NOTES

Polymorphism of Acetaldehyde 2,4-Dinitrophenylhydrazone

By W. M. D. Bryant

In two earlier papers the writer reported the melting point and optical crystallographic constants of acetaldehyde 2,4-dinitrophenylhydrazone.[1] It was shown in the second paper that this derivative exists in at least two distinct crystalline modifications designated as stable and metastable, respectively. Shortly afterward Ingold, Pritchard and Smith[2] reported two crystalline modifications and commented on their possible identity with the above polymorphs. Their "metastable" modification, however, melted at 146°, while only one melting point (168.5°) was obtained from both of the writer's products. Campbell has recently stated[3] that only one modification exists and that the writer's metastable modification was merely contaminated material. This statement is completely at variance with the writer's previous work and with experiments to be reported below. Further, Campbell has incorrectly quoted this modification as melting at 147° instead of 168.5°. He suggests crotonaldehyde 2,4-dinitrophenylhydrazone as a possible contaminant.

Extending the work reported earlier, it has been possible to duplicate the preparation of the low melting material obtained by Ingold, Campbell, and also by Purgotti.[4] This material recrystallized once from benzene is optically indistinguishable from the stable modification as judged by refractive indices, optic axial angle and the highly characteristic inclined dispersion, but is quite distinct from the writer's metastable form. The material melts fairly sharply at 147° and the melting point is not noticeably depressed on mixing with some of the higher melting stable material. No similar product was obtained on mixing a small amount of crotonaldehyde derivative (m. p. 199.6°) with some of the stable modification.

While it is not proposed that the low melting material is necessarily pure, it appears likely that the contaminant is of a catalytic sort (perhaps a trace of sulfuric acid) and that the low melting point is due to an inhibition of the transition from the stable to the metastable form rather than contamination by another "hydrazone." The fact that the stable and metastable forms previously reported both melted at 168.5° suggests that the transition ordinarily occurs in the solid state prior to fusion in the case of the pure stable modification and that the observed melting point is in both cases really that of the metastable form. It may well be that 147° approximates the melting point of the unchanged stable form. According to this reasoning the two products described by Ingold and by Campbell would both be the stable variety, with the difference that the low melting samples may contain a trace of negative catalytic material.

Ammonia Department
E. I. du Pont de Nemours & Co.
Wilmington, Del.
Received September 19, 1936

---

(1) Bryant, This Journal, **54**, 3758 (1932); **55**, 3201 (1933).

(2) Ingold, Pritchard and Smith, *J. Chem. Soc.*, 86 (1934).

(3) Campbell, *Analyst*, **61**, 391 (1936).

(4) Purgotti, *Gazz. chim. ital.*, **24**, 569 (1894).

Kinetic Medium Effects in the Reaction between Bromoacetate and Thiosulfate Ions

By Sam Eagle and J. C. Warner

An examination of the results of recent studies[1-3] on the rate of reaction of thiosulfate ion with bromoacetate ion in water and in mixed solvents has led us to the conclusion that the facts are in better agreement with Scatchard's theory[4] than is implied in the most recent paper.[3] La Mer and Kamner state that "no simple relation is revealed by plotting log *k* against *D* or 1/*D* either for our data or those of Kappanna. . .in aqueous alcohol solutions." "Although dielectric constants of the solvents employed in this research range from urea (solutions) $D = 88.4$ (25°). . .to dioxane (solutions) $D = 33$ (25°), the velocity constants in the presence of non-electrolytes exceed those for water." "Scatchard's theory of the effect of *D* obviously does not hold for the present data." Scatchard's theory yields

$$\log k^0 - \log k_*{}^0 = \frac{\epsilon^2 \mathbf{Z}_\mathrm{A} \mathbf{Z}_\mathrm{B}}{2.3''k''Ta}\left[\frac{1}{D_*} - \frac{1}{D}\right] \tag{1}$$

---

(1) Kappanna, *J. Indian Chem. Soc.*, **6**, 419 (1929).

(2) Straup and Cohn, This Journal, **57**, 1794 (1935).

