

## 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.<sup>1</sup> 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<sup>2</sup> 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<sup>3</sup> 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.<sup>4</sup> 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.

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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<sup>1-3</sup> 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<sup>4</sup> than is implied in the most recent paper.<sup>3</sup> 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

$$\log k^0 - \log k_*^0 = \frac{e^2 Z_A Z_B}{2.3 k^* T a} \left[ \frac{1}{D_*} - \frac{1}{D} \right] \quad (1)$$

(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).

(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).