[Contribution from the Chemical Laboratories of The Ohio State University]

Addition Compounds of Chromium(VI) Oxide with Heterocyclic Nitrogen Bases. II. Reactions with the Lutidines, Vinylpyridines, 2,4,6-Collidine and α-Picoline[1]

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Reactions of chromium(VI) oxide with the lutidines, mono- and polyvinyl pyridines, 2,4,6-collidine and α-picoline were carried out. 2,6-Lutidine is inert toward chromium(VI) oxide. 2,3-Lutidine reacts slowly with the oxide to give a 1:1 addition product which on standing gradually undergoes oxidation–reduction. 2,4-Lutidine yields impure $CrO_3\cdot 2$(2,4-lutidine) which contains some Cr(III). Oxidation–reduction continues on standing. 2,5-Lutidine yields well-defined crystals of $CrO_3\cdot 2$(2,5-lutidine), which on standing undergoes some oxidation–reduction. 3,5-Lutidine yields stable crystals of $CrO_3\cdot 2$(3,5-lutidine). A similarly stable compound $CrO_3\cdot 2$(3-Et, 4-Me pyridine) is obtained. There is little tendency for chromium(VI) oxide to react with 2,4,6-collidine. Extensive and moderately rapid oxidation–reduction occurs with 4-vinylpyridine, and slower oxidation–reduction with poly-4-vinylpyridine. The reaction of CrO_3 with 2-vinylpyridine is very slow. By running the reactions at lower temperatures, α-picoline can be made to yield a stable, pure 1:1 addition compound without extensive oxidation–reduction. Possible structures for the addition compounds are considered.

In a recent communication from this Laboratory[2] the formation, by chromium(VI) oxide at room temperature, of a series of 1:2 addition compounds with several heterocyclic nitrogen bases was reported. These compounds included $CrO_3\cdot 2C_5H_5N$, $CrO_3\cdot 2$(β-picoline), $CrO_3\cdot 2$(γ-picoline) and $CrO_3\cdot 2$(quinoline). Extensive oxidation–reduction prevented the isolation of compounds of α-picoline and of isoquinoline under these conditions. These studies have now been extended to include other bases and other conditions of temperature.

A. Reaction with the Lutidines and 2,4,6-Collidine

In view of the difference in the behavior of α-picoline and that of β- and γ-picoline toward chromium(VI) oxide it was postulated in the previous communication in this series[3] that methyl groups in the α-position sterically hinder the coördination of chromium(VI) oxide molecules with the basic nitrogen. In order to test this hypothesis it seemed desirable to study the reactions of chromium(VI) oxide with some dialkyl and trialkyl substituted pyridines. Five isomeric lutidines (dimethylpyridines), 3-ethyl-4-methylpyridine and 2,4,6-collidine (trimethylpyridine) were studied.

Materials.—The five lutidines and 3-ethyl-4-methylpyridine were obtained from the Reilly Tar and Chemical Co. The 2,6-isomer was purified by crystallization of the urea complex, steam distillation, treatment with sodium hydroxide to set free the base, drying over sodium hydroxide, and fractional distillation. The 2,3-isomer was likewise converted to the urea complex, which was decomposed by fusion. The lutidine layer was fractionally distilled. The 2,4-, 2,5-, 3,5-lutidines and 3-ethyl-4-methylpyridine were dried over sodium hydroxide and fractionally distilled. 2,4,6-Collidine was purified in the manner suggested by Engel.[3] Commercial collidine (Matheson and Co.) was mixed with methyl alcohol, 85% phosphoric acid added, and the mixture agitated and cooled. The crystalline 2,4,6-collidine phosphate was filtered off, washed with methyl alcohol, and dried (m.p. 177°, literature 178°[3]). The phosphate was then treated with sodium hydroxide to form the free base. The base was dried over barium oxide and fractionally distilled. In all the above distillations approximately the middle third of the distillate was retained.

