# 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.

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[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).

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## 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

$$\log k^0 - \log k_*{}^0 = \frac{\epsilon^2 \mathbf{Z}_A \mathbf{Z}_B}{2.3''k''Ta} \left[\frac{1}{D_*} - \frac{1}{D}\right] \qquad (1)$$

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[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 $k^0$s 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

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

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.

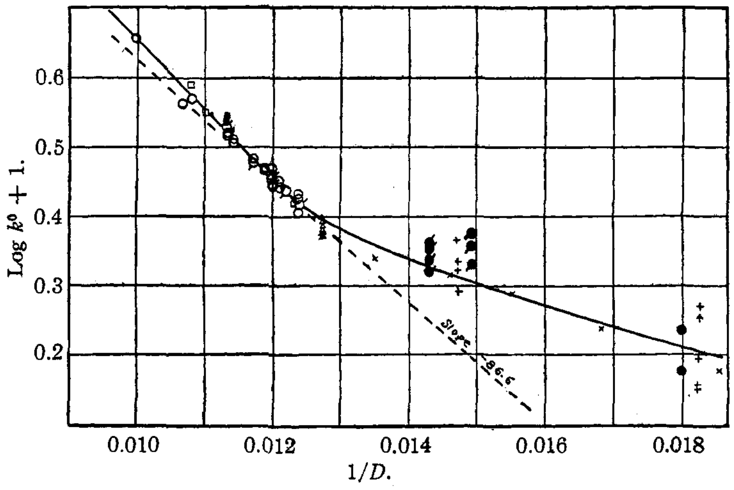

Fig. 1.—$S_2O_3^=$ + $BrAc^-$ at 25°: Kappanna— + $C_2H_5OH$-$H_2O$, ●, sucrose-$H_2O$; La Mer and Kamner—▲, $H_2O$; ■, urea-$H_2O$, ●, glycerol-$H_2O$, ●-, sucrose-$H_2O$; Straup and Cohn—△, $H_2O$, ○, glycine-$H_2O$, ○-, α-alanine-$H_2O$, -○, β-alanine-$H_2O$, □, urea-$H_2O$ × $C_2H_5OH$-$H_2O$.

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.

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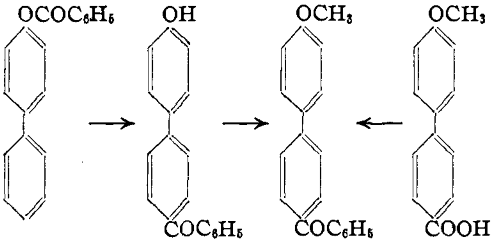
## The Fries Rearrangement of 4-Benzoyloxydiphenyl

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

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[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).