corresponding light hydrogen reaction. Owing to uncertainties in the purity of the deuterium and as to the complete role of exchange reactions, full publication is being deferred.

The catalytic experiments using copper indicated at 0° a ratio of rates H_2/D_2 of 1.59. Since Farkas, Farkas and Rideal [*Proc. Roy. Soc.* (London), **A146,** 630 (1934)] found no exchange at low temperatures over nickel, it is likely that no exchange occurred in this reaction over the comparatively less reactive copper catalyst. However, this point is being investigated. At higher temperatures (184 to 306°) the observed ratio fell from 1.34 to 1.04. How much of this decrease is due to exchange will be determined.

In the homogeneous reaction at 524 and 560° the ratios were 2.10 and 2.0, respectively. This seems to point to a real difference in the activation energies of the homogeneous reactions, but again further investigation (which will be shortly undertaken) is required.

These preliminary results point to the likelihood that comparative rates of hydrogenation can be obtained at 0° on the copper catalyst and at 500–550° in the homogeneous reaction, without serious interference from exchange reactions. Such measurements are now being made with deuterium of known purity.

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PRINCETON, NEW JERSEY
ROBERT N. PEASE
AHLBORN WHEELER

RECEIVED APRIL 15, 1935

THE SEPARATION OF CERTAIN RARE EARTHS

Sir:

It has been shown by Yntema [THIS JOURNAL, **52,** 2782 (1930)] and by Ball and Yntema [*ibid.*, **52,** 4264 (1930)] that europium and ytterbium may be separated from other rare earths by precipitation as sulfate after electrolytic or other reduction to the divalent state. However, because of the small amounts of these elements found in rare earth mixtures, it has still been necessary to resort to fractional crystallization over a period of a year or more before the reduction method becomes applicable.

Using several samples of pure rare earths put at his disposal through the kindness of Professor B. Smith Hopkins of the University of Illinois, the writer has attempted to facilitate the separation of europium through the use of a co-precipitant. In a mixture of terbium group earths too dilute in europium to give any direct precipitate of europous sulfate, it has been found possible to obtain a substantially complete co-precipitation with barium sulfate of all the europium present. The europium is then readily removed from the filtered barium sulfate by repeated washing with a little hot concentrated nitric acid. There seems, therefore, no reason why europium, and probably ytterbium also, cannot be removed practically quantitatively from a crude rare earth mixture in as many days as it formerly took years.

The writer has also examined a possible separation of neodymium and samarium. The mixture of anhydrous chlorides is treated with hydrogen at 700°. This results in reduction of the samarium to $SmCl_2$. Treatment of the resultant mixture with water brings about a reaction probably represented by $6SmCl_2 + 3H_2O \longrightarrow 4SmCl_3 + Sm_2O_3 + 3H_2$, the neodymium trichloride simply dissolving. Part of the samarium is precipitated but seems always to be contaminated with some neodymium. Although the separation obtained is good, as rare earth separations go, it is nevertheless only fractional, and because of its difficulty probably cannot compete with the usual double nitrate fractional crystallization.

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P. W. SELWOOD

RECEIVED APRIL 24, 1935

THE THERMAL REACTION BETWEEN CHLORINE AND FORMALDEHYDE

Sir:

Krauskopf and Rollefson [THIS JOURNAL, **56,** 2542 (1934)] have isolated formyl chloride from the photochemical interaction of chlorine and formaldehyde, and have suggested [*ibid.*, **57,** 590 (1935)] that this substance occurs as an intermediate in the corresponding thermal reaction [Spence and Wild, *Nature*, **132,** 170 (1933); *J. Chem. Soc.*, 1588 (1934)]. Furthermore, they suggest that the excess of carbon monoxide produced in our experiments over that calculated from the pressure change is due not to an induced polymerization of the formaldehyde, but to the presence of formyl chloride, which is produced without change of pressure. If the formyl chloride decomposed in the process of analysis giving HCl and CO, it is claimed that this explanation would account for our results equally well. Consideration of a number of 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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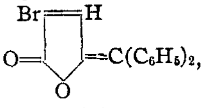
G. K. ROLLEFSON

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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RECEIVED MAY 6, 1935