Chromium(VI) oxide of C.P. grade was dried under vacuum at 140° for two days in the presence of phosphorus(V) oxide, ground to a fine powder, dried again, and stored over phosphorus(V) oxide.

Procedure.—The procedure for carrying out the reactions of chromium(VI) oxide with the various nitrogen bases was similar to that described in the preceding paper[2] and involved the mixing under anhydrous conditions, of chromic anhydride with an excess of the purified base either at room temperature or precooled in an ice-bath, followed by the evaporation of the excess base under reduced pressure at room temperature, and analysis of the solid product. The methods of analysis for Cr(VI) and Cr(III) were essentially the same as those described in the preceding paper.[2] In addition to these analyses the total gain in weight of the sample (due to the taking up of the base) was determined.

Reaction of Chromium(VI) Oxide with the Lutidines.—The addition of chromium(VI) oxide to 2,6-lutidine produces no color in the lutidine, even after standing at room temperature for several days. The product remaining after the lutidine has been evaporated has practically the same weight as the original sample of chromium(VI) oxide; it contains no Cr(III), and contains the theoretical percentage of Cr(VI) for chromium(VI) oxide. It is thus apparent that no reaction between these two substances occurs under the conditions stated.

When chromium(VI) oxide is added to 2,3-lutidine, the liquid gradually colors until, after several days standing at room temperature, it is almost black in color. The chromium oxide is only slightly soluble in the base but is gradually transformed to a light brown solid. The excess lutidine was removed by evaporation under reduced pressure. Analysis of residues thus obtained shows that the light brown solid contains slightly more base than required for the formula $CrO_3\cdot(CH_3)_2C_5H_3N$. (Found: CrO_3, 48.1, 46.8, 47.4, 46.6 (on four different runs); calcd., CrO_3, 48.3). Freshly prepared products contain no Cr(III) but, on standing, oxidation–reduction occurs slowly so that, after two weeks at room temperature, as much as one-sixth of the chromium may have been reduced. Gradual loss of the lutidine also occurs.

When chromium(VI) oxide is added to 2,4-lutidine and shaken for 1.5 hours the crystals change to a dark brown, oily appearing substance without completely dissolving in the supernatant base which assume a very light yellow color. The solid which remains after evaporation of the excess base contains very little Cr(III) and contains almost enough lutidine to correspond to the formula $CrO_3\cdot 2(CH_3)_2C_5H_3N$. (Found: CrO_3, 35.0, 34.3, 35.4 (three different runs); calcd., CrO_3, 31.87). The amount of Cr(III) steadily increases as the product stands at room temperature.

Chromium(VI) oxide dissolves readily in 2,5-lutidine at room temperature to yield a reddish solution which upon evaporation yields well-defined, orthorhombic, reddish-brown crystals. The composition of the freshly prepared product corresponds to the formula $CrO_3\cdot 2(CH_3)_2C_5H_3N$ with virtually no Cr(III) present. (Found: CrO_3, 31.8, 32.6, 30.6 (three different runs); calcd., CrO_3, 31.9). On standing at room temperature, these crystals slowly change color to dark brown and they assume a pasty consistency. This is accompanied by the separation of liquid lutidine and the reduction of considerable quantities of Cr(VI) to Cr(III).

The reaction of chromium(VI) oxide with 3,5-lutidine occurs with much vigor and evolution of heat, and unless the lutidine is precooled the mixture tends to inflame. With cooling of the reaction chamber by means of an ice-bath the reaction proceeds smoothly. The solid oxide swells to more than twice its original bulk before going into solution. The

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[1] Presented in part before the April, 1951, Meeting of the Am. Chem. Soc. at Cleveland, Ohio.

[2] H. H. Sisler, J. D. Bush and O. E. Accountius, This Journal, **70**, 3827 (1948).

