

## NOTES

## 6-Methyl-5,8-quinoline Quinone

BY W. G. CHRISTIANSEN AND M. A. DOLLIVER

In the course of an investigation of compounds having antihemorrhagic activity, 6-methyl-5,8-quinoline quinone has been prepared. According to the method of Nolting and Trautmann,<sup>1</sup> 6-methylquinoline was converted to 5-hydroxy-6-methylquinoline. This, in turn, was coupled with diazotized sulfanilic acid, and the product reduced with stannous chloride to the amine which was oxidized to the quinone by means of potassium dichromate as in the method for the preparation of quinoline quinone reported by O. Fischer and E. Renouf.<sup>2</sup>

6-Methyl-5,8-quinoline quinone is obtained as yellow needles, m. p. 167–168° (uncor.), from benzene-petroleum ether mixture. It is readily soluble in dilute hydrochloric acid and gives a positive Craven test<sup>3</sup> for quinones.

*Anal.* Calcd. for C<sub>10</sub>H<sub>7</sub>O<sub>2</sub>N: C, 69.4; H, 4.1. Found: C, 69.4; H, 4.2.

Biological tests<sup>4</sup> showed that the compound had low, if any, antihemorrhagic activity.

- (1) Nolting and Trautmann, *Ber.*, **23**, 3564 (1890).  
 (2) O. Fischer and E. Renouf, *ibid.*, **17**, 1642 (1884).  
 (3) Craven, *J. Chem. Soc.*, 1605 (1931).  
 (4) Ansbacher, *Proc. Soc. Exp. Biol. Med.*, in press.

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## Electric Moments of the Mercuric Halides in Dioxane. A Correction

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Dielectric constants of solutions of the mercuric halides in 1,4-dioxane were measured a few years ago in this Laboratory. The values reported<sup>1</sup> for the electric moments were, in Debye units, 1.29, 1.06, and 0.58 for the chloride, bromide and iodide, respectively. These values were calculated with the aid of the electronic polarizations, 30.36, 55.30 and 94.28, reported by Bergmann and Engel<sup>2</sup> for the halides in benzene solution. It is now evident that these values of the molar refractions are far too large. They are

- (1) Curran and Wenzke, *THIS JOURNAL*, **57**, 2162 (1935).  
 (2) Bergmann and Engel, *Z. physik. Chem.*, **13B**, 247 (1931).

much greater than the total polarizations of the mercuric halides in the vapor state reported by Braune and Linke.<sup>3</sup> Consistent with these values of the total polarizations are the molar refractions listed by Fajans<sup>4</sup> for mercuric chloride, bromide, and iodide in the vapor state, and for the chloride and bromide in water solution. As the solution values are slightly lower than the refractions in the vapor state, and as the former are needed to calculate the electric moments of the halides in solution, the molar refraction of mercuric iodide in dioxane has been determined. The data obtained are listed in Table I.

TABLE I

INDICES OF REFRACTION, DENSITIES AND MOLAR REFRACTIONS OF SOLUTIONS OF MERCURIC IODIDE IN DIOXANE AT 25°

$c_2$	$n_D$	$d$	$MR_{12}$	$MR_2$
0.00000	1.41966	1.0273	21.699	
.01146	1.42539	1.0775	21.933	42.1
.01167	1.42546	1.0785	21.934	41.8
.01201	1.42566	1.0798	21.947	42.3

The average value for the molar refraction of mercuric iodide calculated from the data of Table I is 42.1. This is somewhat lower than the value reported by Fajans for the vapor, 44.76. The electric moments of the mercuric halides have been recalculated from the solute polarizations at infinite dilution previously reported<sup>1</sup> with the aid of the new value for the molar refraction of mercuric iodide and the values reported by Fajans for the chloride and bromide in water solution. The corrected moments are listed in Table II.

TABLE II

POLARIZATIONS, MOLAR REFRACTIONS AND ELECTRIC MOMENTS AT 25°

	$P_\infty$	$MR_D$	$\mu$
Mercuric chloride	65.0	22.9	1.43
Mercuric bromide	78.6	30.1	1.53
Mercuric iodide	101.4	42.1	1.67

The dielectric constants of the mercuric halides in the vapor state<sup>3</sup> reveal that these molecules are linear. The electric moments of the halides in dioxane listed in Table II indicate a non-linear configuration. This is probably due to the formation of O-Hg dipole-dipole bonds, similar

- (3) Braune and Linke, *ibid.*, **31B**, 12 (1935).  
 (4) Fajans, *Z. Elektrochem.*, **34**, 517 (1928).

to the ion-dipole bonds between oxygen and metal cations in hydrates. The formation of these bonds results in steric repulsion between the methylene groups of dioxane and the halogen atoms, forcing the mercury to assume a valence angle less than 180°. This steric effect is greatest for mercuric iodide; this molecule has the smallest mercury valence angle and therefore the largest electric moment. Further evidence for this type of bonding will be presented in a paper on the electric moments of some organomercuric halides to be published<sup>5</sup> shortly.

