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Vanadium-catalyzed carboxylation of linear and cyclic C_5 and C_6 alkanes

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Abstract

Cyclopentane, cyclohexane, pentane, and hexane are carbonylated in single-pot processes and under mild conditions to carboxylic acids (highest yields of 54–33% and turnover numbers [TONs] of 76–50) by vanadium (IV) and (V) complexes in TFA. These complexes present N,O- or O,O-ligands, namely basic forms of aminoalcohols and of (hydroxyimino)dicarboxylic acids, trifluoroacetate, or triflate. The effects of various parameters (e.g., catalyst type, oxidizing agent, CO pressure, temperature, reaction time, type of solvent) were investigated. The use of either too low or too high CO pressures is discouraged, because the former promote the formation of trifluoroacetate esters and the latter, above a certain level, do not result in higher yields or TONs of the carboxylic acids. Carbon- and oxygen-centered radical mechanisms are suggested by experiments with radical traps and by acid product distribution.

Keywords: Vanadium catalyst; Carboxylation; Homogeneous catalysis; Alkane; Carbon monoxide

1. Introduction

Functionalization of saturated hydrocarbons (alkanes) is attracting great attention, and their conversion into more valuable products, like carboxylic acids, is a matter of current interest. Alkanes are unreactive by most conventional synthetic methods, and their partial oxidation with homogeneous metal catalysts has been recognized as one of the most promising approaches [1–12]. The most important general commercial methods of producing carboxylic acids include aldehyde oxidation, carboxylation of olefins (Koch synthesis), paraffin oxidation, and alkali fusion of alcohols [13]. However, saturated hydrocarbons, the main components of petroleum oil, are abundantly available and cheaper, and their direct conversion to carboxylic acids constitutes one of the most promising routes for the synthesis of the latter.

Fujiwara's group has already reported the catalytic carboxylation of alkanes by CO using such catalysts as $Pd(OAc)_2$ [14–17], $Cu(OAc)_2$ [14,15,17], Mg [18,19], $CaCl_2$ [20], and $Co(OAc)_2$ [21,22], but the yields or turnover numbers (TONs) and selectivities toward carboxylic acids are usually modest. Hence a main aim of the current work is to find a more active homogeneous catalytic system for an alkane-based synthetic method of carboxylic acids. Another objective is to provide a contribution toward the expansion of the still-underdeveloped field of catalysis with vanadium coordination compounds [23,24].

For such purposes, we have addressed some vanadium (IV) or (V) complexes (like Amavadine and related models) with N,O ligands, which we have previously found to be active, under mild conditions, for the single-pot conversion of methane into acetic acid [25] with and without the presence of CO, and for the peroxidative halogenation, hydroxylation, and oxygenation of alkanes into organohalides, alcohols, and ketones, respectively [26,27]. Here we report the results of the extension of the methane carboxylation reaction to liquid alkanes. We show that such vanadium (IV) and (V) complexes and related complexes, using $K_2S_2O_8$ as an oxidizing agent and trifluoroacetic acid (TFA) as a solvent, in mild conditions, catalyze the conversion of linear (pentane and hexane) and cyclic (cyclopentane and cyclohexane) C_5 and C_6 alkanes, in the presence of CO, into carboxylic acids with good yields (up to 50%).

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2. Experimental

2.1. Materials

The following compounds were used as received from the supplier: carbon monoxide (Air Products), dinitrogen (Air Liquid Portugal), cyclopentane (Fluka), cyclohexane (Aldrich), pentane (Lab-Scan), hexane (Fluka), potassium peroxodisulfate (Fluka), ammonium peroxodisulfate (Fluka), *tert*-butyl hydroperoxide solution, 70% in water (Fluka), TFA (Aldrich), *n*-butyric acid (Aldrich), and diethyl ether (Lab-Scan). The following complexes, applied as catalysts, were prepared according to published methods: $[VO\{N(CH_2CH_2O)_3\}]$ **1** [28,29], $Ca[V(HIDA)_2]$ (HIDA = basic form of 2,2′-(hydroxyimino)diacetic acid) **2** [30], $Ca[V(HIDPA)_2]$ (HIDPA = basic form of 2,2′-(hydroxyimino)dipropionic acid) **3** [30], $[VO(ada)(H_2O)]$ (ada = basic form of *N*-2-acetamidoiminodiacetic acid) **4** [31], $[VO(Hheida)(H_2O)]$ (Hheida = dibasic form of 2-hydroxyethyliminodiacetic acid) **5** [31], and $[VO(CF_3SO_3)_2] \cdot 2H_2O$ **8** [32]. Complexes $[VO\{N(CH_2COO)(CH_2CH_2O)(CH_2CH_2OH)\}]$ **6** and $[VO(CF_3COO)_2] \cdot 2H_2O$ **7** were prepared as described below, whereas $VOSO_4 \cdot 5H_2O$ **9** (Merck), V_2O_4 **10** (Merck), and V_2O_5 **11** (Aldrich), the other catalysts, were used as received.