[3] K. H. Engel, U. S. Patent 2,408,975 (to Allied Chem. and Dye Corp.), October 8, 1946.

evaporation of the excess lutidine leaves a deposit of brilliant, light yellow crystals corresponding to the formula $CrO_3 \cdot 2(CH_3)_2C_5H_3N$, and containing no Cr(III). (Found: CrO_3, 31.0, 30.8, 31.8 (three different runs); calcd., CrO_3, 31.9). The product is stable at room temperature and undergoes no change on long standing at this temperature. The substance is insoluble in petroleum ether and carbon tetrachloride, slightly soluble in benzene and carbon disulfide, and readily soluble in water (with hydrolysis).

The reaction of chromium(VI) oxide with 3-ethyl-4-methylpyridine occurs slowly but the solid oxide gradually swells to form a fluffy, brownish-yellow solid. Because of its low volatility the excess base is not readily removed by evaporation even at very low pressures. The solid compound was therefore isolated by filtering off the supernatant liquid. More product was obtained by precipitation from the supernatant liquid with dry petroleum ether. Products obtained by either of these methods correspond closely to the formula $CrO_3 \cdot 2(CH_3)(C_2H_5)C_5H_3N$ and contain no Cr(III). (Found: CrO_3, 29.1, 29.6, 28.9 (three different runs); calcd., CrO_3, 29.24). Heating the mixture of chromium oxide and 3-ethyl-4-methylpyridine to 35° results in the reduction of some of the chromium.

The addition of chromium(VI) oxide to 2,4,6-collidine gives no evidence of reaction except for a very faint color in the base which we believe results from a trace of impurity. Analysis of a sample of the solid oxide after it stood for 12 hours at room temperature in contact with the collidine indicated that it was essentially chromium(VI) oxide with only traces of Cr(III), and that very little, if any, coördination with 2,4,6-collidine had occurred. Longer standing at room temperature produces some Cr(III).

B. Reaction with 2-Vinyl-, 4-Vinyl- and Poly-4-vinylpyridine

In order to compare the effect of methyl and vinyl substituents on the pyridine molecule on the reaction with chromium(VI) oxide the reactions of the oxide with 4-vinyl- and 2-vinylpyridine were carried out. Further it was thought that chromium(VI) oxide might react with polyvinylpyridine to form cross linked polymers by coördinating with nitrogen atoms in different polyvinylpyridine chains. Hence the reaction of chromium(VI) oxide with poly-4-vinylpyridine was studied.

Materials.—2-Vinylpyridine and 4-vinylpyridine containing an inhibitor to prevent polymerization were obtained from the Reilly Tar and Chemical Corporation. They were separated from the inhibitor by distillation. The purified monomers could be stored for several days at −70° under a nitrogen atmosphere without polymerization. Poly-4-vinylpyridine was prepared from the monomer by the method of Fuoss and Straus.[4] In order to obtain a fraction of a relatively narrow range of molecular weight the polymer was fractionally precipitated by controlled addition of benzene to a 3% solution of the polymer in *t*-butyl alcohol. Nitromethane was purified by the method suggested by Wright[5] and was finally fractionally distilled.

Reaction with 2-Vinylpyridine.—The procedure followed was similar to that used for the lutidines. Chromium(VI) oxide was found to be only slightly soluble in the base and the appearance of the solid chromium oxide sample did not change much. After standing for a period of time the liquid base was evaporated and the brownish-red, powdery residue analyzed. The results of three typical experiments are listed in Table I.

TABLE I

REACTION OF CHROMIUM(VI) OXIDE WITH 2-VINYLPYRIDINE (23°)

Time of contact, hr.	% Cr (total)	% Cr(VI)	% Cr(III)	Fraction of chromium reduced
12	42.3	36.1	6.2	0.15
12	47.7	38.8	8.9	.19
24	46.0	32.6	13.4	.29

The above results indicate that chromium(VI) oxide is slowly reduced by 2-vinylpyridine at room temperature, but that there is little tendency for 2-vinylpyridine to coördinate with the oxide since the percentage of chromium is only slightly less than in chromium(VI) oxide.

