LXII.—*The Period of Induction of the Reaction between Ammonium Sulphide and Formaldehyde Solutions.*

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WHEN an aqueous solution of formaldehyde is added to ordinary yellow ammonium sulphide solution, the mixture first becomes colourless, then evolves heat, and finally, after a definite induction period, deposits a white and frequently slightly gummy precipitate. A colourless solution of ammonium hydrogen sulphide shows the last two effects. The new substance, after isolation and purification by thorough washing with hot water and air-drying, is usually a faintly yellow, amorphous powder, m. p. (vague) 150—200°, having a characteristic odour (especially on volatilisation), and is not soluble without decomposition in any common solvent or in dilute acid.

Constitution.—As a test for individuality, four samples were prepared for analysis, the conditions being as follows: (1) from concentrated yellow ammonium sulphide solution and an excess of 40% aqueous formaldehyde, (2) from 40% aqueous formaldehyde and an excess of concentrated yellow ammonium sulphide solution, (3) from more dilute solutions with neither in excess, and (4) as (3) except that freshly prepared ammonium hydrogen sulphide was employed. The analyses of these specimens are given in Cols. 1—4, and Col. 5 contains those of miscellaneous specimens; they correspond roughly to the formula $(CH_2)_3NHS$, which requires C, 40·9; H, 6·8; N, 15·9; S, 35·6%, although the predominating compound formed, whatever it may be, is clearly accompanied by varying amounts of other products.

	(1).	(2).	(3).	(4).	(5).
C, %	36·13	32·5	35·8	36·5	—
H, %	6·09	5·72	6·11	6·2	—
N, %	14·0	13·7	16·6	15·7	16·1, 15·8, 16·4
S, %	37·0	—	37·6	40·5	31·9, 36·9, 35·9, 33·5, 31·8

The possibility that the development of heat is due to the formation of hexamethylenetetramine from formaldehyde and ammonia, and therefore that the above substance is identical with "thiometaformaldehyde," $(CH_2S)_x$, isolated by Wohl (*Ber.*, 1886, **19**, 2345) by passing hydrogen sulphide through boiling ammoniacal hexamine solution, is manifestly untenable in view of the nitrogen content. Incidentally, however, we thought it desirable to repeat Wohl's preparation, and we always obtained products containing nitrogen—in two experiments, as much as 4%. Wohl's product, therefore, cannot be a chemical individual, but probably contains chiefly trithioformaldehyde along with other substances, *e.g.*, of the nitrogenous type now described by us.

The results obtained when aqueous formaldehyde was mixed with aqueous solutions of either methylamine, dimethylamine, ethylamine, or diethylamine, saturated with hydrogen sulphide, were similar to those obtained with ammonia, in that ill-defined white substances were produced after a preliminary development of heat and a period of induction. Only from the first-named amine was a solid derivative produced; it had m. p. 43—50° and was evidently a mixture. Treatment of its ethereal solution with methyl iodide gave, after a few days' standing, a crystalline methiodide, m. p. 161—162°, identical (m. p., analysis, and mixed m. p.) with the corresponding derivative (m. p. 161—163° decomp.) which Wohl prepared from a substance, "methylthioformaldin," $(CH_2)_3S_2NCH_3$ (I), m. p. 65°, obtained by shaking 30% methylamine solution with dilute aqueous formaldehyde which had been previously saturated with hydrogen sulphide.

The products from the other three amines were apparently impure mixtures giving variable analyses and not yielding crystalline methiodides. They were not further investigated.

The Period of Induction.—This was examined fully only in the case of ammonium sulphide-formaldehyde, and, except with very dilute solutions, was quite well defined and amenable to measurement.

Method. Two stock solutions of ammonium sulphide and formaldehyde were made up immediately before use by appropriate dilution of the commercial 16% and 40% solutions respectively. The formaldehyde was standardised by the method of Blank and Finkenberger (*Ber.*, 1898, **31**, 2979; *Analyst*, 1899, **24**, 92), whilst the ammonium sulphide, considerably diluted, was satisfactorily estimated by addition to acidified ferric sulphate solution as described by Mohr ("Titrirmethode," 1896, 257) for hydrogen sulphide solutions. From these parent solutions, by accurately diluting various volumes to a standard volume, solutions of known concentrations were obtained. These were preserved in vessels immersed in a thermostat.

Three sets of experiments were made: (1) formalin concentration constant, ammonium sulphide variable; (2) ammonium sulphide concentration constant, formalin variable; (3) concentrations of both reagents constant, temperature variable.

In the first and second sets, observations were conducted by placing 5 c.c. of each solution in one of a pair of dry boiling tubes and then as rapidly as possible pouring the ammonium sulphide into the formaldehyde solution. In the third case, both the stock solutions and the boiling tubes were sunk in the same large, mechanically stirred water-bath; 15 minutes before each experiment, 10 c.c. of formalin and 20 c.c. of ammonium sulphide were placed in their respective boiling tubes and allowed to attain the temperature of the bath, and the ammonium sulphide was added to the formalin as before.

A stop-watch was started at the moment when addition was completed; a small helical glass mechanical stirrer was used in the formalin tube, although results reproducible to 1—1·5 secs. were obtainable without it. A black background and a good side-light assisted determination of the moment when a bluish-white cloudiness first appeared. This was always taken as the end-point.

