with the normal molybdate is practically non-existent in the system Na_2MoO_4–MoO_3–H_2O at 25°. The isothermally invariant solution in equilibrium with both solid phases is in fact practically coincident with the point representing the aqueous solubility of the pure normal molybdate. This solution contained no detectable concentration of molybdic oxide, and had the composition, therefore, of 0.00% MoO_3 and 39.48% Na_2MoO_4.

The second solid phase listed in Table II, the hydrated dimolybdate, was a fine white solid which settled slowly to form a milky mass. By graphical estimation of the intersection of the tie-lines in this region, it was evident that the solid was either the hexa- or the pentahydrate of $Na_2Mo_2O_7$. The intersections of these tie-lines with the line representing the ratio of Na_2MoO_4 to MoO_3 corresponding to the dimolybdate, were calculated by suitable simultaneous equations, in terms of the percentage of water at the point of intersection (last column of Table II). The nine tie-lines involved gave an average water content for the solid phase of 22.7%, to be compared with the theoretical values of 23.60 for the hexahydrate and 20.47 for the pentahydrate. These results show the hexahydrate to be the more probable formula, but they cannot be called conclusive.

This salt was reported as hexahydrated by Rosenheim,[6] who presented analytical figures in support of it, and as pentahydrated by Frey (Soubarew-Châtelain),[7] with no supporting data. Bye,[5,8] most recently, again gives the hexahydrate formula, as established by analysis of the separated solid phase and by the method of wet residues; no experimental data for either of the methods, however, are given in his article. The present observations may be taken as adding evidence for the formula of the salt as a hexahydrate.

---

(6) Rosenheim, *Z. anorg. allgem. Chem.*, **96**, 143 (1916).

(7) Frey (Soubarew-Châtelain), *Compt. rend.*, **211**, 503 (1940); **208**, 1153 (1939).

(8) The article by Bye (ref. 5), reporting an almost complete study of the system Na_2O–MoO_3–H_2O at 24°, and including therefore the portion of the system Na_2MoO_4–MoO_3–H_2O here described, came to our attention only after the present article was written and, in fact, ready for printing.

DEPARTMENT OF CHEMISTRY
NEW YORK UNIVERSITY
NEW YORK, N. Y.

RECEIVED MAY 10, 1944

Measurement of the Rate of Reaction of Potassium Iodide with Organic Chlorides in Dilute Acetone Solution

BY KENNETH L. SENIOR, RICHARD R. HETRICK AND JOHN G. MILLER

Recently[1] the rates of reaction of certain organic chlorides with potassium iodide in dilute acetone solution were measured by the analytical procedure based on the Andrews titration method as established for such reactions by Conant and co-workers.[2] At dilutions where the total concentration of reactants was less than 0.125 molar, the specific rates showed an irregular increase in value with increasing dilution. This behavior could not be attributed satisfactorily to salt or medium effects. Although the possibility of interference by acetone in the titration was recognized, this appeared unlikely especially in view of the constancy of each specific rate value measured over a wide range of reaction times.

Further investigation of the problem is reported here, using benzyl chloride as organic chloride. The same behavior of the specific rate values was obtained, when using the Andrews procedure, as reported in the previous study.

The reliability of the analytical procedure was then tested by analyzing a carefully prepared solution of potassium iodide by the Andrews, the permanganate,[3] and the Volhard methods. In the absence of acetone the results for each of the methods, run in triplicate, were within 0.1% of the theoretical. On repeating the analyses with addition of various amounts of acetone, the results obtained with the Andrews and permanganate methods varied as much as 25% from the theoretical, even though the values obtained by these two methods were in close agreement. The presence of acetone did not cause any appreciable error in the Volhard method.

While no complete study was made of the nature of the interference by the acetone, it was evident that a large part of the acetone dissolves in the chloroform and that when the acetone is present in large amount the sensitivity of the chloroform layer as an indicator for free iodine is impaired. Thus the end-point of the Andrews titration, shown by the absence of iodine color in the chloroform layer, is reached too soon and in the rate measurements a low estimate of the amount of unreacted iodide is obtained, causing an erroneous and high value of the specific rate. For higher iodide concentrations the error will be negligible and there the method has proved successful in rate studies. The irregularity in the behavior of the specific rate values for the dilute solutions is probably due to the differences in the amount of acetone present in the samples titrated and the differing concentrations of the iodate solutions used.

The interference of the acetone was further demonstrated by using the aqueous layer as an indicator. It had been observed that after the chloroform layer had become colorless, the water layer still showed a fleeting brownish-yellow color of iodine upon addition of more iodate or permanganate. Taking the point at which further addition of iodate produced no fleeting brownish-yellow color in the aqueous layer as the end-point gave specific rate values which were in very

---

(1) Skolnik, Day and Miller, THIS JOURNAL, **65**, 1858 (1943).

(2) Conant and Kirner, *ibid.*, **46**, 232 (1924); Conant and Hussey, *ibid.*, **47**, 476 (1925).