(3) La Mer and Kamner, *ibid.*, **57**, 2669 (1935).

(4) Scatchard, *Chem. Rev.*, **10**, 229 (1932).

In testing the theory, La Mer and Kamner have used rate constants over the range $\mu = 0.002$–0.05. In most of their experiments in solvents of dielectric constant less than water, the primary salt effect is larger than the effect of decreasing the dielectric constant and as a consequence the experimental rates are higher in the mixed solvents than in water. It must be emphasized that the k^0s in equation (1) from Scatchard's theory are rate constants at zero ionic strength. We have calculated k^0 values from the data of the above investigators[1-3] by the well-known relation

$$\log k/k^0 = \frac{\epsilon^2 \mathbf{Z}_A \mathbf{Z}_B}{2.3D''k''T}\frac{\kappa}{1+\kappa a} \qquad (2)$$

using Straup and Cohn's value, $a = 5.6$ Å. The rate constants at zero ionic strength (k^0) show a uniform decrease with decrease in dielectric constant. In the figure, we have plotted log k^0 against $1/D$ for all the experiments of Straup and Cohn, for all experiments of La Mer and Kamner at 25° except those in 1.47% sucrose and in 50.3% dioxane ($k^0 = 0.039$, $1/D = 0.030$), and for all experiments of Kappanna at 25° except those in 50% sucrose ($k^0 = 0.16 - 0.19$, $1/D = 0.0204$), 60% ethyl alcohol ($k^0 = 0.13 - 0.15$, $1/D = 0.023$) and 80% alcohol ($k^0 = 0.09 - 0.11$, $1/D = 0.031$). The inclusion of these values at the lower dielectric constants would have required an undesirable contraction of the abscissa. The spread in k^0 values calculated from experimental rate constants at different ionic strengths does not imply experimental error but more probably points to the inadequacy of equation (2) for extrapolating to zero ionic strength. The "theoretical" slope using $a = 5.6$ Å. in equation (1) is shown in the figure.

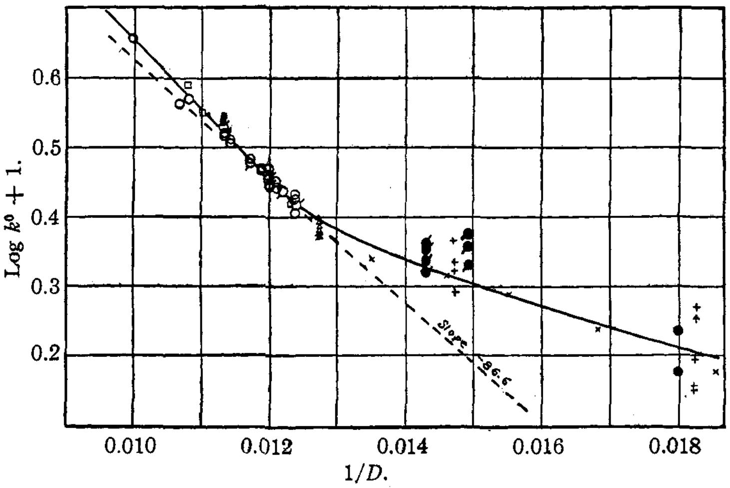


Fig. 1.—$S_2O_3^=$ + $BrAc^-$ at 25°: Kappanna— + C_2H_5OH-H_2O, ●, sucrose-H_2O; La Mer and Kamner— ▲, H_2O; ■, urea-H_2O, ●, glycerol-H_2O, ●-, sucrose-H_2O; Straup and Cohn—△, H_2O, ○, glycine-H_2O, ○-, α-alanine-H_2O, -○, β-alanine-H_2O, □, urea-H_2O × C_2H_5OH-H_2O.

