reagents. From their similarity to the bromotetranitronaphthalenes studied by Merz and Weith[1] one is tentatively designated as 4-chloro-1,3,6,8-tetranitronaphthalene, the other as 4-chloro-1,3,5,8-tetranitronaphthalene; the first corresponding to Merz and Weith's 4-bromo-1,3,6,8-tetranitronaphthalene of melting point 189°, the second to their 4-bromo-1,3,5,8-tetranitronaphthalene of melting point 245°. The 4-chloro-1,3,6,8-tetranitronaphthalene in benzene suspension with ammonia gave Merz and Weith's 1-amino-2,4,5,7-tetranitronaphthalene (4-amino-1,3,6,8-tetranitronaphthalene) of melting point 194°.

Merz and Weith prepared the bromotetranitronaphthalenes by a two-stage nitration involving intermediate precipitation of the partially nitrated material. They mention but do not describe in detail, a one-stage method which apparently, gave very low yields. The following process is much shorter than the two-stage method and gave yields fully equal to those obtained with it. However, the recovery of purified product was still low, amounting to some 25–27 parts of crystalline benzene-soluble chlorotetranitro compound, and 8–12 parts crude benzene-insoluble isomer, per 100 parts chloronaphthalene. For the acid nitration mixture, a smaller amount of oleum of higher sulfur trioxide content probably would be better than the 20% fuming sulfuric acid specified; however, it was not available for trial at the time the work was done.

Procedure.—One hundred grams (84 ml.) of 1-chloronaphthalene was dropped very slowly into 400 g. (270 ml.) of fuming nitric acid of specific gravity 1.50, the latter being swirled and kept cold in a bath of ice and water. The liquid was then added slowly to a cooled mixture of 400 g. (270 ml.) of the fuming nitric acid with 800 g. (435 ml.) oleum or fuming sulfuric acid of 20% sulfur trioxide content contained in a two-liter erlenmeyer flask, and kept at a temperature below 45°. The flask finally was heated in a boiling water-bath for one hour after the temperature of the mixture had reached 92°. After cooling, the nitration mixture was poured on crushed ice, the diluted acid syphoned off and the solid washed first by decantation, then in a buchner funnel (without pressing) until the acidity of the wash water was below $N/100$; the drained solid was then dried on filter paper supported on a pad of news-print. The granulated material held water very tenaciously, and although all surface moisture soon passed off, it was necessary to air-dry for several weeks.

The dry product was extracted with benzene in a large soxhlet tube, the soluble fraction crystallizing from the extract, and being further purified by recrystallization from benzene. Several methods were tried for the purification of the benzene-insoluble isomer, crystallization from glacial acetic acid probably giving the best results though the compound is not very soluble in this solvent, even at the boiling temperature. The crude 4-chloro-1,3,5,8-tetranitronaphthalene was more soluble in boiling *p*-dioxane but did not crystallize rapidly from the solution. The impurities in the crude extracted material increased the solubility of the 4-chloro-1,3,5,8-tetranitronaphthalene in dioxane and much lessened the tendency toward crystallization. Hot chlorobenzene, and hot 2,2′-dichlorodiethyl ether as solvents gave crystals of lower purity.

4-Chloro-1,3,6,8-tetranitronaphthalene.—This isomer was soluble in 4 to 4.5 parts of boiling benzene, approximately four-fifths separating on cooling in pale yellow needles containing an equimolecular amount of solvent. The crystallized compound when heated in a capillary tube fused and lost benzene at about 110°; however, 0.5 g. when exposed in an open dish at summer temperature effloresced rather rapidly, about four-fifths of the benzene passing off in 24 hours. The benzene compound was soluble in somewhat less than 110 parts of boiling 95% alcohol; in two parts of boiling glacial acetic acid; and in less than 14 parts of glacial acetic acid at 25°. It was very soluble in *p*-dioxane, dissolving in about its own weight of this liquid at 25°. Melting point of crystallized substance after heating for 30 minutes at 110°, 176°.

Anal. Calcd. for $C_{10}H_3(NO_2)_4Cl \cdot C_6H_6$: C_6H_6, 18.57. Found: (loss on heating for 30 minutes at 110°), C_6H_6, 18.48. Calcd. for benzene-free substance, $C_{10}H_3(NO_2)_4Cl$: Cl, 10.35. Found: Cl, 10.41.

