

4.2.2.18 The Copper/Methoxide System in Dry Solvents

The solvent most commonly used in the work with the copper/methoxide system, diethyl carbitol, is very hygroscopic. It was felt that water in the solvent could be causing the loss of methoxide and the formation of sodium formate. Reaction of methoxide with water produces hydroxide and methanol and reaction of hydroxide with CO could produce formate. Therefore, it was decided to examine the reactivity of the copper/methoxide system in carefully dried solvents. The results of these experiments are summarized in Table 55.

In DEC dried by refluxing several days over sodium, the gas uptake was lower than expected, but the products were normal, including the usual brown solids containing sodium formate. It was felt that the low activity might be due to solvent decomposition so a milder drying procedure was tried. The DEC was predried over 4A molecular sieves and then refluxed over calcium hydride. The results were about the same, except that the selectivity to methyl formate was unusually high. Gas chromatographic analysis showed that the dried DEC contained no detectable water and that undried DEC contained about 0.1% water, so an experiment was tried with 0.1% water as an additive, but full activity was not restored. Since drying the DEC also removed dissolved oxygen, an experiment was tried in which the dry DEC was saturated with oxygen before reaction, but no difference in reactivity was observed. Finally, a standard experiment with undried DEC was run and it too showed lower than usual activity. One experiment in tetrahydrofuran dried over sodium/benzophenone showed the same results as the DEC experiments. The cause of the lower than usual activity is unknown. However, these experiments clearly demonstrate that water is not causing the loss of methoxide and/or formation of formate. Completely dry solvents produce the same formate-containing solids as are produced with undried solvent.

Table 55. The Copper/Methoxide System in Dry Solvents

SGHAM-G-#	91	93	94	96	97	95
1 Catalyst	CuI	CuI	CuI	CuI	CuI	CuI
2 mmol	5	5	5	5	5	5
3 NaOMe, mmol	110	110	110	110	110	110
4 Solvent ^a	DEC ^b	DEC ^c	DEC ^c	DEC ^c	DEC	THF ^d
5 mL	75	75	75	75	75	75
6 Additive	none	none	H ₂ O	O ₂	none	none
7 mmol ^e	-	-	2	Sat.	0	0
8 Press, psi	2000	2000	2000	2000	2000	2000
9 H ₂ /CO	1:1	1:1	1:1	1:1	1:1	1:1
10 Temp., °C	110	110	110	110	110	110
11 Time, hrs	3	3	3	3	3	3
12 Uptake, psi	1620	1420	1800	1720	1600	1840
13 Wt.% MeOH	4.0	0.1	2.2	2.3	NA ^f	3.0
14 Wt.% MeOF	7.7	8.5	7.3	6.4	NA ^f	8.4
15 Other Prods	none	none	none	none	none	none

Experimental procedure: B(14); Analytical procedure: C(7); Key on page 176.

^a DEC = Diethyl carbitol; THF = tetrahydrofuran.

^b Dried by refluxing over sodium.

^c Dried with 4A mol. sieves, then refluxing over CaH₂.

^d Dried by refluxing over sodium/benzophenone.

^e Sat. = saturated.

^f Not Analyzed.

4.2.2.19 Investigation of a Complex Reducing Agent

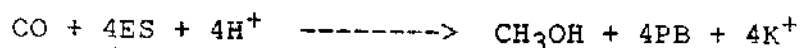
It was noted that the copper/methoxide system has some features in common with a class of heterogeneous reducing agents known as the complex reducing agents, or CRA's. CRA's are prepared from a transition metal salt, sodium hydride and an alcohol which reacts with part of the sodium hydride to form the sodium alkoxide [1]. Thus the CRA's contain a transition metal, hydride and alkoxide, similar to the systems containing copper hydride and sodium methoxide. CRA's have been reported to reduce substrates such as alkyl and aryl halides [2], aldehydes, ketones [3], alkenes and alkynes [4]. In the presence of CO, CRA's will carbonylate aryl halides [5]. The similarity of CRA's to the copper methoxide system prompted an experiment in which the CRA prepared from copper(I) iodide, sodium hydride and tert-amyl alcohol was used as a catalyst for CO hydrogenation. Although this material did reduce bromobenzene to benzene as reported in the literature, it did not catalyze the hydrogenation of CO in diethyl carbitol. No other work was done with the CRA's.