In mixed solvents of dielectric constant greater than water there is good agreement with the theory. The somewhat steeper experimental slope may be attributed to the "salting in" of the highly polar non-aqueous constituents of the solvent. In solvents of dielectric constant less than water, the rate decreases less rapidly with decrease in dielectric constant than required by the approximate equation (1). This deviation might be expected for a variety of reasons. It may be due to a "salting out" of the non-aqueous solvent so that the effective dielectric constant about the reacting ions is less than the dielectric constant according to solvent composition.[5] Since k^0 values are calculated from experimental values at finite ionic strengths, the influence of salting out will be to give calculated values which are higher than the true k^0. Scatchard[4] has already pointed out the limitations imposed upon equation (2) through the neglect of "higher terms" in its derivation. Due to these limitations, equation (2) becomes less adequate for calculating k^0 from an experimental k at constant dielectric constant as the dielectric constant of the solvent is decreased. Due to each of these causes, one would expect the true k^0 to be lower than any calculated by equation (2). This conclusion is supported by our calculations, especially those using Kappanna's data which cover a considerable range of ionic strength. Almost invariably, the lowest k^0 (calculated) is obtained from the experimental k at lowest ionic strength.

The difference in rate constants found by Straup and Cohn in isodielectric solvents is of the same order of magnitude as found by Warner and Warrick[5] for the conversion of ammonium cyanate into urea in isodielectric mixtures of water and various alcohols. These differences might be expected whether the deviations for the simple equations were due to salting in and salting out or to the inadequacy of equation (2). In addition to the factors already discussed, one might at-

---

(5) Warner and Warrick, THIS JOURNAL, 57, 1491 (1935).

tempt to attribute deviations to a change in "a" with solvent or to ion associations which might change the factor $\mathfrak{z}_A\mathfrak{z}_B$ from 2 to 1. Considering all of the limitations imposed in obtaining equations (1) and (2) from the theory, one must conclude that the agreement is as good as could reasonably be expected.

CHEMISTRY LABORATORY
CARNEGIE INSTITUTE OF TECHNOLOGY
SCHENLEY PARK, PITTSBURGH, PA.

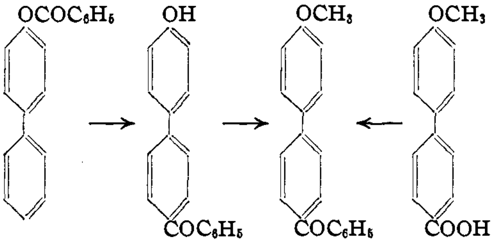
RECEIVED JULY 13, 1936

The Fries Rearrangement of 4-Benzoyloxydiphenyl

BY L. F. FIESER AND CHARLES K. BRADSHER

Having recently reported that the Fries rearrangement of 4-acetoxydiphenyl yields a mixture of 4-hydroxy-3-acetyldiphenyl and 4-hydroxy-4′-acetyldiphenyl,[1] we were interested to note that, in a paper published prior to ours but after the completion of our work, Hey and Jackson[2] obtained only 4-hydroxy-3-benzoyldiphenyl on heating 4-benzoyloxydiphenyl with aluminum chloride in tetrachloroethane solution at 140° and found no evidence of the heteronuclear migration of the benzoyl group. No trace of the alkali-soluble product, m. p. 193–195°, claimed by Blicke and Weinkauff[3] to be produced under identical conditions was observed. The latter investigators had assigned to their product, albeit without satisfactory evidence, the structure of 4-hydroxy-4′-benzoyldiphenyl and had regarded this as a case of heteronuclear rearrangement.

In view of the discrepancy in these two reports and the divergence of our results with the acetate from those of Hey and Jackson with the benzoate, we investigated the rearrangement of the latter ester under conditions similar to those employed with the former.[1] The reagents were brought together in the presence of carbon bisulfide, the solvent was distilled, and the residue heated at 160°. From the resulting mixture a substance identified as 4-hydroxy-4′-benzoyldiphenyl (II), m. p. 194–195° when pure, was isolated in 22% yield. As in other cases, the 4′-derivative is easily separated by virtue of its relatively low solubility. The structure of the substance was established by conversion to the methyl ether (III), which was compared with a sample synthesized by the condensation of the chloride of 4-methoxy-4′-carboxydiphenyl[1] (IV) with benzene. The two samples were found to be identical. The same substance resulted from the Friedel and Crafts reaction of 4-methoxydiphenyl with benzoyl chloride, as stated by Blicke and Weinkauff and by Hey and Jackson, but our results differed from those of the previous investigators in that we isolated not only the 4′-benzoyl derivative (37% yield) but also 4-methoxy-3-benzoyldiphenyl (39% yield).



