same in solutions of the halogen acids as they are for perchloric acid solutions of the same concentrations, and it is important for us to show that this is justified. Evidence that our assumption is correct can be obtained in two ways.

In the first place we have made semi-quantitative experiments to determine the amount of fumaric acid that is produced, both in the perchloric acid solutions and in the halogen acid solutions. The method used was to precipitate the fumaric acid as mercurous fumarate according to the procedure outlined by Ölander.[3] These experiments indicate that, although the decomposition does not go entirely to fumaric acid, this is the principal reaction that occurs. In addition, the amount of fumaric acid that is formed is substantially the same whether the decomposition takes place in perchloric, hydrobromic or hydrochloric acid.

It can be seen in Tables I and II that, as the hydrogen ion is increased from one to three molar, the rate of decomposition of *l*-chlorosuccinic acid increases about 60%, while for *l*-bromosuccinic acid, the rate decreases about 20%. In Ölander's careful investigation of the decomposition of bromosuccinic acid, he concluded that fumaric acid was produced only from the ions of the bromosuccinic acid, β-propionolactonic acid being the intermediate compound. It is difficult to reconcile this conclusion with the present work without making improbable assumptions for the change of activity coefficients with change of the hydrogen-ion concentration. It should be emphasized in this connection that Ölander's work was confined almost entirely to low hydrogen-ion concentrations. Since the production of the lactonic acid is inhibited by hydrogen ions, we should expect the production of fumaric acid to be likewise inhibited if Ölander's views were correct. However, for the chlorosuccinic acid, the rate of decomposition increases with increasing hydrogen on concentration.

It seems much more probable that, under our experimental conditions, the fumaric acid is produced by a direct decomposition of the bromo- or chlorosuccinic acid. Confirmation for this belief may be adduced from the investigations of Rørdam[4] in which he treated β-propionolactonic acid

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[2] Zawidzki and Wyzcalkowska, *Bull. Acad. Polonaise*, (A), 3532 (1927).

[3] Ölander, *Z. physik. Chem.*, **A144**, 49 (1929).

[4] Rørdam, *J. Chem. Soc.*, 2931 (1932).

with solutions whose hydrogen-ion concentration ranged from strong base to strong acid and in all cases found the final product was almost entirely malic acid.

This point is important, since upon it rests the validity of our assumption that the rate of decomposition for these halogen succinic acids is the same in solutions of the halogen acids as it is in solutions of perchloric acid. For, since the lactonic acid reacts rapidly with halogen ions to re-form bromo- or chlorosuccinic acid, if the fumaric acid were produced by a mechanism involving the lactone, the rate of decomposition might be very different in the halogen acids. Our work, however, indicates that this is not the case.

3. The Racemization of *l*-Bromosuccinic Acid in Hydrogen Bromide Solutions.—The reaction here is

$$l\text{-COOHCH}_2\text{CHBrCOOH} + \text{Br}^- \overset{k_2}{=\!=} d\text{-COOHCH}_2\text{CHBrCOOH} + \text{Br}^-$$

and so is pseudo-unimolecular. The perturbing effect of the decomposition of the bromosuccinic acid into the lactonic acid or malic acid was minimized by following the reaction in solutions of two molar hydrogen ion. The reaction was followed polarimetrically and was found to be unimolecular over its complete range. The rate for a given run was obtained by plotting log α, where α is the optical rotation, against the time in minutes and obtaining the slope of the straight line. The rate constant for the reaction as written above was then obtained by a consideration of the decomposition rate of the bromosuccinic acid. The equation that was used for this is

$$k_{\text{obsd.}} = 2k_2b + k_1$$

where b is the concentration of the bromide ion, k_1 is the rate constant for the decomposition reaction, and k_2 is the rate constant for the racemization reaction. For 25 and 35°, the values for k_1 were calculated by means of Equation 1.