1. Brunet, J.J.; Vanderesse, R.; Caubere, P. *J. Organomet. Chem.*, 1978, **157**, 125.
2. Vanderesse, R.; Brunet, J.J.; Caubere, P. *J. Org. Chem.*, 1981, **46**, 1270.
3. Brunet, J.J.; Mordenti, L.; Caubere, P. *J. Org. Chem.*, 1978, **43**, 4804.
4. Brunet, J.J.; Mordenti, L.; Loubinoux, B.; Caubere, P. *Tet. Lett.*, 1977, 1069.
5. Brunet, J.J.; Sidot, C.; Loubinoux, B.; Caubere, P. *J. Org. Chem.*, 1979, **44**, 2199.

4.2.3 Iron Catalysts

4.2.3.1 Introduction

A series of recent publications [1-4] has reported the reduction of CO to methanol at room temperature and one atmosphere of CO pressure by a system composed of Everitt's salt (ES, $K_2Fe^{II}[Fe^{II}(CN)_6]$) coated on a platinum plate, methanol and an iron or chromium complex in aqueous solution. The reduction of CO is accompanied by oxidation of the ES to Prussian Blue (PB, $KFe^{III}[Fe^{II}(CN)_6]$) and consumption of protons from the solution according to the stoichiometry shown below.



The reaction reportedly ceases when all of the ES has been converted to PB. However, the PB may be electrochemically reduced back to ES, thus making the reaction electrocatalytic and increasing the yield of methanol.

Although the Everitt's salt system as reported has only a distant relation to the goal of producing higher alcohol mixtures from synthesis gas, it can be envisioned that logical extensions of this system could lead to the desired reactivity. For example, the combination of electrons supplied electrochemically and protons from the aqueous solution is equivalent to the molecular hydrogen contained in synthesis gas. Also, it is claimed that the only function of the ES is electron transfer, so it should be replaceable by a homogeneous analog. Finally, the product of the reaction may be shifted from methanol to higher alcohols by additives, different reaction conditions, different catalysts or the presence of co-catalysts. With these goals in mind, it was decided to investigate this system, first to verify the literature results, and then to extend them as outlined above.

1. Ogura, K.; Yamasaki, S. *J. Chem. Soc., Faraday Trans. I*, 1985, **81**, 267.
2. Ogura, K.; Kanako, M. *J. Mol. Catalysis*, 1985, **31**, 49.
3. Ogura, K.; Yamasaki, S. *J. Mol. Catalysis*, 1985, **30**, 411.
4. Ogura, K.; Watanabe, H. *J. Chem. Soc., Faraday Trans. I*, 1985, **81**, 1569.

4.2.3.2 Reduction of CO to Methanol by Everitt's Salt System

A series of recent publications has reported the reduction of CO to methanol at room temperature and one atmosphere pressure by a system composed of Everitt's salt (ES, $K_2Fe^{II}[Fe^{II}(CN)_6]$) coated on a platinum plate, methanol and an iron or chromium complex in aqueous solution. The production of methanol from CO under such mild conditions is unprecedented. It was therefore decided to investigate this system as a part of Task 2. Experiments were performed in order to verify the reported CO reduction and to try to extend the use of the Everitt's salt system to syngas reactions.

Stoichiometric reactions were investigated using Procedure B(7) described in Appendix B. Electrocatalytic reactions with the complexes diaquobis(oxalato)chromate and amminepentacyanoferrate were performed using Procedures B(8) and B(9), respectively. High pressure tests were conducted using Procedure B(10). In all cases products were analyzed by Procedure C(6) described in Appendix C.

Before trying to extend the reactivity of this system to the conversion of syngas, it was felt that the reduction of CO to methanol reported in the literature should be verified. Both the stoichiometric reduction, with no potential applied to the Everitt's salt coated electrode, and electrocatalytic reductions were attempted under conditions as close as possible to those in the literature reports. In none of the experiments was any methanol produced. A close examination of the data in the literature reports revealed that for the stoichiometric reductions, the reported yield of methanol was at least 130 times the theoretical yield based on the amount of Everitt's salt available. For the electrocatalytic reduction, methanol was reported to be produced at a rate 275 times that possible based on the current being consumed. It was therefore concluded that the reports of methanol formation at room temperature and one atmosphere are erroneous.

