

Selected reactions of cobalt carbonyl complexes placed under vacuum conditions[☆]

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Dedicated to: Professor László Markó on the occasion of his 70th birthday.

Abstract

There are two main equilibrium reactions involving $\text{Co}_2(\text{CO})_8$ which illustrate the sensitivity of the chemico–physical behavior of cobalt carbonyls to small changes in their immediate environment, such as change in CO partial pressure, addition of hydrogen, presence of a base or application of a vacuum. The first, is the equilibrium reaction of $\text{Co}_2(\text{CO})_8$ with H_2 to yield $\text{HCo}(\text{CO})_4$. Both the kinetics and the equilibrium of this reaction are strongly influenced by the relative p_{CO} in the system. The second is the equilibrium decomposition of $\text{Co}_2(\text{CO})_8$ to $\text{Co}_4(\text{CO})_{12}$. This work examines these reactions and the behavior of some cobalt carbonyls under more drastic conditions, such as vacuum or partial vacuum conditions. The results are discussed as to their possible relevance and role in the mechanism of the hydroformylation (OXO) reaction. Specifically, the formation of the trinuclear cobalt carbonyl hydride, $\text{HCo}_3(\text{CO})_9$, is described and analyzed under conditions which may arise in the semi-stoichiometric OXO reaction, i.e. at low p_{CO} or in the absence of CO. The consequences of the presence of small quantities of $\text{HCo}_3(\text{CO})_9$ in solution on the mechanism of the semi-stoichiometric OXO reaction are discussed. In addition, the decomposition reaction of $\text{Co}_2(\text{CO})_8$ to $\text{Co}_4(\text{CO})_{12}$ is examined in the absence of CO, and some pertinent, previously unreported, thermodynamic parameters are calculated. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cobalt; Metal carbonyls; Vacuum conditions

1. Introduction

Cobalt carbonyl complexes have been the subject of extensive research since the discovery of $\text{Co}_2(\text{CO})_8$ by Mond et al. in 1910. Unlike other transition metal carbonyl complexes, e.g. Fe, Rh, etc., the cobalt compounds demonstrate a remarkable level of complexity, as indicated by their chemico–physical behavior and their chemical properties [2]. In addition to their sensitivity to air [3], they are also very sensitive to small

changes in their immediate environment, i.e. change in CO partial pressure [4], addition of hydrogen [5], presence of a base [3,6] or application of a vacuum [1]. Since cobalt carbonyl complexes are of great importance in catalytic processes, most notably the hydroformylation (OXO) reaction, the changes which inevitably occur in such complex reactions will undoubtedly affect the cobalt carbonyls. The behavior of cobalt carbonyls under the previously accepted mild (i.e. $p_{\text{CO}} < 10$ atm and $p_{\text{H}_2} < 100$ atm, and low temperatures) conditions of the stoichiometric and pseudo-stoichiometric OXO reactions have been extensively investigated [7,8]. Under these conditions (which differ from the more drastic conditions used in the catalytic OXO reaction), there are two main equilibrium reactions involving $\text{Co}_2(\text{CO})_8$ which illustrate the delicate equilibrium among several cobalt carbonyl species as a

[☆] Most of these results were obtained during the course of the Ph.D. work of Rina Tannenbaum [1].

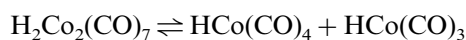
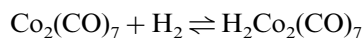
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function of hydrogen and carbon monoxide partial pressures. When $\text{Co}_2(\text{CO})_8$ is placed under medium or high hydrogen pressure, the formation of cobalt tetracarbonyl hydride from dicobalt octacarbonyl can be observed according to Eq. (1):



Eq. (1) must be regarded as one of the key steps in hydrogen activation by cobalt carbonyls, as has been reconfirmed in recent years by important new observations regarding the versatile chemistry of $\text{HCo}(\text{CO})_4$. Carbon monoxide has a retarding effect on the synthesis of $\text{HCo}(\text{CO})_4$ from $\text{Co}_2(\text{CO})_8$, and in order to account for this observation, the following series of equilibria have been suggested [9–12]:



It is obvious, therefore, from these equations, that in the presence of CO, the equilibrium will shift in favor of the coordinatively saturated species, but the actual CO partial pressure present in the reaction mixture will strongly affect this equilibrium. In previous studies [12], we have shown that at constant $p\text{CO}$, the equilibrium of Eq. (1) will be determined by the hydrogen partial pressure. However, $p\text{CO}$ has to be kept sufficiently high during the course of the reaction in order to prevent the formation of $\text{Co}_4(\text{CO})_{12}$, i.e. $p\text{CO}$ ca. 0.6 atm.