TABLE III

Temp., °C.	Concn. of HBr	No. of runs	Average $k_{\text{obs.}} \times 10^3$	Av. dev. in % of indiv. $k_{\text{obsd.}}$	Exptl. $k_2 \times 10^3$	Calcd. $k_2 \times 10^3$
25	2.000	4	0.371[a]	0.5	0.0924	0.0922
35	2.018	4	1.197	0.5	0.296	0.304
50	0.494 plus 1.5 *M* HClO₄	3	1.440	1	1.43	
50	0.991 plus 1 *M* HClO₄	3	3.028	0.5	1.51	
50	1.978	4	6.52	0.5	1.64	1.59
62	2.000	6	21.78	1	5.42	5.37
75	2.000	6	73.3	1	18.2	18.2
88	1.972	3	225.0	0.5	56.7	56.8

[a] This value of the observed rate constant for 25° agrees well with that obtained by Holmberg [*J. prakt. Chem.*, **88**, 553 (1913)] for a solution of 0.261 molar *l*-bromosuccinic acid in 2.00 molar hydrogen bromide. Holmberg's observed rate was 0.367 × 10^{-3}.

The results for this reaction at the various temperatures are collected in Table III. The initial concentration of *l*-bromosuccinic acid was 0.180 molar at all temperatures except 50°, where it was 0.178 molar.

The results for two molar hydrogen bromide solutions give the heat of activation, 21800 ± 50 calories. The calculated values for k_2 which are given in Table III have been obtained from the expression[5]

$$k_2 = 1.49 \times 10^{10}\, e^{-21,800/RT}$$

4. The Reaction of *l*-Chlorosuccinic Acid and Chloride Ion, $l\text{-COOHCH}_2\text{CHClCOOH} + \text{Cl}^- \overset{k_4}{=\!=} d\text{-COOHCH}_2\text{CHClCOOH} + \text{Cl}^-$.—The methods of investigation for this reaction were identical with those for the preceding one. In our previous work, since we set k_3, the rate of decomposition of the chlorosuccinic acid, equal to zero, the value that was given for the rate constant of the reaction as written above was too large. The values that have been listed in Table IV, however, have been obtained by utilizing the rate of decomposition in the same manner as was done for the analogous racemization of *l*-bromosuccinic acid. The inital concentration of *l*-chlorosuccinic acid was 0.180 molar at all temperatures.

TABLE IV

INITIAL *l*-CHLOROSUCCINIC ACID = 0.180 *M*

Temp., °C.	Concn. HCl	No. of runs	Average $k_{\text{obsd.}} \times 10^4$	Av. dev. in % of indiv. $k_{\text{obsd.}}$	Exptl. $k_4 \times 10^4$	Calcd. $k_4 \times 10^4$
50	1.978	6	0.420	1	0.0867	0.0871
62	2.000	6	1.69	2	0.350	0.347
75	2.000	8	6.56	1	1.35	1.39
88	1.972	4	24.4	0.5	5.17	5.06

The Arrhenius equation for this reaction is

$$k_4 = 0.842 \times 10^{10}\, e^{-24,770/RT} \qquad (4)$$

The agreement between the experimental and calculated rate constants that are given in Table IV indicates that the value for the heat of activation, 24,770 cal., is correct to ±150 cal.

5. The Reaction Between *l*-Chlorosuccinic Acid and Bromide Ion to Give *d*-Bromosuccinic Acid and Chloride Ion, $l\text{-COOHCH}_2\text{CHCl-COOH} + \text{Br}^- \xrightarrow{k_5} d\text{-COOHCH}_2\text{CHBrCOOH} + \text{Cl}^-$.—This reaction was followed polarimetrically

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(5) These more accurate values for the collision factor and the heat of activation supplant those quoted by Olson and Voge [THIS JOURNAL, **56**, 1690 (1934)] which were preliminary results obtained from work at only two temperatures.

and the specific rate constant was determined by the methods previously described with, however, one change. Previously, k_3, the decomposition rate of the chlorosuccinic acid, was set equal to zero. More accurate work has shown its value to be large enough to influence significantly the determination of k_5. When the decomposition rate is included, the approximate equations, under the same assumptions as were outlined in the previous paper, are

$$w' = a\ e^{-(k_5c+k_3)t}$$

$$(z - x) = \frac{k_5ca}{2k_2c + k_1 - k_5c - k_3}\ \frac{e^{(2k_2c + k_1 - k_5c - k_3)t} - 1}{e^{(2k_2c + k_1)t}}$$

As before, w' is the concentration of *l*-chlorosuccinic acid at time t, z and x, the concentrations of *d*- and *l*-bromosuccinic acids, c, the initial concentration of the bromide ion, and a, the initial concentration of the *l*-chlorosuccinic acid. Thus the k_5 of our earlier paper is very nearly the sum of the present k_5 plus k_3/c, where c is again the initial bromide ion concentration. Using these corrected expressions, the agreement between the experimental points and the curve that is calculated from the best value of k_5 is again excellent. The results for this reaction for the various temperatures are given in Table V.

