

348. *The Thermal Reaction between Chlorine and Gaseous
Formaldehyde. Part I.*

By ROBERT SPENCE and WILLIAM WILD.

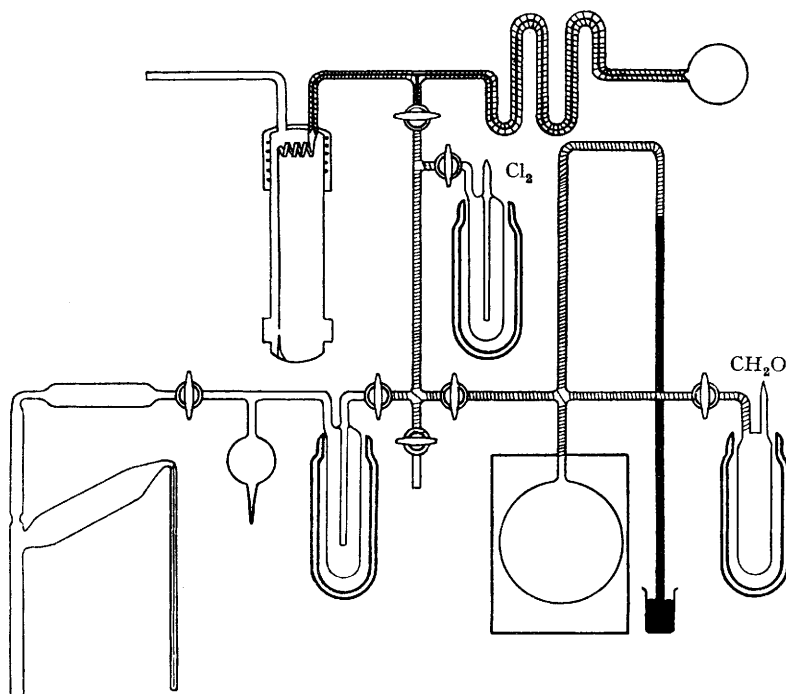
SOLID paraformaldehyde reacts with chlorine when heated in the dark yielding carbon monoxide and hydrogen chloride, whilst in bright sunlight the process goes a stage further to give carbonyl chloride (Tishtchenko, *J. Russ. Phys. Chem. Soc.*, 1887, **19**, 479; Brochet, *Compt. rend.*, 1895, **121**, 1156). We have found that gaseous monomeric formaldehyde

behaves similarly (*Nature*, 1933, **132**, 170); at 150° in the dark, the change can be represented by the equation $\text{H}\cdot\text{CHO} + \text{Cl}_2 \longrightarrow \text{CO} + 2\text{HCl}$. The reaction forms an interesting parallel to the thermal hydrogen-chlorine combination, the evidence in regard to which is somewhat conflicting (Sirk, *Z. physikal. Chem.*, 1908, **61**, 545; Melander, *Ark. Kemi, Min., Geol.*, 1914, **5**, No. 12; Sachtleben, Diss., Hanover, 1914; Christiansen, *Z. physikal. Chem.*, 1929, *B*, **2**, 405). Although the formaldehyde reaction has the apparent advantage that the rate can be followed by observation of the pressure change, closer examination has revealed complications which make the interpretation of such measurements a difficult matter. On this account, considerable importance has been attached to analytical data, and the results of investigations covering a wide range of conditions are presented below.

EXPERIMENTAL.

Chlorine was prepared from anhydrous A.R. copper chloride (Rollefson, *J. Amer. Chem. Soc.*, 1929, **51**, 770; cf. Loeb, *Physical Rev.*, 1930, **35**, 184) and stored in a vessel cooled in liquid air. Formaldehyde was obtained from the liquid monomeride, prepared by distillation of paraformaldehyde according to an improved method, which will be described in another place.

FIG. 1.



Apparatus and Procedure.—The general arrangement of the apparatus was essentially that described in a previous communication (J., 1933, 1193). As before, in order to prevent the polymerisation reaction which occurs at room temperatures (*ibid.*), the connecting tubing was covered with asbestos wrapped with nichrome wire, and heated electrically to 80°. All stopcocks were lubricated with Apiezon grease. Chlorine entered the reaction bulb directly from the storage vessel, and, being the first to be admitted, its pressure could be accurately determined in every case. Gaseous formaldehyde, temporarily stored in a 500 ml. bulb maintained at 100° and previously filled by vaporisation of the liquid, was quickly added to the chlorine so that, in all but those reactions which began with great rapidity, its pressure could be determined with fair accuracy.