4-Chloro-1,3,5,8-tetranitronaphthalene.—This compound was nearly insoluble in benzene and in alcohol. It dissolved in about 40 parts of boiling glacial acetic acid, approximately one-half separating in small yellowish white needles on cooling. It was soluble in 11 parts of boiling *p*-dioxane from which it crystallized in almost white, very fine needles; m.p. 259°.

Anal. Calcd.: Cl_2, 10.35. Found: Cl_2, 10.20.

The chlorotetranitronaphthalenes when dissolved at room temperature in very dilute alcoholic potassium hydroxide gave intensely red solutions that if tested immediately with silver salts showed only traces of chlorides. After warming or standing, the solutions gave heavy precipitates of silver chloride. Both isomers react with simple primary amines, even at high dilutions, to give deeply colored brown or yellow secondary amines.

It is apparent that the chlorotetranitronaphthalenes are acids, though not proton donors. However, because of the high lability given to the halogen by the ortho and para nitro groups the compounds behave as acid chlorides in most of their common reactions.

Grateful acknowledgment is made to Dr. J. O. Maloney for use of the facilities of the Kansas University Research Foundation in connection with this work.

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[1] V. Merz and W. Weith, *Ber.*, **15**, 2708 (1882).

Stability of Chromium Oxides

BY M. A. MOSESMAN

RECEIVED AUGUST 17, 1953

The recently described work of Schwartz, Fankuchen and Ward[1] on the thermal decomposition of chromium trioxide suggests that the results of some experiments we conducted along similar lines during the first half of 1951 might prove of interest. The objective of these experiments was to establish the stability of a promoted, alumina-supported chromic oxide catalyst under the reducing and oxidizing conditions to which the catalyst is subjected during the process of paraffin aromatization. In view of the desirability of studying such a reaction system *in situ* by X-ray diffraction, the previously described apparatus[2] utilizing a beryllium microreactor was employed.

The first phase of this work was devoted to a study of the thermal stability of bulk chromium trioxide in order to provide a reference case for subsequent investigation of the above-mentioned catalyst. Interest in the thermal characteristics of CrO_3 was predicated on the fact that the general preparative procedure for such catalysts involves the use of this water-soluble oxide for impregnating the support, followed by drying and calcination of the resulting mixture at temperatures sufficient to convert CrO_3 to Cr_2O_3. After drying for several weeks at 100°, C.P. CrO_3 was charged to the microreactor and the apparatus assembled and evacu-

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[1] R. S. Schwartz, I. Fankuchen and R. Ward, THIS JOURNAL, **74**, 1676 (1952).

[2] M. A. Mosesman, *ibid.*, **73**, 5635 (1951).

ated. With the system maintained continuously under vacuum (approximately 1 mm.), the temperature was increased slowly in relatively small increments to 396° over a period of 585 hours during which 40 diffraction patterns were obtained. No change in the diffraction pattern was observed until after 25 hours of operation at 215°. The change, however, did not represent decomposition of CrO_3 to Cr_2O_3; instead, a number of reflections distinct from those attributable to chromium in both of these structures was noted. Moreover, these unidentified lines persisted over a period of about 375 hours while the temperature was being increased from 215 to 396°. Operations at the latter temperature for 19 hours finally yielded a diffraction pattern showing only the presence of Cr_2O_3. That the unknown material observed in the temperature range of 215 to 396° bears a close resemblance to the phase I (Cr_3O_8) reported by Fankuchen, *et al.*,[1] is apparent from the diffraction patterns shown in Table I.

TABLE I

X-RAY POWDER PATTERNS

This work		Cr_3O_8[1,a]	
d, Å.	Intensity	*d*, Å.	Intensity
11.6	M	11.8	M
6.01	VW	6.19	W
		5.84	W
4.91	VW	4.95	VVW
4.49	VW	4.49	VW
3.78	S	3.88	S
		3.72	M
3.30	MS	3.34	MS
3.05	MS	3.08	MS
2.61	W	2.60	VVW

[a] Only comparable lines listed.

Although there is no apparent explanation for the failure to observe the other oxidation states, Cr_2O_5 and CrO_2, reported by Fankuchen, *et al.*,[1] as intermediates between CrO_3 and Cr_2O_3, it is possible that the heat treatments may not have been sufficiently severe.

