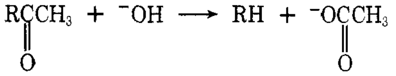
Table I. Ferrocenecarboxylic Acids via Oxygenation

Reaction	Yield,[a] %	Reaction	Yield,[a] %
1a → **2a**	80	**1e** → **2b**	83
1b → **2a**	86	**1f** → **2b**	86
1c → **2a**	51	**1g** → **2a**	34
1d → **2a**	25	**2b**	17

[a] Satisfactory analytical and ir data were obtained.

etylferrocenes are due to a keto cleavage which acetylferrocenes partially can undergo in the presence of strong base.[5]



$$RC(=O)CH_3 + {}^{-}OH \longrightarrow RH + {}^{-}OC(=O)CH_3$$

Thus, oxidation of **1c** gave 40% ferrocene and only 51% **2a.** The oxidation of **1g** yielded 26% ferrocene, 34% **2a,** and only 17% **2b.**

The high conversions of **1a–c** and **1e,f** are very surprising because the corresponding oxidation of mono- and dimethylferrocenes to ferrocenecarboxylic acids never yielded more than 25%.[6] As we could show the lower yields are due to an inhibiting effect caused by oxidation products of HMPT.[7]

Obviously this inhibiting effect does not exist during oxidation of hydroxymethyl, formyl, and acetyl substituted ferrocenes but seems to exist during oxidation of *N,N*-dimethylaminomethylferrocene (**1d**) which yielded only 25% of **2a.** This result leads to the assumption that oxidation products of *N,N*-dimethylamino groups, which are present in HMPT and in **1d,** may inhibit the base-catalyzed oxidation. The inhibiting effect is under further investigation.

Experimental Section

General Procedure. To a solution of freshly sublimed potassium *tert*-butoxide (150 mmol, for one substituent to be oxidized) in 110 ml of freshly distilled HMPT was added under inert atmosphere a solution of **1a–g** (15 mmol) in 20 ml of HMPT. After stirring for 30 min at room temperature dry oxygen was bubbled through the mixture which then was heated to 80 °C for 24 h. The reaction products were poured on ice, and the resulting alkaline solution was extracted with ether. The aqueous phase was acidified with dilute hydrochloric acid. Ferrocenecarboxylic acids **2a,b** precipitating upon acidification were filtered off and dried over phosphorus pentoxide. The acid solution was extracted with ether, and the compounds **2** were obtained after evaporation of the ether extracts. Recrystallization from ethanole was not necessary (**2a,** mp 202–204 °C, lit.[2] mp 205–210 °C; **2b,** mp 250 °C dec, lit.[3b] mp 250 °C dec). Mixtures from **2a** and **2b,** obtained from the oxidation of 1,1′-diacetylferrocene, can be separated by extraction with hot benzene, in which the monocarboxylic acid is soluble.

Registry No.—**1a,** 1273-86-5; **1b,** 12093-10-6; **1c,** 1271-55-2; **1d,** 1271-86-9; **1e,** 1291-48-1; **1f,** 1271-48-3; **1g,** 1273-94-5; **2a,** 1271-42-7; **2b,** 1293-87-4.

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Hydrogenation of Cyclohexene Catalyzed by First Row Transition Metal Stearates

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Among the most unusual and promising catalysts for homogeneous hydrogenation of olefins and aromatics are the transition metal stearates reported by Tulupov.[1–4] A good brief summary can be found in James' book[5] and Tulupov has published on the kinetics and mechanism of the reaction[6] and on the interaction of the metals with cyclohexene[7] in addition to two reviews.[8] We have attempted to repeat some of Tulupov's work and failed.

