the molecular weight of the —CF_2— unit. These mixtures could not be resolved by any means now at our disposal.

It seems that in this reaction, the completely fluorinated molecule may have been formed at first, and then literally smashed by impacting high energy fluorine atoms. In this connection it is of interest that when certain fluorinations were conducted in an experimental glass reactor they were clearly seen to be accompanied, except under the mildest conditions, by intermittent or even continuous bluish flashing or glowing, indicating that a certain amount of combustion was nearly always taking place. Subsequently, the numerous fragments presumably polymerized to form the highly complex mixture actually observed. It is clear from the structure of $C_{11}F_{20}$, or, for that matter of any other similar fluorocarbon, that such a process would result in the formation of a product having an average composition very close to that represented by the formula $(CF_2)_x$. It is equally possible, of course, that the fragmentation and polymerization could have taken place, either wholly or in part, prior to the complete substitution of the hydrogen by the fluorine.

These results, taken together, provide concrete support for the assumption that the primary attack of elementary fluorine on the aromatic nucleus is one of addition, followed in most cases by varying degrees of substitution, fragmentation and polymerization.

Summary

The compound 4-chloro-1,3-*bis*-(trifluoromethyl)-benzene, $C_6H_3Cl(CF_3)_2$, has been fluorinated in the vapor phase over a metal wire catalyst under mild conditions, yielding the tetrafluoride addition product having the exact composition required by the formula $C_6H_3F_4Cl(CF_3)_2$, but presumably consisting of a mixture of isomers, together with the completely fluorinated molecules $C_6F_{10}(CF_3)_2$, $C_6F_{11}(CF_3)$ and C_6F_{12}. Good evidence also has been presented to show that the related difluoride $C_6H_3F_2Cl(CF_3)_2$, and fluorohexafluoride $C_6H_3F_7(CF_3)_2$ were formed at the same time.

Benzotrifluoride, under similar conditions, yielded the expected completely fluorinated molecules $C_6F_{11}(CF_3)$ and C_6F_{12}; together with two distinct isomeric mixtures having the exact composition corresponding to the formula $C_6HF_{10}(CF_3)$, but apparently no stable addition products.

1-Methylnaphthalene, when fluorinated at somewhat higher temperatures and recycled, yielded only a small amount of the completely fluorinated molecule $C_{11}F_{20}$. Most of the product consisted of a clear, stable, highly complex liquid mixture of fragmentation and polymerization products. This mixture could not be separated by distillation, but numerous portions had average high molecular weights which corresponded closely to the formula $(CF_2)_x$.

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Magnesium Dichromate and its Hydrates

BY WINSLOW H. HARTFORD

The state of the literature regarding magnesium dichromate is confused. It is reported by Reinitzer[1] that magnesium dichromate is soluble in alcohol, but no details are given of the preparation or composition of the salt. This is the reference on which Mellor[2] reports the existence of the compound, while Friend[3] states that it has not been prepared. An American patent[4] discloses the preparation of a paste of magnesium dichromate crystals by evaporation of a solution of magnesium chloride and sodium dichromate, separation of sodium chloride, and allowing the resulting solution to cool. No analysis of the product or properties of the material, other than great solubility, are given.

Further investigation of this problem yielded the following previously undescribed compounds.

Experimental

$MgCr_2O_7 \cdot 5H_2O$.—In a typical experiment, 500 g. of magnesium oxide (U. S. P.) was added slowly with agitation to a solution of 2500 g. of technical chromium trioxide in 5 liters of water. The *p*H, as measured by a glass electrode meter, was then adjusted by the addition of magnesium oxide or chromium trioxide as needed to 2.8–3.0. The solution has a dark color due to small quantities of Cr^{+++}; this may be removed by electrolytic oxidation at 4–6 v. using lead electrodes. It is then filtered, concentrated to a volume of 2.5 liters (sp. gr. 1.74 at b. p.) and allowed to crystallize with agitation and slow cooling. The solution is very viscous and has a strong tendency to supersaturate; therefore it is desirable to seed when the mixture has cooled to about 60°. This may be conveniently done by wetting a glass rod with the solution, drying out partially over a low flame and adding the crust to the solution, or by chilling a small sample until crystals separate and pouring the slurry back into the main container. A crop of bright red-orange crystals was obtained on cooling to room temperature; the product was centrifuged and dried by passing a stream of dry air over the material in a rotating dryer at 50°. The yield is approximately 2 kg.

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(1) B. Reinitzer, *Z. angew. Chem.*, **26**, 456 (1913).

(2) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., New York, 1931, Vol. XI, 341.

(3) J. N. Friend, editor, "A Text-Book of Inorganic Chemistry," VII, part 3, J. F. Lippincott Co., Philadelphia, 1926, p. 56.

(4) G. Kranzlein and A. Voss, "Process for the Preparation of Magnesium Chromates," U. S. Patent 1,632,299; June 14, 1927.

Crystals of the same properties were obtained when the crystallizing solution had a *p*H between 0 and 5 and at final temperatures ranging from 0 to 30°. The conditions specified above are preferred, however, as at high *p*H there is danger of a small amount of magnesium chromate separating during concentration, while at low *p*H, the mother liquors contain excess chromic acid which tends to adhere to the crystal. The viscosity of the mother liquor at low temperature renders its separation difficult in spite of the slightly increased crystal yield.