I II III IV

We are in agreement with both pairs of investigators regarding the properties of the various compounds, and the differences in the results appear to be due to variations in the conditions of the reactions and the methods of separating the products. We are inclined to believe that the conditions for the Fries rearrangement specified by Blicke and Weinkauff are not very satisfactory, for although these workers undoubtedly obtained 4-hydroxy-4′-benzoyldiphenyl, we were no more able to duplicate their results, at least in one small-scale experiment, than were Hey and Jackson.

That under slightly different conditions the benzoyl group migrates to an appreciable and unmistakable extent to the 4′-position is consistent with the findings regarding the acetyl migration.[1] We do not, however, regard these examples of heteronuclear migration as having any great theoretical significance, for the evidence available indicates that the Fries reaction is not a true rearrangement but an intermolecular acylation.[4]

Experimental Part

Fries Rearrangement.—4-Benzoyloxydiphenyl (5 g.) was mixed thoroughly with finely powdered aluminum chloride (4.7 g.) and carbon bisulfide (25 cc.) and the solvent was removed by distillation from the steam-bath. The residue was heated for thirty minutes in an oil-bath maintained at 160°, and after cooling and adding ice and

---

[1] Fieser and Bradsher, THIS JOURNAL, **58**, 1738 (1936).

[2] Hey and Jackson, *J. Chem. Soc.*, 802 (1936).

[3] Blicke and Weinkauff, THIS JOURNAL, **54**, 330 (1932).

[4] Rosenmund and Schnurr, *Ann.*, **460**, 56 (1928); Cox, THIS JOURNAL, **52**, 352 (1930).

dilute hydrochloric acid the product was taken up in ether. The ethereal solution was washed with dilute acid and with water and extracted with 2.5% sodium hydroxide, and on acidifying the alkaline extract there was obtained 4 g. of grayish material. On two crystallizations from benzene this afforded nearly pure **4-methoxy-4'-benzoyldiphenyl**, m. p. 193–195°, yield 1.1 g. (22%). A small amount of a highly colored impurity was removed on reprecipitation from an alkaline solution, and further crystallization from benzene gave round, faintly yellow crystal-clusters, m. p. 194–195°.

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.18; H, 5.14. Found: C, 83.42; H, 5.14.

No pure products were isolated from the mother liquor. On conducting the rearrangement according to Blicke and Weinkauff[3] the alkali-soluble product amounted to only about 2% of the ester used and it consisted largely of 4-hydroxydiphenyl.

The acetate formed colorless plates, m. p. 127–128°, from methyl alcohol.

Anal. Calcd. for $C_{21}H_{16}O_3$: C, 79.72; H, 5.09. Found: C, 80.00; H, 5.39.

The methyl ether, prepared with the use of dimethyl sulfate and alkali, crystallized from benzene as colorless needles, m. p. 165–166°. It was identified by comparison with the samples described below.

Friedel and Crafts Reaction.—A solution of 10 g. of 4-methoxydiphenyl and 6.9 cc. of benzoyl chloride in 130 cc. of tetrachloroethane was cooled to −10° and 8 g. of aluminum chloride was added all at once. The mixture was stirred mechanically and allowed to come to room temperature. After eighteen hours ice and acid were added, the solvent was removed with steam, and the moist product was taken up in benzene. On concentrating the solution to a volume of 50 cc. and cooling, 5.8 g. of nearly pure **4-methoxy-4'-benzoyldiphenyl**, m. p. 165–167°, crystallized. The mother liquor was concentrated to a volume of 25 cc. and treated with petroleum ether. The material which separated on one crystallization from methyl alcohol gave 6.1 g. of a product melting at 91–92° (flat needles). This substance is insoluble in alkali and depresses the melting point of 4-methoxydiphenyl; it is undoubtedly 4-methoxy-3-benzoyldiphenyl, which Hey and Jackson[2] prepared by a synthesis establishing the structure and for which they report the melting point 93°.