4.2.3.3 Study of Everitt's Salt System Under Syngas Pressure

While investigating the room temperature, one atmosphere reactivity of the Everitt's salt system, two important discoveries were made. First, the aquo- and amminepentacyanoferrate complexes reported to catalyze the reduction of CO to methanol were not the actual species present during the reaction. Electrochemical studies confirmed other literature reports that these complexes react rapidly with CO to form a very stable carbonyl complex, and it is this complex which is present in the Everitt's salt systems using the pentacyanoferrate catalyst precursors. The high formal potential of the Fe(III/II) couple of the carbonylpentacyanoferrate complex suggested that the carbonyl ligand might be highly activated and thus reactive under more extreme conditions. Second, it was found that molecular hydrogen, the second component of syngas, could reduce Prussian Blue to Everitt's salt when the Prussian Blue was coated on a platinum substrate. Thus if the Everitt's salt system were reactive at higher temperatures and pressures, the electrochemical reduction of Prussian Blue to Everitt's salt would be unnecessary since this would be accomplished by the hydrogen. It was therefore decided to attempt the reduction of CO at elevated temperatures and pressures with the Everitt's salt system and 1:1 syngas as the source of the CO and H₂.

Experiments were conducted under various conditions of pressure and temperature as outlined in Table 56. No methanol was produced with either the pentacyanoferrate or the bis(oxalato)-chromate homogeneous catalyst. It was therefore concluded that this system is unlikely to lead to a homogeneous catalyst for the production of higher alcohol mixtures from syngas, so no further work was done on it.

Key to Table 56

SGHAM-G-#

1 Catalyst	Catalyst precursor; anionic complex charged.
2 mM	Concentration of catalyst complex.
3 PB, mol $\times 10^{-6}$	Total moles of Prussian Blue on 8 cm ² Pt foil.
4 MeOH, mM	Concentration of methanol added initially.
5 Solvent	Solvent used.
6 Electrolyte	Either 0.1 M KCl or pH 3.5 phthalate buffer.
7 pH	pH of solution, adjusted with HCl or buffer.
8 mL	Volume of catalyst solution charged.
9 Pressure, psi	Reaction pressure.
10 H ₂ /CO	Syngas composition, molar (volume) ratio.
11 Temp., °C	Reaction temperature; maximum temp. for #28.
12 Time, hrs	Total reaction time in hours.
13 Uptake, psi	Gas uptake during reaction in psi.
14 Stab. PB	Stability of Prussian Blue coating in reaction.
15 Stab. Cat	Stability of catalyst complex during reaction.
16 Products	Reaction products detected by GC analysis.

Table 56. Pressure Experiments with the Everitt's Salt System

SGHAM-G-#	28	29	30	31	32
1 Catalyst	$\text{Fe}(\text{CN})_5^{3-}$	$\text{Fe}(\text{CN})_5^{3-}$	$\text{Fe}(\text{CN})_5^{3-}$	$\text{Fe}(\text{CN})_5^{3-}$	$\text{Cr}(\text{C}_2\text{O}_4)^{2-}$
2 mM	10	10	10	10	14
3 PB, mol x 10^{-6}	2.4	2.4	2.4	2.4	2.4
4 MeOH, mM	20	20	20	20	20
5 Solvent	Water	Water	Water	Water	Water
6 Electrolyte	KCl	KCl	KCl	Phthalate	Phthalate
7 pH	3.5	3.5	3.5	3.5	3.5
8 mL	172	179	188	180	177
9 Pressure, psi	2000	4000	4000	4000	4000
10 H ₂ /CO	1:1	1:1	1:1	1:1	1:1
11 Temp., °C	200	100	100	100	100
12 Time, hrs	5.5	5.0	4.5	4.0	3.5
13 Uptake, psi	0	50	0	30	0
14 Stab. PB	Poor	Poor	Poor	Fair	Good
15 Stab. Cat	Poor	Good	--	Fair	Good
16 Products	None	None	None	None	None

Experimental procedure: B(10); Analytical procedure: C(6); Key on page 208.

4.2.4 Other Catalysts

4.2.4.1 Introduction

Several novel metal complex-solvent combinations have been tested for catalytic activity. Solvents were chosen for these studies based on their anticipated interactions with the catalytic species. Some of these combinations have shown alcohol production, but the rates are quite low.

