

Lithium-Promoted Hydrogenation of Carbon Dioxide to Formates by Heterobimetallic Hydrido Zinc Alkoxide Clusters

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General Considerations: All manipulations were carried out under anaerobic conditions in dry argon using standard Schlenk techniques. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. NMR spectra were recorded on a BrukerAvance 250 (250.1 MHz (1H)), Bruker ARX200 (200 MHz (1H)) and Bruker DRX400 (400 MHz (1H)) spectrometers at ambient temperature.

IR Measurements: The in situ CO₂ adsorption studies in solution were performed on a Nicolet FTIR spectrometer equipped with a home made glass reactor connected to an IR liquid cell with NaCl windows. The spectra were run at room temperature at a spectral resolution of 4 cm⁻¹ accumulating 20 scans. A concentrated solution of the nanocomposite in toluene was transferred under inert atmosphere in the glass reactor and was circulated continuously through the liquid cell. The flow rates of the gases passing through the solution were 25 ml/min.

Formation of [Zn(HCO₂)₂·2H₂O] in solution: A solution of [(HZnOtBu)₃(thf·LiOtBu)] **1b** (0.25 g, 0.43 mmol) in ca. 20 mL THF was treated with CO₂ for 20 min at room temperature and stirred at this temperature for 1 h. The volatile components of the solution were removed in vacuo. Colourless crystals suitable for X-ray diffraction were isolated after recrystallization of the residue in THF at -30°C. Yield: 0.3 g (1.2 mmol, 98%); IR: 3436 cm⁻¹ (O-H), 2970 cm⁻¹, 2869 cm⁻¹ und 2736 cm⁻¹ (C-H), vs 1608 cm⁻¹ and vs 1376 cm⁻¹ (HCOO). ¹H NMR

(298 K, 250.1 MHz, D₂O): $\delta = 8.26$ ppm (s) ; ¹³C{¹H}-NMR (298 K, 62.9 MHz, D₂O): $\delta = 173.9$ ppm.

Crystal data for C₂H₆O₆Zn, $M_r=191.44$, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.6803(9)$, $b = 7.1241(10)$, $c = 9.3060(12)$ Å, $\beta = 97.664(3)^\circ$, $V = 570.3(1)$ Å³, $\rho_{\text{calcd}} = 2.229$ g cm⁻³, $\mu = 4.265$ mm⁻¹, $Z = 4$, $\lambda = 0.71073$ Å, $T = 213$ K, 209 reflections collected ($\pm h, \pm k, \pm l$), [Θ range: 3.71 to 25.02], 926 independent ($R_{\text{int}}=0.019$) and 734 observed reflections [$I > 2\sigma(I)$], 110 refined parameters, $R = 0.022$, $wR_2 = 0.062$. CCDC-650772 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Quantum Chemical Calculations and assignment of vibration bands: The assignments of characteristic vibration modes of the formate ion is based on quantum chemical calculations. The calculations were performed with the program package Turbomole.¹ The geometries were optimized at the DFT level employing the resolution of identity approach² and using the BP functional.³ A TZVP basis set was used for all atoms besides the C(CH₃)₃ groups and for tetrahydrofuran. Here, the basis set was reduced to DZ. From test calculations on smaller molecules like H₂O, HCOO⁻, and HCOOH, we estimate an accuracy for the vibration frequencies of about 30 cm⁻¹ compared to the experimental values.⁴ The relative shifts of comparable vibrations, like Zn-H, in different compounds, should be even more accurate. The two different conformers **A** and **B** of the hypothetical initial products [**1a** + CO₂] and [**1b** + CO₂] have been considered (Fig. 1). Conformer **B** has stronger binding energies of 0.477 eV for **1a-B** and 0.533 eV for **1b-B**, respectively. From literature it is known that formate can adopt symmetric chelating. We observed for the hypothetical insertion product **1a+CO₂**, that the potential energy surface is very flat with respect to the change between the symmetric and the monodentate form. The energy of a symmetric HCO₂ group is only 0.01 eV higher than the energy of **1a-B**.

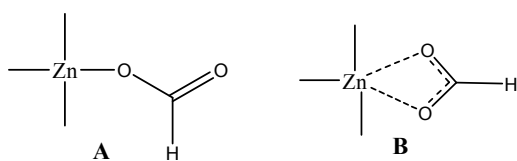


Fig. 1: Coordination modes of postulated formate species from the initial insertion of CO₂ into the Zn-H bond of **1a** and **1b**, respectively.

Tab.1. Experimental and calculated values for selected stretching vibration modes.

a) Experimental

	$\nu(\text{ZnH})$	$\nu_{\text{as}}(\text{HCO}_2)$	$\nu_{\text{s}}(\text{HCO}_2)$	$\nu(\text{HCO}_2)$
1a	1796-1813	-	-	-
1b	1769	-	-	-
1a + CO ₂	1798-1813	1650-1600	1331	2700-2800
1b + CO ₂	1769,1793	1659-1633	1330	2700-2800

b) Calculated

		$\nu(\text{ZnH})$	$\nu_{\text{as}}(\text{HCO}_2)$	$\nu_{\text{s}}(\text{HCO}_2)$	$\nu(\text{HCO}_2)$
1a		1809,1810, 1815			
1b		1777,1780, 1786			
1a +CO ₂	A	1826,1830	1710	1203	2758
1b +CO ₂	B	1821, 1826	1638	1248	2893
1a +CO ₂ sym.	B	1815,1819	1553	1341 (1285)	2960
1b +CO ₂	A	1798,1800	1701	1214	2772
1b +CO ₂	B	1788, 1797	1645	1249	2868

In Figure 1 the calculated stretching frequencies of the different coordination modes for the postulated HCO₂ species from the reaction of **2** with CO₂ and the experimental stretching

frequencies are compared to a selection of literature values for zinc formate. Table 1 shows the comparison between the experimental data a) and the theoretical values b) for the reactions of **1** and **2** with CO₂.

The experimentally observed shift in the Zn-H stretching frequencies between compound **1** and **2** is well reproduced in the calculations. An unequivocal assignment of the formate species to one or more of the HCO₂ coordination modes took shape with difficulty. The experimentally observed C-H stretching frequency between 2700 and 2800 cm⁻¹ is in good agreement with the calculated values for conformer A. The respecting CO stretching frequencies $\nu_s(\text{OCO})$ and $\nu_{as}(\text{OCO})$ are in the same region as solvent bands. The situation for conformer B is just reverse. While the CH frequency should be covered by other vibrations, the CO stretching frequencies should be observable. The difference between a symmetric and an asymmetric chelating mode may be derived from the difference $\Delta\nu$ of $\nu_s(\text{OCO})$ and $\nu_{as}(\text{OCO})$. In general the observed difference is smaller for symmetric chelating modes than for asymmetric chelating modes. The obtained $\nu_s(\text{HCO}_2)$ frequencies in the 1633-1659 cm⁻¹ region are postulated to apply to the conformer B. Here, it has to be considered, that the energies of the symmetric and the asymmetric form of B are almost identical, while the vibration modes are strongly influenced by small changes in the geometry. Our conclusion is, that both conformers A and B contribute to the vibration spectra.

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