**Experimental**

The refractive indices listed in Table I were determined with a Pulfrich refractometer. The densities were measured with an Ostwald-Sprengel pycnometer of approximately 5 ml. capacity. Commercial 1,4-dioxane was refluxed over sodium and distilled through a Widmer column in an all-glass still. Merck U. S. P. mercuric iodide was heated to remove moisture before making up solutions. The concentrations were limited by the low solubility of mercuric iodide in dioxane. This solvent was used because, with the exception of methylene iodide, it is better than any of those listed by Bell.<sup>6</sup>

(5) Presented before the Physical and Inorganic Division at the Cincinnati Meeting of the American Chemical Society, April, 1940.  
 (6) Bell, *J. Chem. Soc.*, 1381 (1931).

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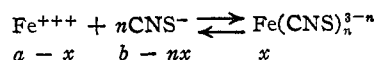
**Ferric Thiocyanate**

BY SYLVAN M. EDMONDS AND NATHAN BIRNBAUM

For some time we have been conducting a photometric study of the equilibrium involved in a ferric thiocyanate solution. Unaware of the work of Bent and French,<sup>1</sup> we have duplicated many of their measurements using a high precision balance type photoelectric colorimeter similar to that described by Withrow, Shrewsbury and Kraybill.<sup>2</sup> It seems worth while, nevertheless, to record here some of our results and to call attention to a rather striking series of experiments which differ from those of Bent and French and also point rather conclusively to the existence of the FeCNS<sup>++</sup> ion. Measurements were made at unit ionic strength (1 M perchloric acid) of mixtures of ferric perchlorate and ammonium thiocyanate. In this way the effect of hydrolysis can be ignored and the complicating factor of chloride ion is absent. Writing the equation for the reac-

(1) Bent and French, *THIS JOURNAL*, **63**, 568 (1941).  
 (2) Withrow, Shrewsbury and Kraybill, *Ind. Eng. Chem., Anal. Ed.*, **8**, 214 (1936).

tion between ferric ion and thiocyanate in the general form



we have

$$\frac{(a-x)(b-nx)^n}{x} = K \tag{1}$$

By confining measurements to conditions where  $b \gg a$  or  $x$  this simplifies to

$$\frac{(a-x)b^n}{x} = K$$

For a fixed cell length and concentration of ferric ion  $a$ ,  $K$  may be evaluated from any two measurements of the transmission by simultaneous solution of the two equations

$$(a-x)b^n/x = (a-y)d^n/y$$

and

$$y/x = \log I_y / \log I_x$$

whence

$$K = \frac{b^n d^n (\log I_y - \log I_x)}{d^n \log I_x - b^n \log I_y}$$

By selecting  $n = 1$ , reasonably reproducible values for  $K$  were obtained, *viz.*,  $K = 0.0079 \pm 0.0006$ . This is as good as can be expected considering the difference method employed in its calculation. Higher values for  $n$  yield values for  $K$  which vary by several hundred per cent. for small changes in  $a$  or  $b$ .

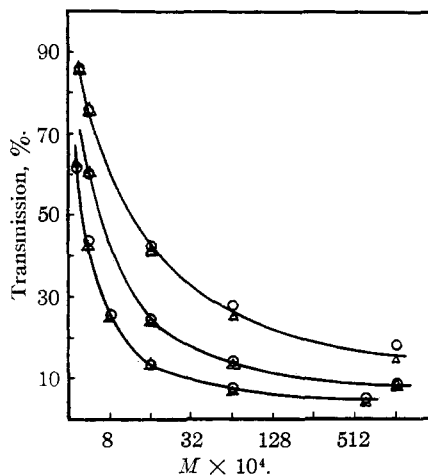


Fig. 1.—Circles indicate CNS<sup>-</sup> and triangles Fe<sup>+++</sup> when the other ion concentration is  $5 \times 10^{-4}$  for upper curve,  $10^{-3}$  for middle curve and  $2 \times 10^{-3}$  for the lower.

In Fig. 1 are shown three series of measurements wherein at a given fixed concentration of ferric or thiocyanate ion the per cent. transmission for a constant cell length is plotted against the other ion concentration. It will be noted that