Reaction with 4-Vinylpyridine.—When chromium(VI) oxide is added to 4-vinylpyridine the liquid immediately turns red-brown in color. The chromium oxide changes to a brownish, powdery-appearing material. Evaporation of the excess of base leaves a brown powder. Runs were made at temperatures of from 0 to 25° with times of contact from 12 to 24 hours. The total percentage of chromium in the various products varied from 18.3% to 21.5% indicating that a considerable amount of the base had been taken up. Analysis for Cr(VI) and Cr(III) showed, however, that from 58 to 86% of the chromium had been reduced. The various products obtained were not homogeneous and the analysis varied with the portion of the mass from which the sample was taken.

Reaction with Poly-4-vinylpyridine.—The reaction was carried out by adding solid polyvinylpyridine to a saturated solution of the chromium(VI) oxide in nitromethane until precipitation ceased (run no. 1), by adding the solid chromium oxide to a nitromethane solution of the polymer until precipitation ceased (run no. 2), and by mixing a nitromethane solution of the polymer with a nitromethane solution of the oxide until precipitation ceased (run no. 3). In each case the precipitate was removed from supernatant liquid, dried, weighed and analyzed. The results of three typical experiments are listed in Table II.

TABLE II

REACTION OF CHROMIUM(VI) OXIDE WITH POLY-4-VINYLPYRIDINE (23°)

No. of run	Time of contact, hr.	% Cr (total)	% Cr(VI)	% Cr(III)	Fraction of Cr reduced
1	1	41.5	35.5	6.0	0.14
2	2	44.4	34.6	9.8	.22
3	..	38.4	31.7	6.7	.17

Tests on the polymer had shown the absence of any material volatile on heating in a vacuum. It is, therefore, necessary to assume that the polymer contained none of the monomer, and that the reduction obtained above is due to reaction with the polymer. The high percentage of chromium in the product indicates that there is very little evidence for coördination of the polymeric base with the chromium oxide. The reason for this lack of coördination probably relates to the configuration of the polymerized base, but there is at present little basis for speculation on this point.

C. Reaction with α-Picoline at Low Temperatures

The fact that at room temperature chromium(VI) oxide is considerably reduced by α-picoline has been previously reported.[3] It was thought that this oxidation–reduction could be at least partially inhibited by running the reaction at low temperatures and thus make possible the preparation of chromium(VI) oxide addition compound of α-picoline. The α-picoline was purified as previously described.[2]

0.59 g. of chromium(VI) oxide was added to 135 ml. of α-picoline which had been precooled to about −60°. Initially, the chromium oxide did not dissolve, but as the temperature was allowed to rise the quantity of chromium oxide appeared to decrease, the solution became slightly yellow and a bright yellow solid began to precipitate. Finally after the temperature had been allowed to rise to 0° with continuous agitation over a period of three hours all the original chromium oxide had disappeared. Seventy ml. of dry petroleum ether was added to the mixture causing the precipitation of more yellow solid, and the excess α-picoline and the petroleum ether were removed by evaporation at 0° and very low pressure. The dry, fluffy, gold-colored product obtained was analyzed for total Cr and for Cr(VI). Found: Cr(VI), 25.3; Cr (total), 25.3. Calcd. for $CrO_3 \cdot CH_3C_5H_4N$: Cr(VI), 26.94. The product was kept in a desiccator in the dark over phosphorus(V) oxide for one month at room temperature and again analyzed. Found: Cr(VI), 26.1; Cr (total), 26.2. It thus appears that the 1:1 addition compound of CrO_3 and α-picoline may be formed at temperatures below 0° without appreciable oxidation–reduction and further that, if properly purified, it can be kept without decomposition at room temperature for extended periods of time.

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(4) R. M. Fuoss and V. P. Straus, *Ann. of N. Y. Acad. Sci.*, **51**, 836 (1949).

(5) C. P. Wright, *et al.*, *J. Chem. Soc.*, 200 (1931).