Fachinetti has reported [13] that in pentane or hexane solutions, containing almost equimolar quantities of $\text{HCo}(\text{CO})_4$ and $\text{Co}_2(\text{CO})_8$, the unstable trinuclear hydride, $\text{HCo}_3(\text{CO})_9$, also characterized by X-ray diffraction analysis [14,15], is formed transiently according to Eq. (2):

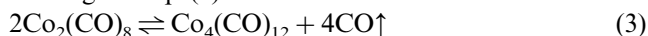


Within the context of the stoichiometric OXO reaction where CO is practically absent, the formation of such a trinuclear cobalt carbonyl complex containing a hydrogen atom is highly possible, even if such a formation is not observed. One can speculate that $\text{HCo}_3(\text{CO})_9$ might form in very small concentrations, and since it is not in direct equilibrium with hydrogen, it can react very fast with an olefin to form a π -complex, which in turn carries on the OXO reaction.

To shed new experimental light upon the chemistry of this trinuclear hydride, we shall describe in this work our direct observations of the in situ formation of $\text{HCo}_3(\text{CO})_9$ during the course of the stoichiometric

OXO reaction, which was conducted either in the absence of CO, or under very low CO partial pressure ($p\text{CO} < 0.6$ atm).

The second equilibrium reaction of great importance is the $\text{Co}(\text{CO})_4$ to $\text{Co}(\text{CO})_3$ transformation according to Eq. (3):



This equilibrium reaction was studied in great detail by Bor et al. [4,17,18], who constructed a three-dimensional equilibrium diagram of the stability regions of $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ as a function of CO partial pressure. It was found that at low $p\text{CO}$, the equilibrium shifts strongly in favor of $\text{Co}_4(\text{CO})_{12}$. In the last phase of the stoichiometric OXO reaction (which was initiated by the introduction of an olefin into a hydrocarbon solution containing equilibrated amounts of $\text{Co}_2(\text{CO})_8$ and $\text{HCo}(\text{CO})_4$), when all the CO in the gas phase has already reacted to give the aldehyde, $\text{Co}_2(\text{CO})_8$ will be destabilized and a rapid $\text{Co}(\text{CO})_4$ to $\text{Co}(\text{CO})_3$ transformation can be expected.

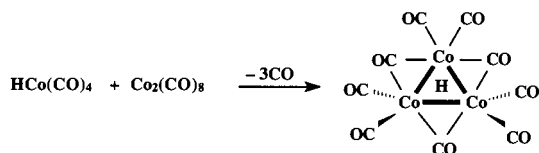
In this work we also examine the $\text{Co}(\text{CO})_4$ to $\text{Co}(\text{CO})_3$ transformation in the extreme case where $\text{Co}_2(\text{CO})_8$ is placed under vacuum (0.01–0.02 mmHg), and the solution stirred thoroughly to avoid dependence on diffusional rates. Preliminary qualitative results [19] have shown that if a solution of $\text{Co}_2(\text{CO})_8$ which has been kept under $p\text{CO}$ is placed under vacuum for a short time to remove the CO, the formation of $\text{Co}_4(\text{CO})_{12}$ starts immediately even at room temperature, and reaches ca. 10% $\text{Co}_4(\text{CO})_{12}$ in approximately 1 h. During this time, the reaction slows down due to the presence of CO liberated in the reaction, according to the equilibrium law in equation Eq. (3). If the solution is again evacuated for a short time, the reaction becomes fast and $\text{Co}_4(\text{CO})_{12}$ increases from ca. 14% to ca. 27% in approximately 1 h. Surprisingly enough, even though this rapid rate of decomposition of $\text{Co}_2(\text{CO})_8$ to $\text{Co}_4(\text{CO})_{12}$ has been qualitatively observed under vacuum, no quantitative thermodynamic or kinetic data have been reported.

In this paper, therefore, we shall examine the behavior of some cobalt carbonyls under vacuum or partial vacuum conditions, and the results shall be discussed as to their possible relevance and role in the mechanism of the OXO reaction.