TABLE V

Temp., °C.	Molar concn. of *l*-chloro	Molar concn. of HBr	No. of runs	Exptl. $k_5 \times 10^4$	Calcd. $k_5 \times 10^4$
50	0.178	1.978	5	0.435	0.440
62	.180	2.000	6	1.66	1.64
75	.180	2.000	7	5.90	6.10
88	.180	1.972	9	21.2	20.9

The rate constants at this constant hydrogen-ion concentration give for the Arrhenius expression

$$k_5 = 0.624 \times 10^{10}\ e^{-23,540/RT} \tag{5}$$

The comparison between the experimental values of k_5 and those calculated from Equation 5 indicates that the value for the heat of activation is accurate to about ±150 cal.

6. **The Reaction between Chloride Ion and *l*-Bromosuccinic Acid,** *l*-$COOHCH_2CHBrCOOH + Cl^- \xrightarrow{k_6}$ *d*-$COOHCH_2CHClCOOH + Br^-$, which is simply the reverse of the reaction discussed in the preceding section.

This reaction was handled in exactly the same way as in our previous paper. The introduction of a specific value for k_3 changes slightly the rather complicated solutions of the rate equations in that, for the former $2k_4b$ and k_5b, there must be substituted $2k_4b + k_3$ and $k_5b + k_3$. Other than this, the change of k_3 from zero to the correct value has a completely negligible effect.[6]

The data for this reaction at the various temperatures are summarized in Table VI.

TABLE VI

Temp., °C.	Molar concn. of *l*-bromo	Molar concn. of HCl	No. of runs	Exptl. $k_6 \times 10^3$	Calcd. $k_6 \times 10^3$
50	0.178	1.978	5	0.233	0.234
62	.180	2.000	3	0.871	0.874
75	.180	2.000	5	3.30	3.30
88	.180	1.972	3	11.30	11.30

The calculated rate constants have been obtained from the Arrhenius expression

$$k_6 = 3.95 \times 10^{10}\ e^{-\frac{23,650 \pm 40}{RT}} \tag{6}$$

It is worthwhile mentioning that, due to the mathematical labor involved in calculating k_5 and k_6, no attempt was made to calculate a constant for each run, but only a constant for the composite data from the several runs. The excellent agreement shown by the plots for the experimental data for k_5 and k_6, as given in the previous paper, gives some idea of the accuracy of the work.

Discussion

The values for the heats of activation and collision factors that are given in Equations 1 to 6 were all obtained in the usual manner by plotting the logarithms of the rate constants against the reciprocal temperatures. In Fig. 1, the plots for the several reactions are collected. It is obvious from this figure that there is no apparent temperature coefficient of the heats of activation for any of the reactions.

The method of least squares was also used to calculate the heats of activation and their probable errors. The results for the heats of activation agree very closely with the values that obtain from the graphical method. The values for the probable errors that are secured by this method all lie within the limits that we have set in the various sections.

In Table VII the constants of the Arrhenius equations for the various reactions have been collected.

TABLE VII

No.	Reaction	*Z* factor × 10^{-10} for time in sec.	ΔE, cal.
1	*l*-bromo = fum.	0.755	24010 ± 100
2	*l*-chloro = fum.	0.313	24220 ± 80
3	*l*-bromo + Br^-	1.49	21800 ± 50
4	*l*-chloro + Cl^-	0.842	24770 ± 150
5	*l*-chloro + Br^-	0.624	23540 ± 150
6	*l*-bromo + Cl^-	3.95	23650 ± 40

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[6] In the expressions for $x - z$ and C on page 1297 of our previous paper, k_4 should replace k_3.

These results for the heats of activation and the collision factors exhibit some interesting regularities. For the decomposition of the two halogen succinic acids into fumaric acid the heats of activation are almost identical. For the bimolecular reactions, the value for the reaction of bromosuccinic acid with bromide ion is lowest, 21.8 kcal., that for chlorosuccinic acid with chloride ion is highest, 24.77 kcal. and the values for the two exchange reactions are intermediate, 23.54 and 23.65 kcal.