Briefly, Tulupov reported the reduction of cyclohexene in ethanol by hydrogen at ca. 1 atm at room temperature in the presence of stearate salts of Ni(II), Cu(II), Co(II), Cr(III), Fe(III), Sc(III), Ti(IV), and Zn(II). He also reports the hydrogenation of benzene catalyzed by stearate salts of Ni(II), Co(II), Fe(III), and Pb(II). There is little precedent for these observations in the literature. It is well known that Cu(I) carboxylate salts catalyze the reduction of benzoquinone[9] in quinoline and this reaction has been studied by two groups.[10,11] Also Rh(II) acetate is known to catalyze the hydrogenation of olefins in a variety of solvents.[12] A number of salts reported as active in ethanol by Tulupov have been reported to be inactive in aqueous systems,[13] consistent with Tulupov's claim of inhibition by water. Neither the Rh(II) nor Cu(I) work serves as confirmation of Tulupov's reports since the Cu(I) system was run in a solvent very different from ethanol and Tupulov did not study any rhodium systems. A thorough literature search yielded no reports of attempts to repeat Tulupov's studies.

Results

A number of stearate salts were prepared using Koenig's procedure,[14] the same one used by Tulupov. After a number of washings, pure salts having acceptable analyses were obtained. When we attempted to dissolve the Ni(II) stearate in anhydrous ethanol (Tulupov[2] reports the solubility as 4.21×10^{-3} M/l.), the ethanol remained colorless and all the salt was recovered by filtration. Two very tiny crystals of Ni(II) stearate were placed in an Erlenmeyer flask with ca. 100 ml of ethanol and allowed to stand for 6 h with occasional shaking. They did not dissolve. Warming the flask until the Ni(II) stearate melted did not result in any room temperature solubility. Similar observations were made with Cu(II) stearate (reported[3] solubility 4.02×10^{-4} M/l.) except that we did note some small solubility in hot ethanol. Koenig[14] reports that these two salts are insoluble in methanol but soluble in amyl alcohol.

A number of attempts were made to hydrogenate cyclohexene and some of them are reported in Table I. All reactions were run in Parr hydrogenators in which other catalytic hydrogenations had successfully been carried out. In no case was any reaction observed. With reaction no. 7, assuming that Tulupov's[3] reported reaction rate in ethanol would be unchanged in isobutyl alcohol, we can calculate a pressure drop of ca. 5.3 psi under our reaction conditions. We could detect a pressure drop of ca. 0.2 psi. The reactions were run with commercial anhydrous ethanol and with ethanol dried by refluxing over Mg and distillation under dry N_2 onto molecular sieves (3A). Two different batches of sodium stearate were used. The cyclohexene gave only two peaks on gas chromatography; one, having a slightly larger retention time than

Table I. Attempted Catalytic Hydrogenation of Cyclohexene Using Tulupov's Catalysts

Rxn	"Catalyst"	Solvent	Temp, °C	H_2 pressure, psia	Rxn time, h	Pressure drop, psi
1	Ni(II) stearate	Hexanes	$\sim$23	37	48	0
2	Ni(II) stearate	Hexanes	60	38	60	0
3	$NiCl_2$	Ethanol	$\sim$23	45	37	0
4	$NiCl_2 \cdot 6H_2O$	Ethanol	$\sim$23	47	43	0
5	$NiCl_2$/stearic acid[2]	Ethanol	$\sim$23	45	36	0
6	$NiCl_2 \cdot 6H_2O$/stearic acid	Ethanol	$\sim$23	35	24	0
7	Cu(II) stearate	Isobutyl alcohol	50	38	28	0
8	$CoCl_2$	Ethanol	$\sim$23	46	67	0
9	$CoCl_2$/stearic acid	Ethanol	$\sim$23	47	36	0
10	Ni(II) stearate[a]	Hexanes	$\sim$23	49	42	0

[a] The olefin used was norbornene.

cyclohexene, had an area less than 0.1% of the cyclohexene peak area.

Discussion

We have been unable to reproduce Tulupov's reported reactions or catalyst solubilities. Since both $NiCl_2$ and stearic acid are quite soluble in ethanol, the reported solubility may be due to impure Ni(II) stearate contaminated with the compounds from which it is made. It does take extensive washing to remove these.