2. Results and discussion

2.1. Formation and decomposition of $\text{HCo}_3(\text{CO})_9$

It has been reported by Fachinetti [13–15] that $\text{Co}_2(\text{CO})_8$ and $\text{HCo}(\text{CO})_4$ may give rise to a reaction whose product is an unsaturated, electron deficient,



Scheme 1. Schematic structural representation of the unsaturated, electron deficient, trinuclear cobalt complex containing a hydrogen atom face-bridged to the three cobalt atoms.

trinuclear cobalt complex containing a hydrogen atom face-bridged to the three cobalt atoms, as shown in Scheme 1. We have reproduced the synthesis conditions of this compound which were described by Fachinetti [13], by utilizing an alkane solution containing equilibrated concentrations of $\text{Co}_2(\text{CO})_8$ and $\text{HCo}(\text{CO})_4$. This solution was obtained by the reaction of $\text{Co}_2(\text{CO})_8$ with H_2 at high $p\text{H}_2$ and low $p\text{CO}$, to prevent $\text{Co}_2(\text{CO})_8$ decomposition [4,16–18], and was frequently used for the study of the stoichiometric OXO reaction [1,12,20]. An IR spectrum of the equilibrated mixture is shown in Fig. 1. $\text{HCo}_3(\text{CO})_9$ contains bridging CO ligands (at least in the solid state [14,15]), and hence, to be able to indicate the presence of this compound in the reaction mixture, special attention was devoted to the analysis of the bridging carbonyl region. It is noteworthy to mention, that similar to the IR spectra of other cobalt carbonyl complexes, the terminal carbonyl re-

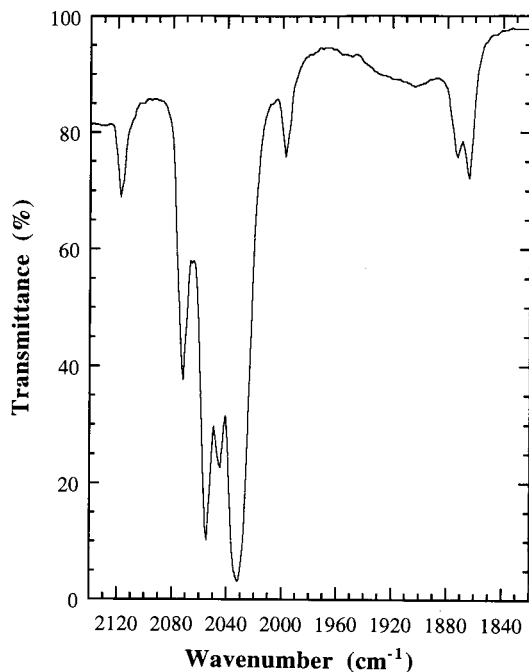


Fig. 1. The IR absorption spectrum of an hexane solution containing equilibrated concentrations of $\text{Co}_2(\text{CO})_8$ and $\text{HCo}(\text{CO})_4$. This solution was obtained by the reaction of $\text{Co}_2(\text{CO})_8$ with H_2 at high $p\text{H}_2$ and low $p\text{CO}$, to prevent $\text{Co}_2(\text{CO})_8$ decomposition, and was frequently used for the study of the stoichiometric OXO reaction.

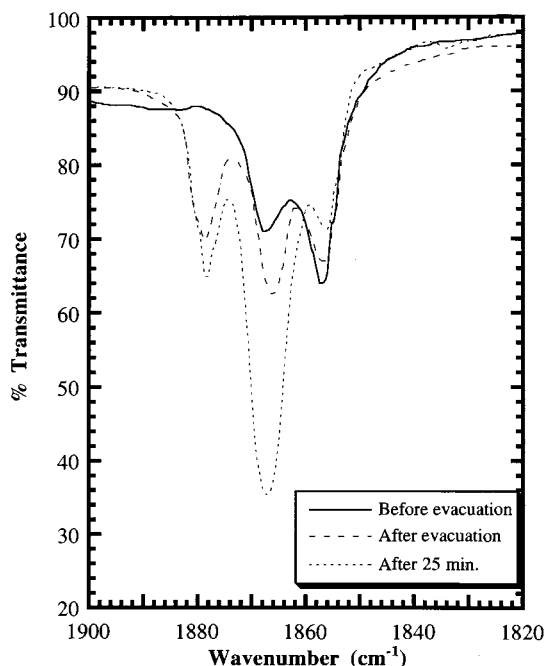


Fig. 2. The IR absorption spectrum of the formation of $\text{HCo}_3(\text{CO})_9$. $\text{HCo}_3(\text{CO})_9$ exhibits a strong IR absorption band at 1879 cm^{-1} , corresponding to the bridged carbonyl stretching mode.