Experiments were also carried out with a novel ligand in combination with cobalt and copper complexes. It was thought that a combination of properties of the ligand could lead to a catalyst with high activity.

Two experiments were done to investigate a literature report claiming conversion of H_2/CO to methanol under conditions of one atmosphere and $20^\circ C$. The catalyst was a metalloporphyrin/colloidal platinum/ligand combination in a variety of solvents. Other experiments involved selected complexes of palladium and rhenium.

4.2.4.2 Investigation of Novel Solvent-Metal Combinations

We had previously postulated that the nitrogen-containing organic solvent N-phenylcarbazole may provide nucleophilic activation of homogeneous catalysts. Additional evaluations of other N-phenylcarbazole/M (M = transition metal complex) combinations were conducted under similar conditions, and results are given in Table 57. These reactions were all begun at 210°C; if catalytic activity was not observed at this temperature after one hour (by monitoring gas uptake), the temperature was raised to 240°C. After another hour the temperature was raised further to 270°C if activity was not observed. It was found that an inactive system resulted with M = $\text{Mn}_2(\text{CO})_{10}$, while traces of alcohols (methanol and ethanol) were noted when M = $\text{Fe}_3(\text{CO})_{12}$, $\text{Cu}(\text{CH}_3\text{CO}_2)_2$, $\text{Pd}(\text{acac})_2$, $\text{Ru}_3(\text{CO})_{12}$, $\text{Rh}(\text{CO})_2(\text{acac})$, or $\text{Ru}_3(\text{CO})_{12}/\text{I}_2$. The volatility of N-phenylcarbazole caused undesirable complications during the recovery of the reaction products in these runs.

Key to Table 57

SGHAM-V-#

1 Catalyst	Catalyst precursor; complex charged.
2 mmol	Amount of designated complex added.
3 Solvent	Solvent used; Tol = toluene; Sulf = sulfolane.
4 mL	Amounts of solvents employed.
5 Promoter	Promoters used.
6 mmol	Amounts of promoters added.
7 Pressure, psi	Reaction pressure.
8 H ₂ /CO	Syngas composition, molar (volume) ratio.
9 Temp., °C (Max.)	Max. reaction temperature; all began at 210°C.
10 Time, hrs	Total reaction time in hours.
11 Wt.% MeOH	Percent by weight of individual products in final reaction solution.
12 Wt.% EtOH	
13 Wt.% n-PrOH	

Table 57. Experiments with Transition Metal/Solvent Couples

SGHAM-V-#	3-2	3-4	3-7	3-10
1 Catalyst	Mn ₂ (CO) ₁₀	Ru ₃ (CO) ₁₂	Pd(acac) ₂	Fe ₃ (CO) ₁₂
2 mmol	7.8	0.75	0.84	2.4
3 Solvent	TMB ^a	TMB ^a	N-PC ^b /Tol	N-PC ^b /Tol
4 mL	75	75	30/45	30/45
5 Promoter	-	-	-	-
6 mmol	-	-	-	-
7 Pressure, psi	6000	6000	6000	6000
8 H ₂ /CO	1:1	1:1	1:1	1:1
9 Temp., °C (Max.)	240	240	240	240
10 Time, hrs	3	3	3	3
11 Wt.% MeOH	30 ^c	25 ^c	1.5	0.1
12 Wt.% EtOH	-	-	0.5	-
13 Wt.% n-PROH	-	-	-	-

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 212.

^a Trimethoxyboroxine.

^b N-Phenylcarbazole.

^c Due to solvent decomposition.

Table 57. Experiments with Metal/Solvent Couples (Cont'd)

SGHAM-V-#	3-12	3-17	3-19	3-24
1 Catalyst	Cu(AcO) ₂	Ru ₃ (CO) ₁₂	Ru ₃ (CO) ₁₂	Rh(CO) ₂ (acac)
2 mmol	18.5	3.1	3.1	3.0
3 Solvent	N-PC ^a /Tol	N-PC ^a /Tol	N-PC ^a /Tol	N-PC ^a /Sulf
4 mL	30/45	30/45	30/45	30/45
5 Promoter	-	I ₂	I ₂	-
6 mmol	-	8.0	8.0	-
7 Pressure, psi	6000	6000	6000	6000
8 H ₂ /CO	1:1	1:1	1:1	1:1
9 Temp., °C (Max.)	270	210	260	240
10 Time, hrs	3	3	3	3
11 Wt.% MeOH	0.3	3.2	1.9	2.0
12 Wt.% EtOH	0.1	1.2	0.2	0.3
13 Wt.% n-PrOH	-	-	-	-

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 212.

