The compounds studied were obtained according to our previous work [1].

### CONCLUSIONS

Under conditions of electron-impact mass spectrometry, nitromethylpyridines form molecular ions whose stability depends on the position of the substituent. The nature of the fragmentation of the molecular ions permits us to distinguish trinitromethyl from dinitromethyl substituents.

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REDUCTION OF CARBON MONOXIDE BY CHROMOUS HYDROXIDE

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The mild reduction of CO in aqueous and methanolic media, detected for pyrocatechol complexes and V(II) hydroxides [1, 2], is apparently a common reaction for protic nitrogen-fixing systems [3]. In the present work, we discovered that CO is readily reduced by the Cr(II)-HO<sup>-</sup> system even though this system has only weak nitrogen-fixing capacity [4] and efficiently reduced N<sub>2</sub> only in the presence of molybdenum compounds [5].

### EXPERIMENTAL

A sample of  $CrCl_2 \cdot 4H_2O$  was obtained by dissolving metallic chromium in aqueous HCl. The starting reagent solutions and the Rittenberg vessels containing these solutions were stored in a chamber filled with argon. The experimental method including the procedures with <sup>14</sup>CO were carried out by analogy to our previous work [2]. The PMR spectra were taken on a Bruker SXP-4-100 spectrometer.

# RESULTS AND DISCUSSION

The Cr(II) complexes obtained upon the addition of base to aqueous, water-methanol, or methanolic solutions of chromous salts are relatively stable in vacuum or under argon. Only a small portion of Cr(II) is oxidized to Cr(III):

$$2Cr(II) + 2H^{+} \rightarrow 2Cr(III) + H_{2}$$
(1)

UDC 542.941.7:5 5.262.3-31

by the protons of the medium (Table 1, experiment 1-3), and even after several days, unreacted Cr(II) may be detected after acidification by titration in the reaction mixture.

When  $Cr(OH)_2$  is generated and shaken in a CO atmosphere, methane is obtained in addition to  $H_2$ :

$$CO + 6Cr(II) + 6H^{+} \rightarrow CH_{4} + H_{2}O + 6Cr(III)$$
(2)

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TABLE 1.	Yield o	f H <sub>2</sub> in	an Ar	Atmosphere	and of H <sub>2</sub>
and CH <sub>4</sub> in	a CO A	tmosphe	re and	the Fractio	on of 👘
Unreacted	Cr(II)	in the	Cr(II)-	-NaOH-CH <sub>3</sub> OH	(-H <sub>2</sub> 0)
system					

Experiment	Water content	Yield of H <sub>2</sub>	Unreacted						
No.	in the solvent, vol. %	H <sub>2</sub>	CH₄	Ct(II), %					
Ar atmosphere									
1 2 3	Traces 5 100	10,3 31,2 32,8	Traces »	86,0 65,5 63,0					
$CO   atmosphere (p_{CO} = 1 atm)$									
4 5 6 7 8 9	<b>Traces</b> 5 10 50 85 100	6,8 2,7 6,0 13,3 14,2 15,1	14,9 32,7 27,2 28,0 16,8 18,0	13,0 10,2 5,9 7,5 11,6 10,0					

\*Containing 0.375 mmole Cr(II) and 3.75 mmoles NaOH. The total volume of the reaction mixture was 7.5 ml, and the reaction time was 24 h. Methanol was the solvent in experiments 1 and 4, while water was the solvent in experiments 3 and 9.

as well as a small amount of ethane [about 1% relative to Cr(II)]. Table 1 indicates that the extent of the oxidation of Cr(II) under these conditions is about 90%, while the consumption of Cr(II) in reactions (1) and (2) in all the experiments is significantly less and, thus, the formation of  $CH_4$  and  $C_2H_6$  is not the only pathway for the reduction of carbon monoxide. Aldehydes, alcohols, and carboxylic acids are possible products of the reductive reactions of CO on chromous hydroxide in addition to hydrocarbons.

Formaldehyde, which is formed in significant amounts from CO on V(II) pyrocatechol complexes in methanol [1, 2], was not detected either in methanolic or water-methanol solutions (by analysis with chromotropic acid in  $H_2SO_4$  after removal of the Cr hydroxide precipitate).