gion is characterized by considerable band overlap of the various carbonyl bands of the cobalt carbonyl complexes present in solution [20]. On the other hand, in the equilibrated octacarbonyl/hydride mixture, only $\text{Co}_2(\text{CO})_8$ has absorption bands in the bridging region, a medium absorption band at 1858 cm^{-1} and a shoulder at 1867 cm^{-1} . Upon consecutive evacuations of the reaction vessel for short periods, the formation of a new cobalt complex was observed, as shown in Fig. 2. It has been reported that the complex $\text{HCo}_3(\text{CO})_9$ exhibits a strong IR absorption band at 1879 cm^{-1} , corresponding to the bridging carbonyl stretching mode [13]. $\text{HCo}_3(\text{CO})_9$ may be characterized by two additional absorption bands, at 2037 and 2054 cm^{-1} , corresponding to the terminal carbonyls stretching modes. Unfortunately, these bands cannot be observed because they overlap with absorption bands of $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ which are also present in the system. The 1879 cm^{-1} band increased as the evacuation procedure was repeated. The reproducible occurrence of this bridging CO absorption band seems to be an unequivocal indication for the transient formation of $\text{HCo}_3(\text{CO})_9$, under the given conditions.

Had the formation of the $\text{HCo}_3(\text{CO})_9$ carbonyl complex been a reversible equilibrium process, it would have been obvious to expect that it would be stabilized by hydrogen at elevated pressures, similar to $\text{HCo}(\text{CO})_4$. However, when pressurizing the system with 100 atm of H_2 , $\text{HCo}_3(\text{CO})_9$ was not stabilized, but decomposed rather quickly to give $\text{Co}_4(\text{CO})_{12}$, as shown

in Fig. 3. The decomposition of $\text{HCo}_3(\text{CO})_9$ is characterized by the decrease in the intensity of the 1879 cm^{-1} band and increase in the intensity of the 1867 cm^{-1} band which corresponds to the bridging carbonyl stretching of $\text{Co}_4(\text{CO})_{12}$. After 90 min, the band corresponding to $\text{HCo}_3(\text{CO})_9$ disappeared, and all detectable cobalt was in the form of $\text{Co}_4(\text{CO})_{12}$. No traces of $\text{Co}_2(\text{CO})_8$ were detected during the decomposition and hence it seems to be a direct recombination of the $\text{Co}(\text{CO})_3$ groups.

These observations demonstrate that $\text{HCo}_3(\text{CO})_9$ is a metastable species which forms transiently under these conditions and no H_2 and/or CO pressure regions stabilize it.

2.2. Decomposition of $\text{Co}_2(\text{CO})_8$ under vacuum

The lability of $\text{Co}_2(\text{CO})_8$ in the absence of CO partial pressure (which gives it a unique position in the series of the 3d metal carbonyls) has been investigated in a relatively non-volatile solvent (*n*-dodecane, b.p. 216°C). Ungváry and Markó reported [21] that the kinetic equation for this decomposition in the presence of CO is second-order with respect to $\text{Co}_2(\text{CO})_8$ concentration and an inverse second-order with respect to CO concentration, as shown below:

$$\text{Rate} = \frac{d[\text{Co}_4(\text{CO})_{12}]}{dt} = k_{\text{obs}}[\text{Co}_2(\text{CO})_8]^2[\text{CO}]^{-2} \quad (4)$$