^a N-phenylcarbazole.

4.2.4.3 Effects of Solvents on Rhodium Catalysts

Previous results showed that the use of the solvents 3,4,5-trimethoxytoluene and 2,4,6-trimethoxytoluene resulted in unusually stable cobalt catalysts. Therefore several reactions were carried out with related solvents and the more reactive rhodium catalyst to determine whether catalyst stability could also be improved in this system. Results are given in Table 58. Mixtures of methanol and ethanol were obtained in solvents 1,2-dimethoxybenzene and 2-methoxyphenol with promoted rhodium catalyst systems, and solvent stability appeared satisfactory in these initial tests. Productivities were lower than desirable, however.

Table 58. Effects of Solvents on Rhodium Catalysts

SGHAM-V-#	3-29	3-32	3-35	3-54
1 Catalyst	RCA ^a	RCA ^a	RCA ^a	RCA ^a
2 mmol	3.0	3.0	3.0	1.5
3 Solvent	DMT ^b	DMB ^c	DMB ^c	DMB ^c /EtOH
4 mL	75	75	75	50/50
5 Promoter	NMM ^d	NMM ^d	NMM ^d	Na
6 mmol	3.0	5.0	5.0	15.5
7 Pressure, psi	6000	6000	6000	2000
8 H ₂ /CO	1:1	1:1	1:1	0:1
9 Temp., °C	220	220	240	90
10 Time, hrs	1.5	3.5	3.0	1.5
11 Wt.% MeOH	15.0 ^e	1.3	1.0	-
12 Wt.% EtOH	1.2	0.2	0.10	-
13 Solids	some	trace	little	some
14 Solv. Decomp.	70.0	-	trace	37.0

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 140.

^a Rh(CO)₂(acac).

^b 2,5-Dimethoxytetrahydrofuran.

^c 1,2-Dimethoxybenzene.

^d N-Methylmorpholine.

^e Formed mainly as a result of solvent decomposition.

Table 58. Effects of Solvents on Rhodium Catalysts (Cont'd)

SGHAM-V-#	3-64	3-74
1 Catalyst	RCA ^a	RCA ^a
2 mmol	3.0	3.0
3 Solvent	2-MP ^f	2-MP ^f
4 mL	75	75
5 Promoter	NMM ^d	CsHCO ₂
6 mmol	5.0	0.50
7 Pressure, psi	6000	6000
8 H ₂ /CO	1:1	1:1
9 Temp., °C	240	260
10 Time, hrs	5.0	6.0
11 Wt.% MeOH	0.35	1.3
12 Wt.% EtOH	0.60	0.3
13 Solids	none	some
14 Solv. Decomp.	5.0	15.0

Experimental procedure: B(3); Analytical procedure: C(3); Key on page 140.

^a Rh(CO)₂(acac).

^d N-Methylmorpholine.

^f 2-Methoxyphenol.

4.2.4.4 Low Pressure Runs with Cu and Co Complexes

Borohydride-reduced cobalt and copper complexes containing a novel ligand which possesses a highly acidic functionality have been evaluated for the conversion of syngas to alcohols under relatively mild conditions (100°C and 950 psi 2:1 H₂/CO). Both polar and nonpolar solvents have been tested. In this novel approach, it was anticipated that the highly acidic functional group would serve as a potent activator. The screening experiments, shown in Table 59, have not shown significant gas uptake or product formation. Initially it was thought that sodium borohydride insolubility in nonpolar solvents precluded metal reduction/activation; however, reaction in a polar solvent also did not result in catalyst activation.

