

### III.—*The Velocity of Interaction of Iodic and Sulphurous Acids in Various Media.*

By THOMAS STEWART PATTERSON and WILLIAM COLLINS FORSYTH.

IN connexion with the experiments detailed in the preceding paper, we thought it would be of interest to examine some other type of reaction, and chose, as one perhaps allowing of very simple observation, the well known experiment of Landolt on the reduction of iodic acid by sulphurous acid (*Ber.*, 1886, **19**, 1340; 1887, **20**, 745). Dilute solutions of these reagents are mixed, a small quantity of starch solution being present, and after the lapse of a definite time, depending on the concentration of the solutions and the temperature, a blue colour suddenly appears, due to the action of the liberated iodine on the starch. Landolt himself made some experiments regarding the influence of added inactive substances, and found that acids—sulphuric, hydrochloric, oxalic, acetic—hasten the reaction the more the greater is the affinity constant of the acid. Sodium chloride and ammonium chloride were also found to accelerate the reaction, but to a less extent. Similarly, alcohol in the proportion of 7 to 3 of water in the solution reduced the time necessary for the appearance of the blue colour from 102.2 secs. to 90.4 secs. He says that the influence of alcohol is thus not great, and that he was unable to find a liquid which definitely retarded the velocity of the reaction.

For the following experiments our reagents were made as follows: Of a saturated solution of sulphur dioxide, 50 c.c. were diluted to a litre, whilst 10 grams of iodic acid were dissolved in 1 litre of water. For an experiment, 10 c.c. of sulphur dioxide solution were first mixed with 2 c.c. starch solution, and to this were added 100 c.c. of diluent, water, for example. To this mixture 10 c.c. of iodic acid solution were quickly added, the temperature being about 20° in all cases. In the above instance the blue colour flashed out in nineteen seconds. In other experiments, instead of the 100 c.c. of water, 100 c.c. of pure methyl, ethyl, *n*-propyl alcohol, or acetone, or mixtures of these with water in known proportions were added. The colour which appeared in the solution was blue or yellow, according to the proportion of neutral solvent added.

In the case of methyl alcohol the following results were obtained:

Percentage of methyl alcohol in 100 c.c. of added diluent.	Time.
0	19 seconds
50	9    "
100	2    "

It thus appears that the addition of methyl alcohol hastens this reaction very considerably, and practically in direct proportion to the quantity of alcohol added. It was then found that ethyl and *n*-propyl alcohol behaved in a manner quite similar to methyl alcohol, the accuracy of the method of investigation being insufficient to detect any distinct variation.

On the addition of acetone the results were somewhat different, as the following table shows:

Percentage of acetone in 100 c.c. of added diluent.	Time.
0	19 seconds
25	23 "
50	24 "
60	20 "
75	15 "
100	3 "

The velocity of the reaction increases at first as the proportion of acetone increases up to about 50 per cent., to diminish again rapidly thereafter.

It is not possible much to extend the examination of this reaction, since the solvents used must (1) be neutral or acid, and (2) be miscible with water, two conditions which considerably limit the number of available liquids. In addition, although the reaction is one which can be timed fairly accurately, the variation in colour of the starch iodide and also the complexity of the whole reaction render the results at least difficult of interpretation.

We need only remark that an increase in the velocity of a reaction, on the addition of a neutral solvent, to reach a maximum has been observed in numerous cases; thus, Dawson (Trans., 1911, **99**, 1) found the reaction between iodine and acetone with a little sulphuric acid in presence of ethyl alcohol to be very greatly reduced by the addition of small quantities of water, whilst Tubandt (*Annalen*, 1907, **354**, 259) has recorded a somewhat similar observation in regard to the inversion of menthone. For other references Dawson's paper should be consulted.

ORGANIC CHEMISTRY DEPARTMENT,  
UNIVERSITY OF GLASGOW.