Synthesis of 4-Methoxy-4'-benzoyldiphenyl.—A solution of 0.5 g. of 4-methoxy-4'-carboxydiphenyl[1] in 10 cc. of thionyl chloride was refluxed gently for one hour and the excess reagent was removed at reduced pressure. The residue was dissolved in 25 cc. of thiophene-free benzene, 0.3 g. of aluminum chloride was added and the mixture was refluxed for one hour. The reaction product, recovered in the usual way, crystallized from alcohol or benzene as colorless needles, m. p. 165–166°. Mixed melting point determinations of this 4-methoxy-4'-benzoyldiphenyl with both of the samples obtained above indicated the identity of all three preparations.

CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.
RECEIVED AUGUST 12, 1936

A New Synthesis of Morpholine

BY BURT L. HAMPTON AND C. B. POLLARD

Morpholine was first prepared by L. Knorr[1] by heating diethanolamine and an excess of concentrated hydrochloric acid in a sealed tube and then refluxing the reaction mass with potassium hydroxide. Because of low yields Knorr abandoned this method for the sulfuric acid method.[2] In both cases he failed to state his yields. However, Jones and Burns[3] have shown that morpholine is formed in about a 10% yield by the action of sulfuric acid on diethanolamine following the directions of Knorr. Therefore the yield using hydrochloric acid and potassium hydroxide must have been considerably lower. The only other methods for the preparation of morpholine are indirect ones and need not be reviewed here.

In his first preparation Knorr assumed the chlorohydrin of diethanolamine to be formed. Ring closure with loss of hydrogen chloride was then effected by refluxing in potassium hydroxide solution. He based this assumption on the fact that he was able to isolate the chlorohydrin of N-phenyldiethanolamine in a similar reaction; however, he was unable to isolate the chlorohydrin of diethanolamine because of its similarity in properties to the parent substance.

We have shown in this investigation that the chlorohydrin does not necessarily have to be formed and that no dehydrating agent other than that of heat on the hydrochloride is necessary for the formation of morpholine from diethanolamine. This was surprising in view of the work of Knorr.

Preparation.—Diethanolamine (2 moles) is placed in a round-bottomed flask fitted with a thermometer and an air-cooled condenser. Concentrated hydrochloric acid is added slowly until the solution is acid to litmus. The solution is then heated rapidly until the water is driven off, and the temperature of the solution is kept at 200–210° for fifteen hours. The reaction mass is now allowed to cool, an excess of calcium oxide is added, and the mixture subjected to dry distillation. The resulting liquid is dried over solid sodium hydroxide and refluxed over metallic sodium for thirty minutes; it is then subjected to fractionation. The entire product boils at from 126–129° and is practically anhydrous. The yield is around 48%. This procedure offers a rapid

---

[1] Knorr, *Ber.*, **22**, 2081 (1889).

[2] Knorr, *Ann.*, **301**, 1 (1898).

[3] Jones and Burns, THIS JOURNAL, **47**, 2966 (1925).

method for the preparation of morpholine and obviates many steps necessary in other methods.

If instead of subjecting the mixture to dry distillation concentrated sodium hydroxide is added and the solution distilled with steam into hydrochloric acid, a yield of 65% of the hydrochloride of morpholine is obtained. This, when distilled over calcium oxide, gives about 45% of morpholine (based on diethanolamine).

If to the original reaction mass cold sodium hydroxide is added, and the resulting amine layer is extracted with ether, pure morpholine is obtained.

The picrate melts at 145–147°. Knorr gives the melting point of the picrate as 145–147°. N-(2-Chlorocinchoninyl)-morpholine was used for the analysis.

Anal. Calcd. for $C_{14}H_{13}ClN_2O_2$: N, 10.13. Found: N, 10.07.