Once formed, the Cr_2O_3 proved refractory to further change. No change in its diffraction pattern was noted throughout the following consecutive treatments: (1) continued heating *in vacuo* for 240 hours over the temperature range of 396 to 593°; (2) heating in flowing air at 1.2 atmospheres for 612 hours over the temperature range of room temperature to 671° and (3) heating in flowing H_2 at 1.7 atmospheres for 745 hours over the temperature range of 130 to 660°. The results of the latter two treatments are in accord with those reported by Lazier and Vaughen[3] which indicated that only amorphous Cr_2O_3 underwent reduction and oxidation.

In view of the results obtained on bulk Cr_2O_3 by treatment with both air and H_2 at elevated temperatures, it was considered unlikely that the Cr_2O_3 catalyst composed of alumina-supported Cr_2O_3 would prove less stable. Such proved to be the case for a catalyst containing 22% Cr_2O_3 and small quantities of potassium and cerium as promoters. This catalyst, after prior use in a large scale pilot unit, was observed to undergo no change in chromium oxidation state when contacted initially with air over a period of 271 hours in which the temperature was increased from 263 to 660°, and subsequently with H_2 during a period of 249 hours in which the temperature was increased from 263 to 583°. Based on these observations it appears that the rapid and severe deactivation generally experienced with Cr_2O_3–Al_2O_3 catalysts in aromatization processes does not stem primarily from a change in oxidation state of the chromium.

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[3] W. A. Lazier and J. V. Vaughen, THIS JOURNAL, **54**, 3080 (1932).

The Reactivity of the Methyl Group in 2-Methyl-3-nitronaphthalene[1]

BY LEONARD E. MILLER, W. W. HANNEMAN, W. L. ST. JOHN AND R. R. SMEBY

RECEIVED SEPTEMBER 14, 1953

The preparation of 2-methyl-3-nitronaphthalene described in the literature,[2] for which tetralin is the starting material, is tedious and the yields in some of the steps are low or unstated. As a consequence a new synthetic route has been devised.

Commercially available 3-hydroxy-2-naphthoic acid was first converted to its methyl ester I[3] which was then reduced with lithium aluminum hydride according to the method of Nystrom and Brown[4] to give 3-hydroxymethyl-2-naphthol (II) in a yield of 87% of the theoretical amount.[5]

The 3-hydroxymethyl-2-naphthol underwent hydrogenolysis at 142° in the presence of copper–chromium oxide to give 3-methyl-2-naphthol (IIIa) in 87% yield. This procedure is analogous to that used by Cason[6] to convert 4-hydroxy-2-naphthaldehyde to 4-hydroxy-2-methylnaphthalene. When 3-methyl-2-naphthol was mixed with a solid calcium chloride–ammonia complex and heated at 270°, 3-methyl-2-naphthylamine (IIIb) was formed in yields up to 88%. Fries and Hübner[7] have used this technique to prepare 1-methyl-2-naphthylamine from 1-methyl-2-naphthol, another compound which does not undergo the Bucherer reaction satisfactorily.

The methods which have been reported[8] for the conversion of aromatic amines to nitro compounds were not adaptable in our hands for the preparation of 2-methyl-3-nitronaphthalene (IIIc). A

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[1] Presented before the Organic Division at the 118th meeting of the American Chemical Society, Chicago, September 3 to 9, 1950.

[2] V. Veselý and F. Štursa, *Collection Czechoslov. Chem. Commun.*, **6**, 137 (1934); *Chem. Listy*, **29**, 361 (1935).

[3] Cohen and Dudley, *J. Chem. Soc.*, **97**, 1748 (1910).

[4] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 1197 (1947).

[5] After this work had been reported,[1] W. T. Smith, Jr., and L. Campanaro, *ibid.*, **74**, 1107 (1952), described the preparation of this compound in 23% yield, by the direct reduction of 3-hydroxy-2-naphthoic acid. Our over-all yield from the same acid was 77% (88% for the esterification; 88% for the reduction).

[6] J. Cason, THIS JOURNAL, **63**, 831 (1941).

[7] K. Fries and E. Hübner, *Ber.*, **39**, 444 (1906).

[8] (a) H. H. Hodgson and E. R. Ward, *J. Chem. Soc.*, 127 (1947); (b) H. H. Hodgson, A. P. Mahadevan and E. R. Ward, *ibid.*, 1392 (1947); (c) M. F. W. Dunker, E. B. Starkey and G. L. Jenkins, THIS JOURNAL, **58**, 2308 (1936); (d) E. B. Starkey, *ibid.*, **59**, 1479 (1937).