In order to detect  $CH_3OH$ , we used the same method as in our study of vanadium systems [1, 2] and studied the reduction of <sup>14</sup>CO by chromous hydroxide in methanol. Indeed, after the separation of the gaseous reactions products (see Table 1, experiment 4), radioactivity is found in the solution separated from the reaction mixture by freezing. Upon fractionation of the solvent, the label is distributed virtually uniformly in the first fractions, while the later fractions are enriched to a slight but real extent by radioactive reaction products. The <sup>14</sup>C distribution upon additional distillation of the individual fractions diluted by methanol indicated that the yield of <sup>14</sup>CH<sub>3</sub>OH is 38% relative to Cr(II).

In order to detect other products including acids, after removal of the solvent from the reaction mixture, the precipitate was dissolved in dilute  $H_2SO_4$ . Since radioactive products with a high <sup>14</sup>C content are frozen out of this solution together with water we added water an additional two times to the precipitate and methanol and the solvents were frozen out. The total <sup>14</sup>C content in the combined water-methanol solution corresponded to about 1 mole reacted <sup>14</sup>CO per mole Cr(II).

The high radioactivity of the water-methanol solution may be explained by the presence of formate in the reaction products (CO is known readily to add HO<sup>-</sup> in alkaline media); formic acid is formed upon the acidification of this solution. Indeed, after the alkalization of the water-methanol solution, only a slight amount of radioactive products are frozen out with solvent; these products are <sup>14</sup>CH<sub>3</sub>OH and, apparently, <sup>14</sup>C<sub>2</sub>H<sub>5</sub>OH in 4% yield relative to Cr(II). The dry residue did not contain any of the reduction products in significant amounts except for H<sup>14</sup>CO<sub>2</sub>Na. The label is uniformly distributed over the fractions upon the distillation of formate by formic acid. Only the signal for the formic acid H-C proton is seen in the PMR spectrum of formate in dilute D<sub>2</sub>SO<sub>4</sub> in D<sub>2</sub>O (8.2 ppm relative to TMS); the H<sup>14</sup>CO<sub>2</sub>H content calculated from the integral intensities of this signal and the signals of the aromatic protons of  $C_6H_5CO_2$  of known concentration corresponded precisely to that determined in the radioactivity measurements. We should note that chromous hydroxide does not reduce sodium formate.

Thus, the major products of the reduction of CO by chromous hydroxide in methanol are  $CH_4$ ,  $C_2H_6$ , and alcohols; the hydrocarbon yield is about 16%, while the alcohol yield is about 50%. Upon carrying out the reaction in 5-50% aqueous methanol, the  $CH_4$  yield is increased, while the methanol yield drops. Thus, 32.7%  $CH_4$  and 25.6% methanol are formed in 5% aqueous methanol in an experiment with <sup>14</sup>CO (experiment 5).

These data permit certain conclusions relative to the mechanism of the formation of  $CH_4$  from CO in this system. Formaldehyde is readily reduced by chromous hydroxide, apparently to methanol. Less than 1%  $CH_4$  is formed in this reaction. Even less methane is found in the reaction products of  $Cr(OH)_2$  in methanol or aqueous methanol in the absence of CO (experiments 1 and 2). Thus, the major portion of  $CH_4$  in this system is formed on polynuclear species providing for six-electron reduction of CO to  $CH_4$  without the intermediate formation of  $CH_2O$  or  $CH_3OH$ .

In the case of V(II) hydroxide, in contrast to  $Cr(OH)_2$ , methanol is virtually the only product of the reduction of CO [1] (only traces of  $CH_4$  are formed in highly basic media). In view of the many types of coordination of CO and the products of its reduction with polynuclear complexes [6], the differences in the composition of the CO reduction products in these two systems may be related not only to the higher reducing potential of Cr(II) but also to a different extent of polymerization of the hydroxide species in these systems.

# CONCLUSIONS

Chromous hydroxide reduces CO under mild conditions in protic media. The major reactions products are methane and methanol. Methane is formed from CO in the coordination sphere of the complex without the escape of formaldehyde or methanol into the solution.

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