ORGANIC CHEMISTRY LABORATORY
UNIVERSITY OF FLORIDA
GAINESVILLE, FLORIDA
RECEIVED AUGUST 20, 1936

Alkylation of Aromatics with Olefins in the Presence of Boron Fluoride[1]

BY V. N. IPATIEFF AND A. V. GROSSE

In the course of our investigations on hydrocarbon reactions in the presence of metallic halides[2] the alkylation of aromatic hydrocarbons with olefins in the presence of boron fluoride was also accomplished. This fact is interesting in connection with recent similar work of Nieuwland[3] in which the addition of acids, especially sulfuric acid, was considered to play an important part in these condensations.

As has been recently shown in our laboratories[4] the sulfuric acid *per se* is an excellent alkylating catalyst under the conditions used by Nieuwland and the presence of boron fluoride is not necessary. On the other hand, boron fluoride *without acids* is *also* an alkylating catalyst.[5]

The alkylation of aromatic hydrocarbons with olefins, including ethylene,[6] takes place in the presence of boron fluoride in a *nickel-lined*[7] autoclave at room temperature and also at temperatures up to 250°.

In one particular experiment 250 cc. (219 g.) of benzene was treated in a rotating nickel-lined bomb with ethylene in the presence of 18.5 g. of boron fluoride and 2.0 g. of water for eight hours at 20–25°. The initial ethylene pressure was 20 atmospheres, which dropped readily to 10 atmospheres when fresh ethylene was pressed in. In all five refillings were made and 22 g. of ethylene was absorbed.

The reaction product, after washing and drying, was separated into the following fractions:

Charge, 250.0 cc.

Fraction	Boiling points at 760 mm., °C	Volume in cc.	% of total product	$n^{20.0}D$	Remarks: (All fractions water white and stable to $KMnO_4$ solution)
1	80 ± 1.5	180.0	72.0	1.5002	Pure benzene, solidifies in ice
2	81.5–135	1.0	0.4	1.4985	
3	136 ± 1	52.0	21.0	1.4960	Monoethyl benzene; $d^{20.0}_4$ 0.8674
4	137–182	3.5	1.5	1.4958	
5	183 ± 1	7.5	3.0	1.4974	Diethylbenzenes
Bottoms	>184	4.0	1.6	1.5032	
Losses		2.0	0.8		
Total		250.0	100		

As can be seen from these results over 25% of the benzene was alkylated to monoethyl-, diethyl and higher alkylbenzenes. The constants of our monoethylbenzene (see table) are in complete agreement with the values given in the literature (see "I. C. Tables," boil. point at 760 mm. 136°, $n^{20}D$ 1.4959, $d^{20.0}_4$ 0.8669). As a further check oxidation with boiling potassium permanganate solution gave only *benzoic acid,* melting at 122.0°, proving the absence of xylenes.

---

(1) Announced by V. N. Ipatieff before the Organic Section of the American Chemical Society at the Kansas Meeting on April 22, 1936.

(2) V. N. Ipatieff, A. V. Grosse and co-workers, THIS JOURNAL, **57**, 1616, 1722, 2415 (1935); **58**, 913, 915 (1936); *Ind. Eng. Chem.*, **28**, 461 (1936).

(3) S. J. Slanina, F. J. Sowa and J. A. Nieuwland, THIS JOURNAL, **57**, 1547 (1935).

(4) V. N. Ipatieff, B. B. Corson and H. Pines, *ibid.*, **58**, 919 (1936).

(5) For alkylations of paraffins, see Ref. 1, p. 1616.

(6) As contrasted to the actions of sulfuric acid, see Ref. 3.

(7) For the role of nickel, see Ref. 1, pages 1617 and 1618.

UNIVERSAL OIL PRODUCTS CO.
RIVERSIDE, ILL.
RECEIVED JULY 22, 1936

Thermal Type Silver–Silver Chloride Electrodes

BY C. K. RULE AND VICTOR K. LA MER

In connection with an investigation of the temperature coefficients of the e. m. f. of quinhydronesilver chloride cells in deuterium oxide, we have tested the reliability of silver–silver chloride electrodes made by a thermal method analogous to that recommended by Owen[1] and by Keston,[2] respectively, for the corresponding iodide and bromide electrodes. An electrode formed from a coil of platinum wire sealed into a tube of Jena normal glass was covered with a paste composed of seven parts of silver oxide and one part of silver chlorate and heated to decomposition in an electric furnace. No appreciable differences were observed when the percentage of silver chlorate was varied between 8 and 15.