Formaldehyde reacts much more rapidly than hydrogen with chlorine, and in certain circumstances the mixture will explode at 150°. This phase of the reaction has been separately investigated. First, the vessel was maintained at 100° in an oil-bath until the required amounts

of chlorine and formaldehyde had been admitted. The bath was then quickly replaced by another at 160°, thermostatically controlled and provided with a stirrer connected to a slow-speed induction motor by a flexible speedometer drive. Since the gases remained in the apparatus only a short time before explosion, a simple constant-volume mercury manometer was used in these experiments, the mercury surface being covered by a layer of sulphuric acid.

In the case of the slow reaction, the apparatus, constructed of Pyrex glass, was arranged as shown in Fig. 1. An electric oven (not illustrated), comprising a large steel tube suitably wound and enclosed in corrugated asbestos pipe lagging 3" thick, with asbestos plugs 1½" thick inserted into the ends, contained the reaction vessel. The temperature was controlled by a special thermoregulator consisting of two concentric spirals filled with mercury, operating in an atmosphere of nitrogen. The pressure change occurring in the reaction vessel was followed by a Bodenstein quartz spiral manometer, protected from possible explosion shock by a folded capillary tube.

After reaction, the products were completely withdrawn from the bulb through a liquid-air trap by the Töpler pump shown in Fig. 1. In certain experiments a spiral was substituted for the trap, since this appeared to effect a better separation of small quantities of condensable gas. The permanent gases were analysed in a simplified Bone and Wheeler apparatus, in which carbon monoxide was absorbed in ammoniacal cuprous chloride solution, and hydrogen was burned on a platinum spiral in the presence of excess oxygen. The condensable gases were collected in a 150 ml. bulb provided with a tubular extension drawn off to a capillary and immersed in liquid air. After the bulb had been sealed off, the capillary was broken under 10% potassium iodide solution, and the liberated iodine titrated with standard thiosulphate solution. Hydrogen chloride was determined with standard sodium hydroxide, two indicators being used, such that any carbon dioxide formed by the hydrolysis of carbonyl chloride, a possible product of the reaction, could have been detected: in no case was any evidence of this product obtained. Provided that the concentration of chlorine or formaldehyde in the products were small, blank experiments showed that the method could be applied successfully. With high concentrations of each, *i.e.*, 200—300 mm., in the reaction vessel, the analysis showed a deficiency of chlorine and an excess of hydrogen chloride. For complete or almost complete reaction, however, the analysis proved to be satisfactory. The accuracy of the total chlorine determination is illustrated by the following blank experiment: 93.0 mm. of chlorine in the apparatus at 150°, corresponding to 5.72×10^{-4} g.-mol., was withdrawn and analysed; the thiosulphate titration gave 5.7×10^{-4} g.-mol. Again, to check the gas analysis, 3.13×10^{-4} g.-mol. of air was removed from the reaction vessel by the Töpler pump; the volume measured in the gas-analysis apparatus corresponded to 3.12×10^{-4} g.-mol.

The Explosive Reaction.—Explosions could be obtained with the greatest regularity in a vessel which had been activated by a long series of slow reactions, but no evidence could be obtained of the existence of a reproducible pressure limit. Indeed, a vessel subjected to repeated explosions can become so active as to explode certain gas mixtures at temperatures as low as 100°. Detonation was accompanied by a sharp click and the emission of light, the intensity of both increasing with the chlorine concentration. The initial and final quantities (g.-mols. $\times 10^{-4}$) are given in Table I. In those cases in which formaldehyde was in excess, the ratio HCl/CO,

TABLE I.
Analysis of the explosive reaction.

| Reactants. | | | | Products. | | | | | |
|--------------------------------------|---------------------------------------|-------------------|--------------------|-------------------|-------|----------------------------|-------|------------------|---------|
| Cl ₂ , mm. at 100°. | CH ₂ O, mm. at 100°. | Cl ₂ . | CH ₂ O. | Cl ₂ . | HCl. | Total Cl ₂ . | CO. | H ₂ . | HCl/CO. |
| 351.0 | 117.0 | 24.50 | 8.18 | 16.20 | 15.50 | 23.95 | 7.85 | | 1.98 |
| 303.5 | 152.5 | 21.20 | 10.66 | 9.61 | 22.94 | 21.08 | 11.30 | | 2.03 |
| 203.8 | 193.0 | 14.25 | 13.50 | 0.39 | 27.97 | 14.38 | 14.01 | | 2.00 |
| 143.7 | 150.0 | 10.05 | 10.49 | 0.04 | 19.80 | 9.94 | 11.18 | 1.04 | 1.96 |
| 99.0 | 143.0 | 6.91 | 10.00 | 0.06 | 13.02 | 6.57 | 10.05 | 3.38 | 1.95 |
| 99.7 | 217.0 | 6.97 | 15.17 | 0.18 | 12.94 | 6.65 | 15.44 | 8.87 | 1.97 |

col. 10, was calculated after an amount of carbon monoxide equivalent to the hydrogen produced had been subtracted from the total monoxide. The formaldehyde pressures given in Table I could only be obtained approximately, since rapid polymerisation occurred at the protective

layer of sulphuric acid in the manometer, whilst in certain cases in which the surface was particularly active, reaction had already begun at 100°.