Recently Ogg and Polanyi[7] published the results of some theoretical calculations of the heats of activation for reactions of the type

$$X^- + RY = RX + Y^-$$

where X and Y are halogens. Their results, calculated for the reactions of the various halide ions with methyl halides, indicate that the heats of activation should increase with decreasing weight of the halogen. This is just the result that we have obtained. These authors have not given calculations for exchange reactions of the type RBr plus chloride ion, but an extension of their work indicates that theoretically the heat of activation for this reaction should lie between the value for the reaction of RBr with bromide ion and that for the reaction of RCl with chloride ion. Again this is the experimental result. In addition, the calculated difference in the activation energies, which Ogg and Polanyi feel is the most significant result of their work, is approximately the same as found by us.

It is interesting to note that the heats of activation for Reactions 5 and 6, which are merely the forward and reverse reactions of the equilibrium

$$l\text{-chlorosuccinic acid} + Br^- \longleftrightarrow d\text{-bromosuccinic acid} + Cl^-$$

are almost identical. This signifies that, under these experimental conditions, ΔH for this equilibrium is almost zero. This is, of course, not ΔH^0, but if the assumption is made that ΔH^0 is also zero, then this, with the value for the equilibrium constant for this reaction, k_5/k_6, gives for the entropy change for the reaction, $\Delta S^\circ = -3.3$. The difference between the entropies of chloride ion and bromide ion as given by Latimer, Schutz and Hicks[8] is -5.9, which indicates that the entropies of the two organic acids are nearly equal.

There are some interesting regularities in the collision factors that are listed in Table VII. The collision factor is greater in every case for reactions involving bromosuccinic acid than for the corresponding reaction involving chlorosuccinic acid. For the four substitution reactions, those that involve chloride ion have in every case a larger collision factor than the corresponding reaction involving bromide ion.

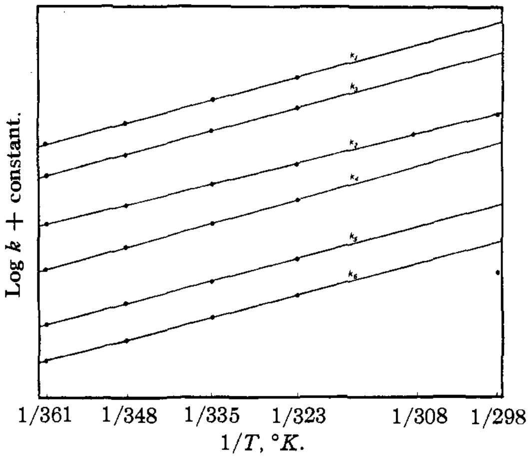

Fig. 1.—Log k against $1/T$ for the assembled reactions.

Moelwyn-Hughes[9] and others have advanced the thesis that the kinetics of reactions in solution can be explained by the same sort of collision theory that has been applied in explaining gaseous reactions with, of course, slight differences due to different conditions. If the equations given by Moelwyn-Hughes are used to calculate the theoretical collision factors for the four substitution reactions, the results vary from 12 to 16×10^{10}, *i. e.*, larger than the observed values by a factor of approximately ten. For these calculations the diameters of the organic molecules were secured from their molecular volumes, and for the halide ions the diameters of the solvated ions as given by Hartley and Raikes[10] were used. The agreement between the observed and calculated values is, of course, all that could be expected considering the approximate character of the calculation. It is interesting, however, that the calculated values are decidedly higher, a fact that is in agreement with the theory of such reactions as developed by Olson[11] which postulates that not every collision, but only collisions with a certain orientation, will lead to reaction.

Summary

The heats of activation and the collision factors

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[7] Ogg and Polanyi, *Trans. Faraday Soc.*, **31**, 604 (1935).

[8] Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 82 (1934).

[9] Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford Univ. Press, Oxford, England, 1933.

[10] Hartley and Raikes, *Trans. Faraday Soc.*, **23**, 394 (1927).

[11] Olson, *J. Chem. Phys.*, **1**, 418 (1933).

for the six related reactions which occur when *l*-bromosuccinic acid is treated with chloride ion in aqueous solution have been determined at temperatures ranging from 25 to 88°. No measurable trends of the heats of activation were found for any of these reactions. The collision factors for the four bimolecular reactions are of the same order of magnitude as those calculated from kinetic theory.