Key to Table 59

SGHAM-REM-#

1 Catalyst	Complex added as catalyst precursor.
2 mmol	Amount of complex in mmoles.
3 Solvent	Solvent used for reaction.
4 mL	Amount of solvent in mL.
5 Additive	Additive included in reaction.
6 mmol	Amount of additive in mmoles.
7 Promoter	Promoter employed.
8 mmol	Amount of promoter in mmoles.
9 Pressure, psi	Reaction pressure in psig.
10 H ₂ /CO	Synthesis gas molar (volume) ratio.
11 Temp., °C	Reaction temperature.
12 Time, hrs	Reaction time in hours.
13 Uptake, psi	Gas uptake in psig.
14 Wt.% MeOH	Amount of methanol observed.
15 Wt.% EtOH	Amount of ethanol observed.

Table 59. Low Pressure Runs with Cobalt and Copper

SGHAM-REM-#	21-2	21-3	21-5
1 Catalyst	Co(OAc) ₂ ·4H ₂ O	CuCl ₂ ·2H ₂ O	Co(OAc) ₂ ·4H ₂ O
2 mmol	0.65	0.65	0.65
3 Solvent	Toluene	Toluene	Toluene
4 mL	35	35	35
5 Additive	A27	A27	A27
6 mmol	0.65	0.65	0.65
7 Promoter	NaBH ₄	NaBH ₄	NaBH ₄
8 mmoles	1.0	1.0	1.0
9 Pressure, psi	965	968	969
10 H ₂ /CO	2:1	2:1	2:1
11 Temp., °C	100	100	100
12 Time, hrs	3.5	1.5	2.0
13 Uptake, psi	-	-	-
14 Wt.% MeOH	-	-	-
15 Wt.% EtOH	-	-	-

Experimental procedure: B(11); Analytical procedure: C(3); Key on page 219.

4.2.4.5 Screening of Various Other Catalysts

Several other potential catalysts were briefly screened for activity. $\text{PdCl}_2/\text{NaOMe}$, a system similar to the active Cu/base system showed no activity. A rhenium complex, $(\text{C}_5\text{Me}_5)\text{Re}(\text{CO})_3$, gave only traces of hydrocarbons even under extreme temperature conditions, 310°C .

Two experiments were done to investigate claims made in a Japanese patent application [1] that reported conversion of H_2/CO to methanol under conditions of 1 atmosphere and 20°C . The catalyst was a metalloporphyrin/colloidal platinum/ligand combination in a variety of solvents. Presumably, the metalloporphyrin binds and activates CO, which is reduced by colloidal platinum-activated H_2 . Experiments M-8 and 9 were done to test this idea. The data are included in Table 60. We did not observe any product formation under conditions similar to those claimed in this patent.

1. Japanese patent application 59-088,436 (1984), to Nihon Mining Co.

Key to Table 60

SGHAM-M-#

1 Catalyst	Compounds added as catalyst precursor.
2 Amount	Amount added.
3 Additive	Catalyst additive employed.
4 Amount	Amount used.
5 Solvent	Reaction solvent.
6 Pressure, psi	Reaction pressure in psia.
7 H ₂ /CO	Syngas molar ratio.
8 Temp., °C	Reaction temperature.
9 Uptake, psi	Gas uptake, psig.
10 Time, h	Reaction time in hours.
11 MeOH, Wt. %	Amounts of products, nd = not detected.
12 EtOH, Wt. %	
13 n-PrOH, Wt. %	
14 n-BuOH, Wt. %	
15 i-BuOH, Wt. %	
16 C ₂ + ROH, Wt. %	Fraction of alcohols higher than methanol.

Table 60. Screening of Metalloporphyrin Complexes

SGHAM-M-#	8	9
1 Catalyst	Fe(TPP)/Coll Pt	Fe(TPP)/Coll Pt
2 Amount	10 mg/10 mL	10 mg/10 mL
3 Additive	imidazole	imidazole
4 Amount	34 mg	34 mg
5 Solvent	H ₂ O/HOAc	H ₂ O/HOAc
6 Pressure, psi	14.7	1500
7 H ₂ /CO	1.0	1.0
8 Temp., °C	20	14
9 Uptake, psi	na	400
10 Time, h	384	5.0
11 MeOH, Wt. %	nd	nd
12 EtOH, Wt. %	nd	nd
13 n-PrOH, Wt. %	nd	nd
14 n-BuOH, Wt. %	nd	nd
15 i-BuOH, Wt. %	nd	nd
16 C ₂ + ROH, Wt. %	na	trace

Experimental procedure: B(1); Analytical procedure: C(1); Key on page 222.