2.1.1. Complex *6*

N,N-bis(2-hydroxyethyl)glycine (bicine) (0.82 g, 5.0 mmol) and $Ba(OH)_2 \cdot 8H_2O$ (1.58 g, 5.00 mmol) were dissolved in deionised water (20 mL) under dinitrogen. The solution was heated and stirred for 30 min, after which $VOSO_4 \cdot 5H_2O$ (1.26 g, 5.00 mmol) was added and the reaction mixture stirred for another 30 min. The formed solid of $BaSO_4$ was separated by filtration, and the filtered dark-blue solution was concentrated under vacuum to yield an oily residue, which was washed with diethyl ether by the freeze-thaw technique to give a dark-blue solid that was filtered off, washed with diethyl ether, and dried under vacuum. Yield 0.662 g (58%). IR (KBr): 951(m) $\nu(V{=}O)$, 1442(m), 1647(w), 3385 cm^{-1}(w,br) $\nu(OH)$. MS (FAB^+): m/z: 228 $[M^+]$; elemental analysis: calcd (%) for $C_6H_{11}O_5NV \cdot 0.5(CH_3CH_2)_2O$ (228): C 36.0, H 6.2, N 6.0; found: C 35.6, H 6.7, N 6.5.

2.1.2. Complex *7*

The synthesis was performed in two steps. In the first step, the salt $Ba(CF_3COO)_2$ was synthesized by the reaction of $Ba(OH)_2 \cdot 8H_2O$ (204.7 mg, 0.65 mmol) with TFA (CF_3COOH) (0.10 mL, 1.3 mmol) in water under dinitrogen (yield 89%). This salt (144.8 mg, 0.58 mmol) was then dissolved in methanol (2 mL), and the solution was added to a methanol solution (2 mL) of $VOSO_4 \cdot 5H_2O$ (146.4 mg, 0.58 mmol). The formed precipitate of $BaSO_4$ was subsequently filtered off, and the filtered bright-blue solution was concentrated under vacuum to give a brown solid, which was dried for a few hours at 120 °C in an oil bath. Yield 122 mg (72%); IR (KBr): 728 (s), 991(m) $\nu(V{=}O)$, 1151(m), 1205(m), 1439(m), 1676(w) $\nu(C{=}O)$, 3400 cm^{-1}(w,br) $\nu(OH)$; elemental analysis: calcd (%) for $C_4O_5F_6V \cdot 2H_2O$ (329): C 14.6, H 1.2; found: C 14.5, H 0.9.

2.2. Instrumentation

C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (ca. 1.18×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000–400 cm^{-1}) were recorded on a Jasco FT/IR–430 instrument in KBr pellets. ^{13}C-$\{^1H\}$ and ^{19}F nuclear magnetic resonance (NMR) spectra were recorded at 22 °C on a Varian UNITY 300 spectrometer using TMS as internal standard (for ^{13}C) and $CFCl_3$ (for ^{19}F).

Gas chromatography (GC) measurements were carried out on a Fisons model 8160 equipped with a flame ionisation detector and a capillary column (DB-WAX; column length, 30 m; i.d., 0.32 mm). Helium was used as the carrier gas. GC-mass spectroscopy (MS) measurements were carried out in a Fisons Trio 2000 mass spectroscope with a coupled gas chromatograph (Carlo Erba Instruments, Auto/HRGC/MS).

2.3. Typical carboxylation procedures and products analysis

The reaction mixtures were prepared as follows. To 0.0625 mmol of the metal complex contained in a 39.0 mL AISI 316 stainless steel autoclave equipped with a Teflon-coated magnetic stirring bar was added the oxidant [either $K_2S_2O_8$ (12.5 mmol), $(NH_4)_2S_2O_8$ (12.5 mmol), or *t*-BuOOH (12.5 mmol)], the substrate [cyclopentane (0.90 mL, 9.58 mmol), cyclohexane (1.00 mL, 9.26 mmol), pentane (1.00 mL, 8.68 mmol), or hexane (1.10 mL, 8.42 mmol)] and 22.0 mL of TFA. Then the autoclave was closed and flushed with dinitrogen three times for replacing the air inside and finally pressurized with 0–60 atm of carbon monoxide. The reaction mixture was vigorously stirred using a magnetic stirrer for 2–20 h at 40–150 °C with an oil bath. After the reaction was complete, the autoclave was cooled using an ice bath, then degassed and opened. To 2.5 mL of the filtered reaction solution was added 6.5 mL of diethyl ether (which led to further precipitation) and 90 µL of *n*-butyric acid (as an inner standard). The obtained mixture was stirred, then filtered off and analyzed by gas chromatography. The reaction products (carboxylic acids) were quantitatively analyzed by GC (1 µL samples) using the inner standard method. The injection temperature was 240 °C, and the column temperature was initially 100 °C for 1 min, then increased by 10 °C/min (or 5 °C/min for the analysis of the hexane products) to 250 °C and held at this value for 1 min.

In some cases, products were also identified by GC-MS and ^{13}C-$\{^1H\}$ NMR of the final reaction solutions. The carboxylic acids of all hydrocarbons were determined by both GC and ^{13}C-$\{^1H\}$ NMR (in $CDCl_3$) spectroscopy, and the esters were identified by ^{13}C-$\{^1H\}$ and ^{19}F NMR spectroscopy. Genuine samples of the esters were synthesized in our laboratory by the reaction of TFA with the corresponding alcohols and their NMR