(3) Kolthoff, Laitinen and Lingane, *ibid.*, **59**, 429 (1937).

good agreement with values reported for higher concentrations. Results of a typical experiment are shown in Table I. In this experiment the molarity of the potassium iodate was 0.00475, the original concentrations of potassium iodide and benzyl chloride were 0.01331 *M* and 0.06655 *M*, respectively, and the temperature was 25.00 ± 0.01°. The data reported by Conant and coworkers[2] for this reaction at 25° and for the concentration range of 0.0134 *M* to 0.04 *M* in potassium iodide and 0.0667 *M* to 0.20 *M* in benzyl chloride yield values of *k* varying from 1.64 to 1.97.

TABLE I

Time, hours	KIO_3, ml.	*k*
0	11.00	..
1.00	9.65	1.99
1.00	9.62	2.04
2.00	8.55	1.94
2.00	8.53	1.95

Since detection of the fleeting and yellow color is very difficult, starch was tried as indicator. The blue coloration produced under the conditions of this analysis was transient also, but much easier to discern than the yellow color. The results obtained with starch agreed very well with those reported in Table I.

Finally, the Andrews titration may be replaced successfully by a potentiometric titration. The cell was prepared by placing a platinum and a normal calomel electrode in a mixture of 25 ml. of distilled water, 25 ml. of concentrated hydrochloric acid and 20 to 25 g. of crushed ice. The vessel was then placed in a large ice-bath to maintain constant temperature during the titration. The solution to be analyzed was added to the cell and titrated potentiometrically with potassium iodate solution. Thorough stirring was needed to establish equilibrium after each addition of iodate. The end-point of the titration was determined by the sharp rise in potential occurring at the end-point of the reaction $KIO_3 + 2KI + 6HCl \rightarrow 3ICl + 3KCl + 3H_2O$. Tests of the method were made with known amounts of potassium iodide both in the absence and presence of acetone and with or without addition of benzyl chloride. The analyses checked to within 0.05% of the correct value.

Table II shows values of the specific rate of the benzyl chloride reaction obtained at 25° in an experiment in which the Andrews titration, using the aqueous layer as indicator, and the potentiometric method were both used. The value marked (starch) is the one obtained in the Andrews titration, starch being added to aid detection of the end-point. The potassium iodate was 0.00475 *M* and the reaction mixture was 0.0354 *M* in potassium iodide and 0.177 *M* in benzyl chloride. Numerous other runs were made, showing that the potentiometric method is fairly accurate in the dilute solution measurements.

TABLE II

Time, hours	KIO_3, ml.	*k*
0	22.40	..
1.00	16.30	1.86 (starch)
1.00	16.35	1.83
2.00	11.65	1.95

It is clear that although reliable rate data may be obtained by the Andrews method for this reaction at higher concentrations, this method must be modified or replaced in work with dilute solutions.

THE DEPARTMENT OF CHEMISTRY AND
CHEMICAL ENGINEERING
UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA, PENNSYLVANIA
RECEIVED MAY 5, 1944

Studies on Oxythiamine

BY MORRIS SOODAK AND LEOPOLD R. CERECEDO

The synthesis of oxythiamine has been reported by Bergel and Todd[1] and by Slobodin and Ziegel.[2] The former workers obtained a product which in doses of 1 mg. showed no antineuritic activity when assayed by the bradycardia method. The substance prepared by Slobodin and Ziegel was found to have only 0.5% of the activity of thiamine when tested on pigeons.

We have prepared oxythiamine by deamination of thiamine with nitrous acid. The procedure was as follows: The nitrous acid gas was generated in a flask which was open to the atmosphere through a small aperture, by the gradual addition (four to six hours) of an excess of 18% HCl to 20–30 g. of sodium nitrite. It was then passed under slight suction through a solution of 4 g. of thiamine hydrochloride in 25 cc. of water. When the thiochrome test indicated that 97–98% of the thiamine had disappeared (occasionally more nitrous acid was required), the solution was evaporated *in vacuo* until an oil was obtained. After addition of a few cc. of 95% ethyl alcohol, the solution was evaporated once more. The oil was dissolved in 75 cc. of absolute ethyl alcohol and to the solution ether added until precipitation was complete. The precipitate was taken up in 75 cc. of absolute ethyl alcohol and dry hydrogen chloride gas passed through the solution for about an hour. Heat was generated, and a white crystalline product was deposited. After cooling, the precipitate was washed with absolute ethyl alcohol and dried. A material melting at 195–200° was obtained. An additional crop of crystals separated out upon addition of absolute ether to the mother liquor. The yield varied between 50 and 70%.

Anal. Calcd. for $C_{12}H_{17}O_2N_3Cl_2S$: C, 42.60; H, 5.00; N, 12.43. Found[3]: C, 42.29; H, 4.97; N, 12.69.

---

[1] Bergel and Todd, *J. Chem. Soc.*, 1504 (1937).

[2] Slobodin and Ziegel, *J. Gen. Chem.* (U. S. S. R.), **11**, 1019 (1941).

[3] 1 mg. of oxythiamine has been found to contain between 1 and 4 μg. of thiamine.