The Slow Reaction.—Reaction in a new vessel, at 150° and with the pressures used, was almost invariably non-explosive and preceded by an induction period. Experiments with constant chlorine concentration and varying formaldehyde concentration show that the rate is materially dependent on the condition of the glass surface. The initial rate after the induction period (maximum rate of pressure change) increases approximately linearly with the formaldehyde concentration (Fig. 2) until finally the mixture explodes. After the first series of experiments (lower curve) the vessel was washed with aqua regia, dried, and a further series of measurements carried out. The surface was now considerably more active, and the experimental rates (upper curve) were of a higher order. The activity of the surface also appeared to increase with the number of experiments. Owing to the variability of the surface factor, therefore, and to the further complication of a sensitised polymerisation of the formaldehyde (see below), only general significance can be attached to these velocity measurements.

The results of analyses of the slow reaction are given in Table II in terms of g.-mol. $\times 10^{-4}$. In every case, more reaction occurred than the amount calculated from the pressure increase (col. 9) according to the equation on p. 1589. This can only be ascribed to a disappearance of formaldehyde due to polymerisation, a process which is generally supposed to be entirely absent at temperatures greater than 100°. Experiments were carried out, therefore, with formaldehyde alone; e.g., 567.0 mm. of formaldehyde decreased to 559.2 mm. in 30 mins., and 228.0 mm. decreased to 224.0 mm. in the same time, at 150°. Part of this decrease may be due to polymerisation at the stop-cock, but there is also a definite deposition of polymeride on the wall of the reaction vessel itself. Visual evidence of its existence was obtained when the vessel was removed from the oven after a series of experiments: the glass was at first quite clear, but gradually a white deposit became evident, which slowly disappeared again. Since in the majority of the experiments, the partial pressure of formaldehyde was less than 250 mm., and the time of contact generally of the order of 30 mins., the maximum amount of polymerisation to be expected could hardly be more than 5 mm. or 0.22×10^{-4} g.-mol. The discrepancy between $\text{CO}_{\text{obs.}}$ and $\text{CO}_{\text{calc.}}$ is about four times as great, and we are obliged to conclude that the polymerisation reaction is catalysed by chlorine.

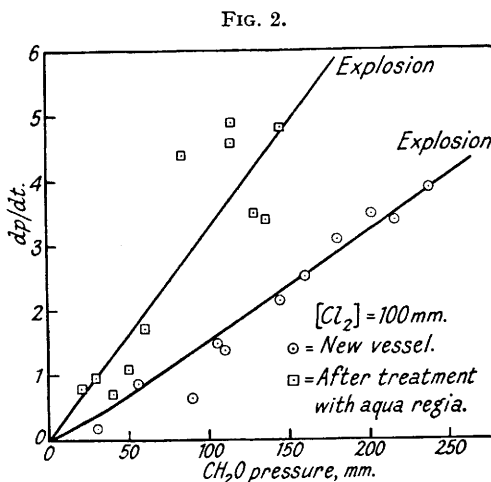


TABLE II.

Analysis of the slow reaction. $v = 116.4 \text{ ml.}; T = 150^\circ; s/v = 1.486.$

| Reactants. | | | | Products. | | | | | |
|------------------------|--------------------------------|-----------------|-------------------------|-----------------|-------|--------------------------|---------------------------|----------------------------|--------------------|
| Cl_2 , mm. | CH_2O , mm. | Cl_2 . | CH_2O . | Cl_2 . | HCl. | Total Cl_2 , | $\text{CO}_{\text{obs.}}$ | $\text{CO}_{\text{calc.}}$ | HCl/ CO . |
| 107.7 | 227.0 | 4.76 | 10.02 | 0.11 | 9.12 | 4.67 | 4.69 | 3.90 | 1.94 |
| * 96.4 | 163.9 | 6.18 | 10.51 | 1.39 | 9.31 | 6.05 | 4.69 | 3.80 | 1.99 |
| 201.4 | 266.6 | 8.89 | 11.77 | 0.22 | 17.30 | 8.87 | 8.52 | 7.53 | 2.03 |
| 211.5 | 175.5 | 9.33 | 7.74 | 4.97 | 8.49 | 9.22 | 4.10 | 3.40 | 2.07 |
| 205.0 | 100.5 | 9.05 | 4.44 | 6.41 | 5.76 | 9.29 | 2.82 | 2.37 | 2.04 |

* In this experiment, $v = 161.0 \text{ ml.}$ and $T = 130^\circ.$

$\text{CO}_{\text{calc.}}$ is the amount of reaction corresponding to the pressure change, the foregoing equation being assumed to apply quantitatively.

