additional experiments has enabled us to decide between the two views. Only two of the unpacked series need be quoted here, *viz.*, J1 and J12.

J1, *T* 140°.
HCHO 197.4 mm.; Cl_2 99.5 mm.

t, min.	*p*, mm.
0	296.9
12	365.9
20	376.8
60	376.7

Δp max. 79.9 mm.
Found: CO 93.9 mm.

$$\frac{\text{HCHO polym.}}{\text{HCHO reacted}} = \frac{14.0}{93.9} = 0.149.$$

J12, *T* 150°.
HCHO 378.0 mm.; Cl_2 53.0 mm.

t, min.	*p*, mm.
0	431.0
8	441.0
17	442.0
27	438.5

Δp max. 11.0 mm.
Found: CO 52.1 mm.

$$\frac{\text{HCHO polym.}}{\text{HCHO reacted}} = \frac{41.1}{52.1} = 0.789.$$

These experiments show how the discrepancy between the theoretical and the observed pressure change increases with the formaldehyde–chlorine ratio. According to Krauskopf and Rollefson's view, 40 mm. of formyl chloride must have been produced in J12 after eight minutes, remained unchanged at 150° for a further nineteen minutes, and must then have been completely decomposed in the process of pumping out over liquid air. However, experiments in a vessel packed with powdered glass gave similar results: *e. g.*, K5 (HCHO 206.0 mm.; Cl_2 168.8 mm.). 15.4 mm. of formaldehyde polymerized in forty-eight minutes before addition of the chlorine, while polymerization during forty-eight minutes of reaction amounted to 27.5 mm. Any formyl chloride present in this case would scarcely decompose at the cooler surface of the tubing leading to the liquid air trap, and once frozen out, the carbon monoxide would be lost to the analysis, resulting in an increase in the HCl/CO ratio. However, our ratios always remained very close to two, and the discrepancy between the amount of reaction and the pressure change must be attributed to an induced polymerization of the formaldehyde. Nevertheless, as we had already pointed out [*J. Soc. Chem. Ind.*, **54,** 83 (1935)] in agreement with Krauskopf and Rollefson, it is probable that formyl chloride occurs as an intermediate in the thermal reaction, but in our opinion, its concentration must be small.

THE UNIVERSITY
LEEDS, ENGLAND

R. SPENCE
W. WILD

RECEIVED APRIL 29, 1935

THE REACTION BETWEEN CHLORINE AND FORMALDEHYDE

Sir:

The experiments described in the note of Spence and Wild indicate that the amount of formyl chloride in the reaction mixtures was too small to be of importance in accounting for the discrepancy between theoretical and observed pressure change. It was not our intention in the previous Note [THIS JOURNAL, **57,** 590 (1935)] to account for the total discrepancy in this manner but only to account for what was left after correcting for the normal amount of polymerization. The data from experiment K5 in the packed reaction vessel (a condition very unfavorable for the existence of formyl chloride) seem to be in favor of the higher rate of polymerization in the presence of chlorine, suggested by Spence and Wild. The failure of the HCl/CO ratio to deviate appreciably from two also supports this view.

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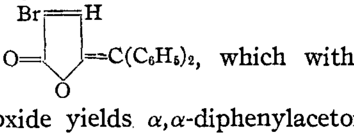
K. B. KRAUSKOPF
G. K. ROLLEFSON

RECEIVED MAY 16, 1935

ORIENTATION IN THE FURAN SERIES. HILL'S 3,5-DIBROMO-2-FUROIC ACID

Sir:

The pivotally significant "3,5-dibromo-2-furoic acid" [Hill and Sanger, *Proc. Am. Acad. Arts. Sci.*, **21,** 135 (1885)] is actually 4,5-dibromo-2-furoic acid. This has been demonstrated as follows: (1) The β-bromo-2-furoic acid, obtained by replacing an α-bromine in the dibromofuroic acid by hydrogen, gives 2,4-furandicarboxylic acid on hydrolysis of the nitrilo-acid secured by heating with potassium cyanide and cuprous cyanide [Rosenmund and Struck, *Ber.*, **52B**, 1749 (1919)]. (2) The dibromofuran, obtained from decarboxylation of the dibromofuroic acid, gives (by a corresponding treatment) 2,3-furandicarboxylic acid. (3) The ethyl ester of the dibromofuroic acid gives with phenylmagnesium bromide the bromocrotolactone,  which with 5% sodium hydroxide yields α,α-diphenylacetone.

By a series of inter-relating reactions it now appears that Hill's structures for 3-sulfo-5-bromo-2-furoic acid, 3-sulfo-5-chloro-2-furoic, and 3,5-dichloro-2-furoic acid warrant revision.

CONTRIBUTION FROM THE
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