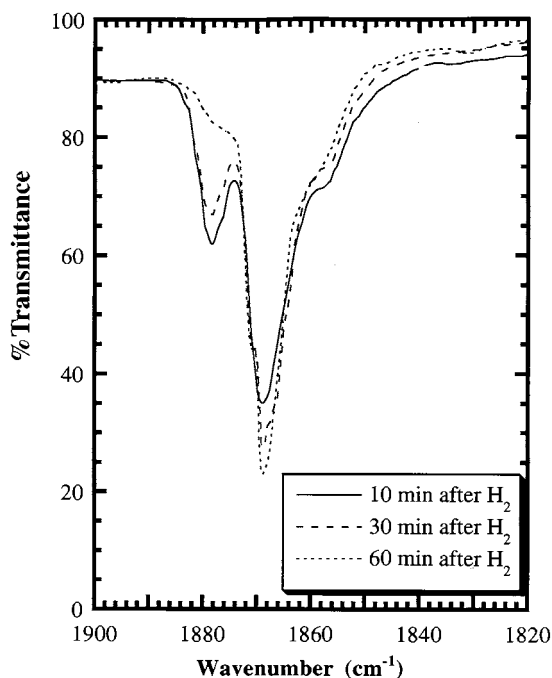


Fig. 3. The IR absorption spectrum of the fast decomposition of $\text{HCo}_3(\text{CO})_9$ to $\text{Co}_4(\text{CO})_{12}$, when pressurizing the system with 100 atm of H_2 .

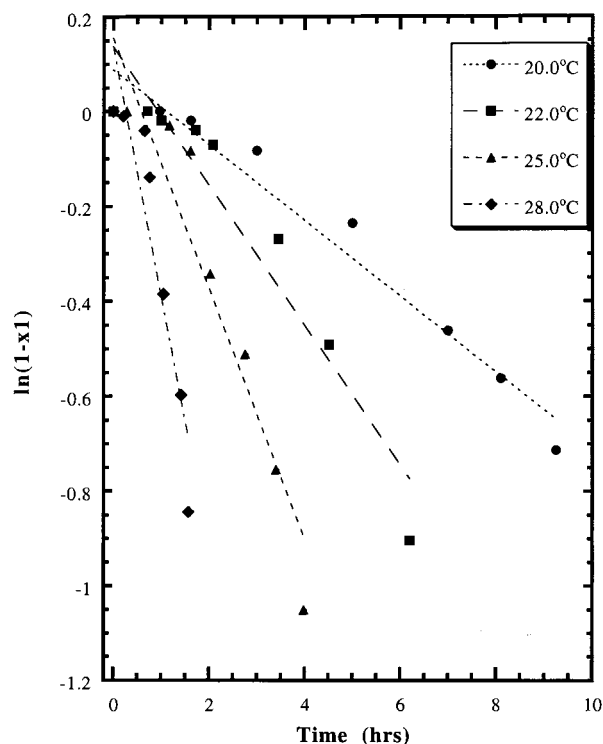


Fig. 4. The decomposition of $\text{Co}_2(\text{CO})_8$ to $\text{Co}_4(\text{CO})_{12}$ at four different temperatures under vacuum. The reaction follows first-order kinetics with respect to the molar fraction of undecomposed $\text{Co}_2(\text{CO})_8$ in solution.

However, under vacuum, the decomposition of $\text{Co}_2(\text{CO})_8$ to $\text{Co}_4(\text{CO})_{12}$ follows first order kinetics with respect to the molar fraction of undecomposed $\text{Co}_2(\text{CO})_8$ in solution, according to Eq. (5) below:

$$\text{Rate} = \frac{d[\text{Co}_4(\text{CO})_{12}]}{dt} = k_{\text{obs}} \left(1 - \frac{[\text{Co}_4(\text{CO})_{12}]_t}{[\text{Co}_2(\text{CO})_8]_0} \right) \quad (5)$$

$$\text{where: } \frac{[\text{Co}_4(\text{CO})_{12}]_t}{[\text{Co}_2(\text{CO})_8]_0} = x_1$$

x_1 = the molar fraction of $\text{Co}_4(\text{CO})_{12}$ in solution.

The various kinetics for four different temperatures are shown in Fig. 4. Since the CO which is released during the decomposition is continuously removed, the reverse reaction (the $\text{Co}_4(\text{CO})_{12}$ to $\text{Co}_2(\text{CO})_8$ transformation) is practically nonexistent. Moreover, the thorough mixing of the reaction solution avoids any dependence on diffusional effects, and therefore the observed rate of decomposition is only dependent on the concentration of the unreacted fraction of $\text{Co}_2(\text{CO})_8$. The temperature dependence of k_{obs} is shown in Fig. 5. Based on this Arrhenius plot, the activation energy, E_a , was calculated to be $40.3 \pm 1.3\text{ kcal mol}^{-1}$, which is consistent with some other neutral metal carbonyl complexes decomposed in the absence of CO (e.g. E_a for $\text{Fe}(\text{CO})_5$ is $34.03\text{ kcal mol}^{-1}$ [22]).