Whilst it is apparent from Fig. 2 that the reaction is influenced by surface variations, general considerations suggest that it occurs to a large extent in the homogeneous gaseous phase. Experimental data obtained with vessels of different surface/volume ratio are set out below.

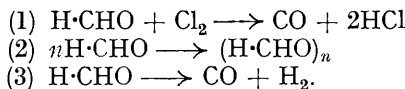
Influence of surface/volume ratio, T = 150°.

| Cl ₂ , mm. | CH ₂ O, mm. | v, ml. | s/v. | Reaction, %. |
|-----------------------|------------------------|--------|--------|--------------|
| 105.3 | 202.2 | 115.4 | 1.486 | 81.0 |
| 101.8 | 203.4 | 77.0 | 8.82 | 76.7 |
| 101.0 | 235.5 | 32.4 | >100.0 | 36.8 |

The figures under col. 5 represent the percentage of the total possible reaction occurring in 48 mins., measured as carbon monoxide. As before, the reaction was accompanied by polymerisation. However, after allowance had been made for the polymerisation which occurs in absence of chlorine, rapid in the case of the packed vessel, the ratio of sensitised polymerisation to reaction was not materially altered. Further details with regard to the polymerisation will be given in a forthcoming paper.

DISCUSSION.

The experimental results (Tables I and II) can be attributed to the occurrence of three reactions:



It is clear from Table I that the explosive reaction proceeds according to (1) so long as chlorine is in excess. Only traces of hydrogen could be detected. Any excess of formaldehyde, however small, is quantitatively decomposed according to equation (3). This sensitised decomposition is characteristic of the explosion and does not occur in the slow reaction, in which no more than traces of hydrogen have ever been observed, no matter how large the excess of formaldehyde. On the other hand, Table II contains evidence of a sensitised polymerisation (2) in the slow reaction, which occurs even in the presence of excess of chlorine. The relative amount of this polymerisation reaction appears to increase with the CH₂O/Cl₂ ratio, but further experiments are necessary before definite conclusions can be drawn.

A detailed discussion of reaction mechanism would be premature at this stage, but the experiments in vessels having different surface/volume ratios are worthy of special consideration. First of all, since there is no increase in the rate with increasing surface, it can be concluded that the reaction is not essentially heterogeneous. The occurrence of an actual decrease in velocity with surface might be interpreted as inhibition of a chain reaction by the wall. The decrease, however, is scarcely greater than the variation possible in a single reaction vessel (Fig. 2), and the only legitimate conclusion that can be drawn is that the velocity is nearly independent of surface/volume ratio, but may tend to decrease as the surface increases. We must suppose, therefore, that the reaction takes place almost entirely in the gaseous phase. Nevertheless, the gradual conditioning of the surface which has been observed indicates that the latter plays a fundamental rôle. A homogeneous reaction at moderate pressures can be influenced by surface only on one condition, *viz.*, that it is a chain reaction. This assumption would be in agreement with Christiansen's conclusion (*loc. cit.*) regarding the thermal hydrogen-chlorine reaction, which exhibits similar behaviour. For instance, Sirk (*loc. cit.*) observed that the velocity depended to a certain extent upon the previous history of the surface, but that no appreciable difference could be observed when the surface was doubled. According to these authors, the rate is independent of the hydrogen concentration, whereas Melander (*loc. cit.*) finds that it varies with the first power of hydrogen concentration. At constant chlorine concentration, the rate of the formaldehyde-chlorine reaction appears to be directly proportional to the formaldehyde concentration (Fig. 2), but it will be necessary first of all to ascertain the precise ratio of polymerisation to reaction at every stage before further progress can be made in this direction.

SUMMARY.

Monomeric formaldehyde and chlorine react at 150° to give carbon monoxide and hydrogen chloride. The explosive reaction is accompanied by light emission, and any excess

of formaldehyde is quantitatively decomposed to hydrogen and carbon monoxide. The slow interaction induces polymerisation of the formaldehyde.

THE UNIVERSITY, LEEDS.

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