

## The Sulphuric Acid Solvent System: A Conductometric Investigation of Solutions of 1,1'-Dianthrimide

R. T. ARNESEN and F. J. LANGMYHR

*Chemical Institute A, University of Oslo, Blindern, Oslo 3, Norway*

A number of papers have been published on the complex formation and the quantitative determination in concentrated sulphuric acid of boron, selenium(IV), tellurium(IV), and germanium with various dianthrimides. In connection with these investigations it was considered of interest to obtain some information on the species formed when dianthrimides are dissolved in sulphuric acid or concentrated sulphuric acid.\*

The present paper describes a conductometric study of solutions of 1,1'-dianthrimide in sulphuric acid.

*Experimental.* The conductometric measurements were made with a Philips measuring bridge PR 9500. The special cell employed was similar to that previously described by Gillespie and Wasif.<sup>1</sup>

During measurement the cell was kept in water, the temperature of the water being adjusted to  $25.0 \pm 0.1^\circ\text{C}$  with the use of a thermostat. The 1,1'-dianthrimide (Fluka AG., Switzerland), concentrated sulphuric acid (95–97%), fuming sulphuric acid (about 15% of sulphur trioxide) and other chemicals were of reagent grade quality. Water from an ion exchange column (Research Model, Illinois Water Treatment Co., U.S.A.) was used.

*Determination of the cell constant.* The cell constant was determined with a solution of potassium chloride. Before use the salt was recrystallized from water and dried to constant weight at  $400^\circ\text{C}$ . 3.7285 g were weighed out, transferred to a 500 ml volumetric flask and dissolved in water. The solution was diluted to volume with water. According to Jones and Bradshaw<sup>2</sup> this solution has a specific resistance of 77.78 ohm cm.

\* In accordance with accepted practice 100% sulphuric acid is designated sulphuric acid, while acids of lower strength are designated concentrated sulphuric acid.

*Measurements on the sulphuric acid-water system.* 330.0 g of an acid of strength just above 100% were weighed out in the reservoir of the cell, the temperature was adjusted and the specific conductance was measured. Water was then added in small increments, the specific conductance being measured after each addition. From the resulting concentration specific conductance curve the minimum value was found to correspond to  $(1.05 \pm 0.01) \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ , a value which compared favourably with the precision value of Gillespie, Oubridge and Solomons<sup>3</sup>  $-1.0432 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$  ( $25^\circ\text{C}$ ).

*Measurements on the sulphuric acid – 1,1'-dianthrimide system.* Before each series of measurements 100% sulphuric acid was prepared by adding water to a slightly fuming acid until the specific conductance was  $(1.05 \pm 0.01) \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ .\* An amount of 1,1'-dianthrimide was weighed out and transferred to the reservoir of the cell. After dissolution and adjustment of the

\* As demonstrated by Gillespie, Oubridge and Solomons<sup>3</sup> the minimum in specific conductance does not correspond exactly to 100% acid. This difference is, however, too small to be detected by the present instrument.

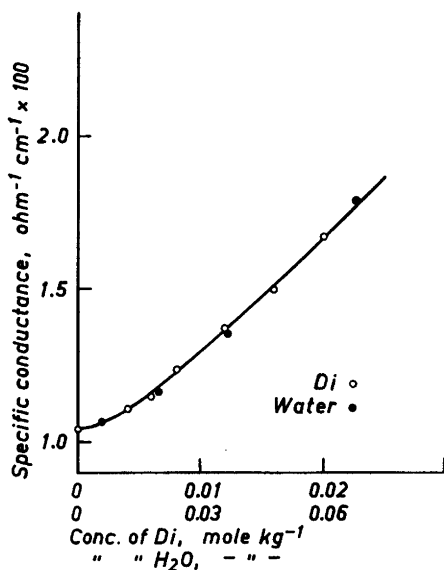


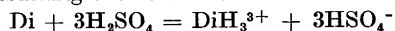
Fig. 1. Specific conductance of solutions of water and of 1,1'-dianthrimide in sulphuric acid. Temperature  $25.0 \pm 0.1^\circ\text{C}$ .

temperature, the specific conductance was measured. New weighed portions were added and dissolved, the specific conductance being measured after each addition.

**Results and discussion.** The experimental data are shown in Fig. 1 which gives the specific conductance as a function of the molality of the solutions of water and 1,1'-dianthrimide (Di). To facilitate comparison the concentrations of the latter reagent were divided by three.

From previous work on the sulphuric acid solvent systems it is known that many organic substances, *e.g.* anthraquinone, behave as bases,<sup>4</sup> that water is completely ionized,<sup>5</sup> and that the conductance of solutions of substances reacting as bases is mainly due to the  $\text{HSO}_4^-$  ions formed by the protolytic reaction.<sup>6</sup>

From Fig. 1 it is seen that one molecule of 1,1'-dianthrimide produced a conductance corresponding to three molecules of water. This result was explained by assuming the reaction



For solutions of anthraquinone in sulphuric acid Hammett and Deyrup<sup>4</sup> showed that one molecule of both reagents participated in the protolytic reaction, the proton being attached to one of the carbonyl groups.

In the present system it was considered as highly probable that two of the three protons were attached to two of the four carbonyl groups, and that the third proton was attached to the imino group.

Previous authors<sup>7</sup> have noted that the colour of solutions of 1,1'-dianthrimide changed by varying the strength of concentrated sulphuric acid. In acids of low strength the solutions were but faintly coloured, while in strong acid they were green, the intensity of the colour increasing with the strength of acid.

This change may be explained by assuming that the first proton is taken up by the most basic group, the imino group, and that the resulting ion only produces a faint colour. By increasing the strength of the acid additional protons are taken up by the chromophore carbonyl groups, this resulting in strongly coloured solutions.

1. Gillespie, R. J. and Wasif, S. *J. Chem. Soc.* **1953** 204.
2. Jones, G. and Bradshaw, B. C. *J. Am. Chem. Soc.* **55** (1933) 1780.

3. Gillespie, R. J., Oubridge, J. V. and Solomons, C. *J. Chem. Soc.* **1957** 1805.
4. Hammett, L. P. and Deyrup, A. J. *J. Am. Chem. Soc.* **55** (1933) 1900.
5. Gillespie, R. J. and White, R. F. M. *Can. J. Chem.* **38** (1960) 1371.
6. Hammett, L. P. and Lowenheim, F. A. *J. Am. Chem. Soc.* **56** (1934) 2620; Gillespie, R. J. and Wasif, S. *J. Chem. Soc.* **1953** 209.
7. Langmyhr, F. J. and Skaar, O. B. *Anal. Chim. Acta* **23** (1960) 28.

Received November 6, 1964.

### 3-Piperidino-Chromanone-(4)

PETER W. FEIT

*Leo Pharmaceutical Products, Ballerup, Denmark*

Earlier, Colonge and Guyot<sup>1</sup> described the reaction of 3-bromochromanone-(4) (I) with piperidine resulting in a yellow solid with m.p. 117°, and suggested it to be 3-piperidino-chromanone-(4) (III). This reaction has been reinvestigated. The isolated compound was not III, but was shown by its melting point (122–122.5°), ultraviolet and infrared spectra to be identical with *o*-hydroxy- $\beta$ -piperidino-acrylophenone (II) obtained according to Winter and Hamilton<sup>2</sup> after treatment of chromone with piperidine. It can therefore