The crystals are extremely deliquescent and therefore could not be examined at length with the microscope, nor any crystal angles conveniently determined. They are, however, uniform in size and shape, and careful examination of several samples failed to reveal the presence of more than one crystal species. The crystals are tabular with truncations at each corner to give a hexagonal or octagonal cross section. They are completely different in appearance from crystals of either magnesium chromate heptahydrate or chromium trioxide, as well as possessing the red-orange color characteristic of dichromate.

The solubility at 25° was determined by agitating an excess of the salt with water in a closed container for eight hours, the temperature of the vessel being thermostatically controlled. A sample was withdrawn by means of a sintered-glass funnel and transferred to a weighing bottle, samples being taken at the end of four and eight hours. The solution was analyzed for magnesium oxide and chromium trioxide:

TABLE I

Time of agitation, 25°	4 Hr.	8 Hr.	
% MgO	9.91	9.88	
% CrO_3	49.00	48.89	
Mole ratio of CrO_3:MgO in solution	1.993	1.995	
% $MgCr_2O_7 \cdot 5H_2O$ in solution[a]	81.1	80.9	Av. 81.0

[a] From average of values for magnesium oxide and chromium trioxide.

Microscopic examination of the residual solid indicated no change in nature of the solid phase, indicating a congruent solubility in water. The density of the saturated solution is 1.712_4^{25} as measured by precision hydrometer.

$MgCr_2O_7 \cdot 5H_2O$ is also soluble in ethanol to the extent of about 200 g./liter[5] of solution at 25°, and to a lesser extent in acetone and other polar organic solvents. These solutions decompose on standing, especially in the light, with oxidation of the organic compound and reduction of the dichromate.

Anal. Two separate batches of material were analyzed. Calcd. for $MgCr_2O_7 \cdot 5H_2O$: MgO, 12.20; CrO_3, 60.53; H_2O, 27.26. Found: 1st batch, MgO, 12.40; CrO_3, 60.29; 2nd batch, MgO, 12.40; CrO_3, 60.37.

Drying of $MgCr_2O_7 \cdot 5H_2O$, even under 75 mm. at 160°, results in the loss of only $4H_2O$; calcd. for loss of $4H_2O$, 21.82; found: 21.71, 21.73. No significant further loss of weight is noted until the compound is heated to 300–320°, when partial decomposition occurs, forming magnesium chromite, magnesium chromate, oxygen and chromic chromates.

$MgCr_2O_7 \cdot H_2O$.—The stability of composition of the intensively dried material over a wide temperature range, as shown above, indicates the existence of $MgCr_2O_7 \cdot H_2O$, while failure to remove the last mole of water shows that the anhydrous salt cannot be prepared under ordinary conditions. In order to determine whether the monohydrate exists as a phase in equilibrium with aqueous solutions of magnesium dichromate, the following procedure was used:

A solution of magnesium dichromate was prepared, as for the formation of the pentahydrate. The *p*H was reduced to 2 by addition of chromic acid, this step being necessary to prevent separation of magnesium chromate in the subsequent operations. The solution was concentrated by boiling to a density of 1.9, when crystals started to separate. A yield of about 35% was taken, and the product separated as brick-red, deliquescent crystals, which appeared under the microscope as irregular needles with poorly developed pyramidal terminations. They were entirely different in appearance from the pentahydrate, but again only a single crystal species was present. They were centrifuged, using a preheated basket, and dried at 75 mm. and 150°. A second batch was dried at 100°. The crystals were unchanged in appearance by either treatment.

Anal. Calcd. for $MgCr_2O_7 \cdot H_2O$: MgO, 15.61; CrO_3, 77.42. Found: 1st batch: MgO, 15.68; CrO_3, 77.12; 2nd batch: MgO, 15.62; CrO_3, 77.18.

Transition Point.—The phase relationships were further determined by cooling curve measurements. A sample of the solid material was agitated in contact with saturated solution and the samples slowly cooled by surrounding the sample with a water jacket maintained at about 15° lower temperature than the sample. The cooling water was agitated. The thermal behavior was studied over the range from 0 to 100°. While there was a strong tendency for the solutions to supercool and the high viscosity rendered good mixing difficult, evidence was obtained of only one transition point in this range. This was checked by three runs, using a different ratio of solid to liquid phase in each case. The following results were obtained, using a calibrated thermometer graduated to 0.2°: $MgCr_2O_7 \cdot 5H_2O \rightleftarrows MgCr_2O_7 \cdot H_2O$, 89.1, 89.6, 89.6°; average 89.4°. The solid phases above and below the transition point were separated and examined. They were the same as the monohydrate and pentahydrate described above.

Summary

This paper reports the preparation for the first time of $MgCr_2O_7 \cdot 5H_2O$ and $MgCr_2O_7 \cdot H_2O$. The transition between the two salts is at 89.4°.

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[5] An accurate value is impossible because of the effect of water in the compound and the alcohol on the solubility, and the rapid decomposition of the solution.