It is more difficult to explain our failure to hydrogenate cyclohexene. Obviously, neither the salts nor their precursors showed any catalytic activity. Since Tulupov observed reactivity with a variety of salts, and we with none, the place to look for the explanation is in those compounds common to all systems: the sodium stearate and cyclohexene. The use of two different batches of sodium stearate from two different manufacturers greatly reduces the probability that there was an inhibitor present. Likewise, use of a second olefin (norbornene, rxn 10) with the same results reduces the possibility of an inhibitor being present in the reactant. It is possible that something is present in Tulupov's stearic acid which is causing the reaction. Having been unable to obtain samples of catalyst from Tulupov, we are not able to investigate this aspect of the problem further. In any event, it is quite clear that all is not well with the reported use of transition metal stearate salts as homogeneous catalysts for olefin hydrogenation.

Experimental Section

Melting points were taken on a Mel-Temp apparatus and were uncorrected. Analytical gas chromatography utilized a Varian Aerograph Model 1400 instrument equipped with a flame ionization detector and using a 0.125 in. × 7 ft 5% SE-30 on 60–80 mesh Chromosorb W column. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Ethanol was dried by refluxing over magnesium and distillation under dry nitrogen onto molecular sieves (3A). Hexanes and isobutyl alcohol were dried over molecular sieves (3A).

Metal Stearates. Sodium stearate (13.5 g, Fischer) was dissolved in 900 ml of water and the mixture was heated and stirred until the solution was clear. The hot soap solution then was poured with vigorous stirring onto a solution containing 6 g of $NiSO_4 \cdot 6H_2O$ or 4 g of $CuSO_4$ in 600 ml of warm water. The precipitates were washed by decantation with water and dried in the air at 115 °C for 15 h. Nickel stearate was also made from the sodium stearate prepared from stearic acid (Emery) and sodium hydroxide.

Nickel(II) stearate: green solid; mp 100 °C; yield 84%. Anal. Calcd for $NiC_{36}H_{70}O_4$: C, 69.09; H, 11.34. Found: C, 69.77; H, 10.70.

Copper(II) stearate: light blue solid; mp 106–108 °C; yield 80%. Anal. Calcd for $CuC_{36}H_{70}O_4$: C, 68.56; H, 11.21. Found: C, 68.51; H, 11.66.

Attempted Catalytic Hydrogenation of Cyclohexene. To a stearate salt ($\sim$1 g) in $\sim$110 ml of warm solvent was added 12 g of cyclohexene (Eastman Kodak). The solution was poured into a 500-ml hydrogenation bottle and the bottle was then mounted on a low-pressure Parr hydrogenator. Air was removed from the system by alternatively filling the system with hydrogen to 35 psi and venting it at least three times. The solution was shaken at ca. 3 atm hydrogen pressure. Similar procedure was also carried out for the hydrogenation of bicyclo[2.2.1]-2-heptene (Aldrich). The pressure of the system was monitored.

Acknowledgment. We are grateful to the Energy Research and Development Administration for support of this work.

Registry No.—Sodium stearate, 822-16-2; nickel(II) stearate, 2223-95-2; copper(II) stearate, 660-60-6; cyclohexene, 110-83-8; bicyclo[2.2.1]-2-heptene, 498-66-8.

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An Aberrant Rearrangement in the Reaction of 1,2-Dibromo-3,3-difluorocyclopropene with Anthracene[1]

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In an attempt to develop a rational synthesis of the as yet unknown, but potentially useful synthon 3,3-difluorocyclopropene (**1a**), we have examined the reaction of anthracene with 1,2-dibromo-3,3-difluorocyclopropene (**1b**).[2] It was anticipated that the [4 + 2] cycloadduct **2** would permit a classical approach to the elusive[3] cyclopropene (**1a**) via reductive