D. Cryoscopic Studies

In order to obtain some evidence as to the molecular complexity of the solute species in solutions cryoscopic measurements were carried out on solutions of chromium(VI) oxide in pyridine, in β-picoline and in γ-picoline. It was assumed that these solutions obey Raoult's law and that satisfactory values for the cryoscopic constants for the three basic solvents could be obtained by averaging the results obtained by determining the freezing points of solutions of pure samples of xylene, toluene and camphor in the respective bases. Values of x, where x is defined by the equation

$$x = K \Big/ \frac{(-\Delta T_f)}{m}$$

and where K = the cryoscopic constant, $-\Delta T_f$ = the lowering of the freezing point of the solvent produced by a molality (moles/1000 g. of solvent) of chromium(VI) oxide equal to m, were calculated and are listed in Table III.

TABLE III

MOLECULAR COMPLEXITY OF CrO_3 COMPLEXES

Solvent	Values of x	Values of m
Pyridine	0.80	0.0691
	.85	.0478
	.87	.0160
	.88	.0596
	.89	.0339
	.95	.0567
β-Picoline	0.80	0.0205
	.87	.0224
	.95	.0252
γ-Picoline	0.79	0.0179
	.81	.0167
	.86	.0356
	.88	.0340
	.92	.0242
	.94	.0175

The results obtained, while not completely rigorous, seem to indicate, however, that there is no dimerization or polymerization of the chromium(IV) oxide complexes in solution in the bases pyridine, β-picoline and γ-picoline. This does not, of course, eliminate the possibility of dimers or polymers in the solid state, but it makes the assumption of such structures considerably less attractive.

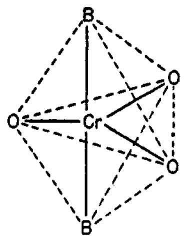
E. Discussion and Conclusions

The results of the studies with the lutidines and with 2,4,6-collidine serve to support our previous conclusion[3] that the coördination of chromium(VI) oxide with the basic nitrogen in pyridine and its derivatives is hindered by the presence of alkyl groups in the α-position. Thus, 2,6-lutidine and 2,4,6-collidine (containing two α-methyl groups) do not coördinate with the oxide at all. Further, α-picoline (α-methyl) yields only a 1:1 compound and even this must be formed at reduced temperatures to avoid extensive oxidation–reduction. Similar behavior is shown by the lutidines which contain one α-methyl group. Thus, 2,3-lutidine yields only a 1:1 compound. The 2,4- and 2,5-isomers yield 1:2 compounds but these undergo oxidation–reduction on standing. The behavior of 2-vinylpyridine seems to indicate that one α-vinyl group prevents or greatly hinders coördination with the nitrogen atom.

Substituted pyridines which contain no α-alkyl groups, however, coördinate much more rapidly than those listed above, and, when the heat of reaction is controlled, form well-defined, stable 1:2 addition compounds with chromium(VI) oxide without appreciable oxidation–reduction. This is shown by the behavior of pyridine, β-picoline, γ-picoline, 3,5-lutidine and 3-ethyl-4-methylpyridine.

Since, in those instances where the nitrogen atom on the substituted pyridine is sterically blocked by two methyl groups, there is very little tendency toward oxidation–reduction, it appears that oxidation–reduction takes place most readily through a mechanism involving prior coördination of the CrO_3 unit with the basic nitrogen, followed by some sort of attack on the α-methyl groups. Even the vinyl group, which we should expect to be fairly susceptible to oxidation by chromium(VI) oxide, is attacked much more slowly when it is in the α-position and is blocking coördination, than when it is in the γ-position.

The cryoscopic studies, though incomplete and not completely rigorous tend to show that, in solution at least, these addition compounds are monomeric, *i.e.*, contain only one CrO_3 unit per molecule of solute. It is, therefore, worth noting that the theoretical calculations of Kimball[6] show that Cr(VI) may have a trigonal bipyramidal configuration such as would give the 1:2 addition compounds discussed above, the structure



hybrid orbitals of either the dsp^3 or d^3sp types would yield such a configuration and orbitals of both of these types are available in Cr(VI).

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[6] G. E. Kimball, *J. Chem. Phys.*, **8**, 198 (1940).