BERKELEY, CALIFORNIA RECEIVED DECEMBER 26, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Thermal Data on Organic Compounds. XVI. Some Heat Capacity, Entropy and Free Energy Data for Typical Benzene Derivatives and Heterocyclic Compounds

BY GEORGE S. PARKS, SAMUEL S. TODD AND WILLIAM A. MOORE

This investigation was undertaken to obtain thermodynamic data for some typical benzene derivatives and heterocyclic compounds, and serves to supplement several previous studies by Parks and his collaborators.[1] In the present case we have measured the heat capacities of triphenylbenzene, nitrobenzene, thiophenol, benzyl alcohol, phthalic acid, phthalic anhydride, pyridine and quinoline.

Materials

Nitrobenzene ($C_6H_5NO_2$).—The sample of nitrobenzene employed was obtained from Eastman "highest purity" material by eight successive fractional crystallizations. Its melting point, determined by a mercury thermometer which had been calibrated by the United States Bureau of Standards, was 5.65° (±0.05°), in good agreement with the "International Critical Tables" value of 5.7°.

Thiophenol (C_6H_5SH).—Eastman "highest purity" thiophenol (b. p. 70–71° at 15 mm. pressure) was found to freeze sharply at −14.9°. Accordingly it was used without further purification.

Benzyl Alcohol ($C_6H_5CH_2OH$).—Eastman "highest purity" benzyl alcohol was subjected to a careful fractional distillation at 86–88° with about 5 mm. pressure. The middle third of the distillate was selected for the present measurements. It melted at −15.5° ("I. C. T." value, −15.3°).

Pyridine (C_5H_5N).—Dr. Poe Liang of this Laboratory had occasion to prepare some very pure pyridine for another investigation. He subjected a high-grade German material (boiling range about 0.5°) to a series of distillations over solid potassium permanganate, potassium hydroxide and barium oxide, and thus obtained a final product boiling within less than 0.1° and having a water content of about 0.02%. He kindly gave us some of this pyridine for our present study. Its melting point was −42.0°, which agrees exactly with the "I. C. T." value.

Quinoline (C_9H_7N).—Eastman synthetic quinoline (b. p. 110–111° at 14 mm.) was subjected to a careful fractional distillation at 78° and about 3 mm. pressure. The middle third of this distillate was then used in our measurements; it showed a sharp melting point at −14.7°, which is considerably above the "I. C. T." value (−19.5°).

1,3,5-Triphenylbenzene ($C_{24}H_{18}$), ***o*-Phthalic Acid** [$C_6H_4(CO_2H)_2$], **and Phthalic Anhydride** ($C_8H_4O_3$).—These were Eastman "highest purity" materials with melting points at 170–171°, 206–208° (dec.) and 129–131°, respectively. All our specific heat measurements on these compounds were made at temperatures at least 100° below the melting points, where moderate amounts of organic impurities could not produce an appreciable effect on our results; hence, these materials were employed without further purification.

Experimental Results

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the fusion data. The apparatus and details of experimental procedure have been fully described in other places.[2] In view of the accuracy of the various measurements involved, the absolute error in the experimental values thereby obtained is probably less than 0.7%, except in so far as impurities in a sample may cause premelting or otherwise influence the results. The fortuitous errors were ordinarily under 0.25%.

On an average about thirty-five specific heat determinations in the temperature interval between 90 and 300°K. were made upon each of the eight compounds investigated. These results were then plotted on a large scale, a smooth curve through the experimental data was drawn, and specific heat values were read off from this curve for various even temperatures. For the sake of spatial economy these derived values, rather than the more numerous experimental ones, are recorded in Table I. They and also the fusion data

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[1] (a) Huffman, Parks and Daniels, THIS JOURNAL, **52**, 1547 (1930); (b) Huffman, Parks and Barmore, *ibid.*, **53**, 3876 (1931); (c) Parks, Huffman and Barmore, *ibid.*, **55**, 2733 (1933); (d) Parks and Light, *ibid.*, **56**, 1511 (1934); (e) Jacobs and Parks, *ibid.*, **56**, 1513 (1934).

[2] Parks, *ibid.*, **47**, 338 (1925); also Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).