FIG. 1.

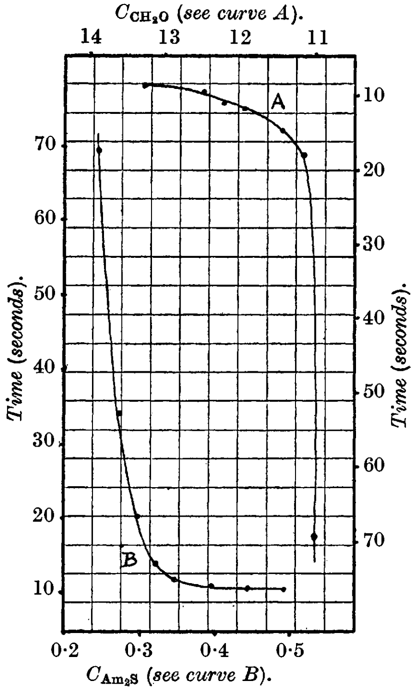
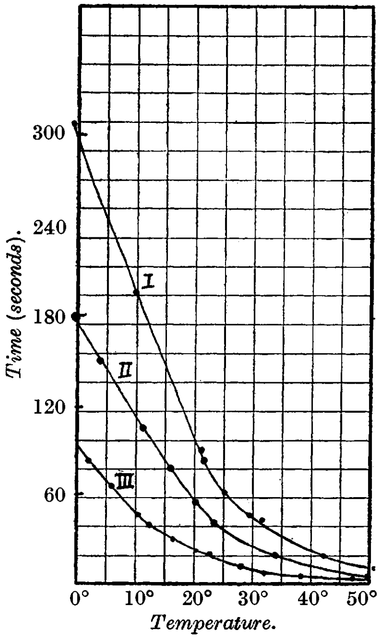


FIG. 2.



The results are summarised in Tables I, II, and III; C_{CH_2O} and C_{Am_2S} represent concentrations of formaldehyde and ammonium sulphide respectively in g.-mols./l., and t is the period of induction in seconds. Fig. 1 represents the data in Tables I and II, and Fig. 2 (Curve I) those in Table III, Curves II and III being derived from other pairs of solutions.

TABLE I.

C_{CH_2O} = 13·3; temp. = 18°.

C_{Am_2S}.	t.	$C_{Am_2S} \times t$.
0·4918	10·1	4·97
0·4426	10·5	4·65
0·3934	10·9	4·25
0·3434	11·8	4·05
0·3197	14·0	4·48
0·2950	20·2	5·96
0·2705	34·0	9·20
0·2459	69·2	17·02
0·1967	*ca.* 900	177·0

TABLE II.

C_{Am_2S} = 0·4918; temp. = 18°.

C_{CH_2O}.	t.	$C_{CH_2O} \times t$.
13·26	9·2	122·0
12·47	10·0	124·7
12·20	11·6	141·6
11·93	12·4	147·9
11·67	15·2	177·4
11·40	15·1	173·3
11·14	18·6	207·1
10·61	116·0	1229·0

TABLE III.

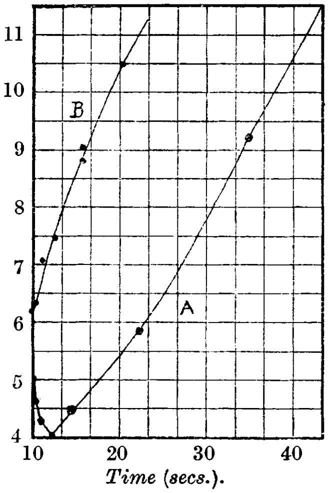
C_{Am_2S} = approx. 0·2; C_{CH_2O} = approx. 1·0

Temp.	–1°	10°	22°	23°	25°	29°	32°	42°	51°	62°
t	312	192	91	83	60	48	43	20	7	*ca.* 0

Discussion.

From the third columns of Tables I and II it will be seen that the period of induction is not even approximately inversely proportional to the concentration of the solutions (compare the case of the interaction of sulphurous and iodic acids; Landolt, *Ber.*, 1886, **19**, 1317), for were it so, then Fig. 3, Curves A and B (the product of concentration and time plotted against time from Tables I and II respectively) would be horizontal straight lines.

FIG. 3.



Curve A : $C_{Am_2S} \times t$.
Curve B : $C_{CH_2O} \times t \div 20$.

As this irregularity in Curve A might have been due to the increasing predominance of a different reaction as the concentration of the added liquid diminished, we roughly examined the natures of the products at the various stages. We found that as the solutions were diluted (the temperature being kept below, say, 20°) the products became more readily soluble in cold hydrochloric acid, clearly indicating a change in chemical nature. On two occasions from very dilute solutions the precipitate was even obtained as white needles, m. p. 125—129° (Found: C, 31·9; H, 5·29; N, 10·1; S, 50·0; residue, 1·49%). This type of product is now under investigation.

Table III and Fig. 2 also suggest that effects of more than one set of reactions are being observed. If the same chain of intermediate reactions leading to precipitation persisted along the whole temperature range studied, then, whatever their velocity accelerations with temperature may be, the curves in this figure should be linear. Actually they display a linearity up to *ca.* 18°, after which they flatten out and join the temperature axis at 60°.

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