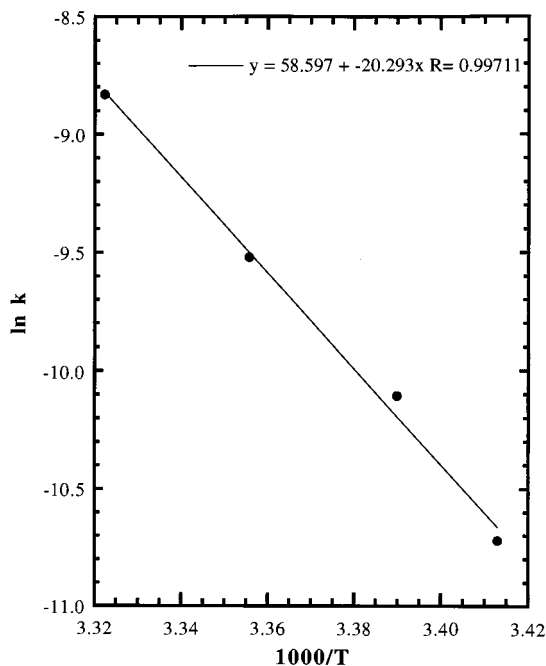


Fig. 5. The Arrhenius plot for the decomposition of $\text{Co}_2(\text{CO})_8$ to $\text{Co}_4(\text{CO})_{12}$ at four different temperatures under vacuum.

3. Experimental

For the in situ synthesis of $\text{HCo}_3(\text{CO})_9$, a hexane solution containing equilibrium concentration of $\text{Co}_2(\text{CO})_8$ and $\text{HCo}(\text{CO})_4$ was used. This solution was obtained by the reaction of $\text{Co}_2(\text{CO})_8$ with H_2 at high $p\text{H}_2$ (100 atm) and low $p\text{CO}$ (0.6 atm, to prevent $\text{Co}_2(\text{CO})_8$ decomposition) in a closed system (1 l autoclave) [11], and was frequently used for the study of the stoichiometric OXO reaction [12]. A detailed description of the experimental method and sampling techniques can be found elsewhere [1,12,20]. The temperature was then set at 35°C , and the solution was allowed to re-equilibrate for 3 days. Then, the gas mixture was flushed and the system was evacuated for 20 s. An IR spectrum was measured immediately, by utilizing a flow-through type high pressure/high temperature cell [12,13], and special attention was paid to the bridging carbonyl region, as shown in Fig. 2. This type of evacuation was repeated four times. After each evacuation, the system was pressurized with 10 atm N_2 to enable the sampling. A cold trap (-80°C dry ice/acetone) was placed between the autoclave and the vacuum pump to avoid the entrance of carbonyls into the pump. When the 1879 cm^{-1} band of $\text{HCo}_3(\text{CO})_9$ did not increase further, the system was pressurized with 100 atm H_2 . After 90 min, the band corresponding to $\text{HCo}_3(\text{CO})_9$ disappeared and all detectable cobalt was in the form of $\text{Co}_4(\text{CO})_{12}$.

The vacuum decomposition of $\text{Co}_2(\text{CO})_8$ to

$\text{Co}_4(\text{CO})_{12}$ was performed by utilizing the same apparatus and the same sampling techniques as described above. The temperature control of the flow-through IR cell was accurate to $\pm 0.2^\circ\text{C}$. In order to take samples, the system was pressurized with 10 atm N_2 which essentially quenched the reaction. Reaction time was calculated to exclude the sampling manipulations.

Spectra were scanned by a Perkin–Elmer model 325 grating IR spectrophotometer. Scanning conditions were: slit program 4.5, spectral slit width 0.87 cm^{-1} (at 1900 cm^{-1}), scanning rate $5\text{--}8\text{ cm}^{-1}\text{ min}^{-1}$, scanning range $2150\text{--}1800\text{ cm}^{-1}$. Solvent absorption was compensated for by the use of a commercial variable path length cell. This variable solvent cell also served as indicator for the optical path in the main cell, which varied between $0.028\text{--}0.033\text{ cm}$.

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