Twelve electrodes immersed in 0.01 *M* hydrochloric acid solution exhibited ±0.02 mv. as the average deviation from the mean. After standing for six weeks this value increased to not more than ±0.04 mv. Freshly made electrodes agreed with the old within this limit.

A comparison of the "thermal" type electrodes with those made by decomposing a paste of silver oxide by heat and then electrolyzing for five hours in 0.2 *M* hydrochloric acid solution at 1.8 milliamperes per electrode showed that the electrolytic type tended to drift and were on the average about 0.04 mv. more positive.

CHANDLER LABORATORY
COLUMBIA UNIVERSITY
NEW YORK, N. Y.

RECEIVED OCTOBER 6, 1936

---

[1] Owen, THIS JOURNAL, **57**, 1526 (1935).

[2] Keston, *ibid.*, **57**, 1671 (1935).

The Heat of Fusion of Stannic Iodide

BY SAMUEL S. TODD AND GEORGE S. PARKS

The changes in heat content of stannic iodide were measured by us in 1928 for the temperature intervals between 27 and 80, 120, 155 and 171°, respectively. A method of mixtures was used with a water calorimeter, the details of the apparatus and experimental procedure being given in a previous paper by Parks and Todd.[1] The sample of stannic iodide studied had been kindly prepared for us by Professor J. H. Hildebrand.

Although the error in the calorimetric measurements themselves was within 1%, considerable uncertainty as to the premelting effect in the crystalline material precluded at that time a reliable calculation of the heat of fusion of stannic iodide from our heat content data. Recently, however, Negishi[2] has obtained accurate information concerning the heat capacities of solid and liquid stannic iodide over a range of temperatures. Using his data and taking the melting point as 144°, we have now calculated the following fusion values from our four determinations pertaining to the 27–155° range: 7.23, 7.19, 7.24 and 7.25 cal. per gram. The mean heat of fusion is 7.23 (±0.14) cal. per gram or 4530 cal. per mole.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY, CALIFORNIA

RECEIVED SEPTEMBER 2, 1936

---

[1] G. S. Parks and S. S. Todd, *Ind. Eng. Chem.*, **21**, 1235 (1929).

[2] G. R. Negishi, THIS JOURNAL, **58**, 2293(1936). Prof. J. H. Hildebrand kindly sent us these essential data prior to publication.

NEW BOOKS

Physical Aspects of Organic Chemistry. By WILLIAM A. WATERS, M.A., Ph.D. (Cantab.), University of Durham. Introduction by Professor T. Martin Lowry, George Routledge and Sons, Ltd., Broadway House. 68–74 Carter Lane, London E.C., England, 1935. xv + 501 pp. 14 × 22 cm. Price, 25s.

The title of this book does not indicate very clearly the nature of its contents. Actually it is largely concerned with current electronic ideas of valence and their application to organic chemistry, especially to details of reaction mechanism. The chapter headings are: Chemical Affinity, Physical Theories of Molecular Structure, Valency, Electrical Dipoles, Chemical Reactivity, Unsaturation, Free Radicals and Their Non-ionic Reactions, Ionization and Ionic Reactions, Acidity, The Reactivity of Halogen Compounds, General Polarity, Hydrolysis and Esterification, Ionotropic Change, Molecular Rearrangement, Conjugation, Aromatic Compounds—I, Aromatic Compounds—II.

But this list does not furnish an adequate indication of the range of topics dealt with. Many of these subjects are exceedingly broad, have a lengthy and complicated history and even today have not reached any state of agreed opinion. One is therefore especially impressed with the skill of presentation. The author states in his preface: "The historical aspect of a rapidly developing subject has been kept continually in view, with the intention of giving a general outline of theoretical organic chemistry rather than