

## TRANSIENT SPECIES OF IMPORTANCE IN THE STOICHIOMETRIC HYDROFORMYLATION REACTION

### I. EVIDENCE FOR $\text{HCo}(\text{CO})_3$ BY MATRIX ISOLATION

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#### Summary

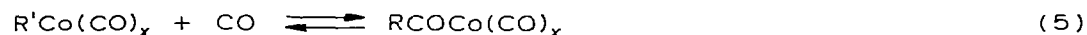
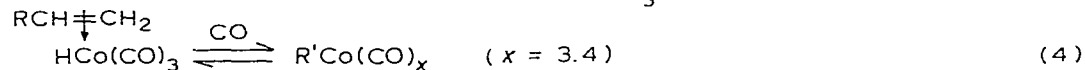
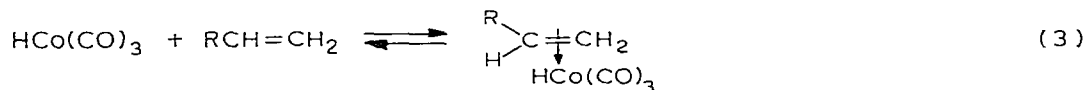
Spectra of  $\text{HCo}(\text{CO})_4$  in a low temperature argon matrix show a weak band at  $2018\text{ cm}^{-1}$ . On irradiation, this band grows rapidly and additional bands (previously too weak to be readily observable) appear at  $2025$  and  $485\text{ cm}^{-1}$ . These three bands are assigned to  $\text{HCo}(\text{CO})_3$ , a coordinatively unsaturated species persistently proposed as an intermediate in the hydroformylation reaction but not previously characterized.

#### Introduction

The hydroformylation reaction with  $\text{HCo}(\text{CO})_4$  is of interest both industrially and as a model for other catalytic systems [1,2]. Although the overall stoichiometric reaction can be represented by a deceptively simple equation (eq. 1), the mechanism is actually highly complex.



Several intermediates have been postulated, but there is no firm evidence for their existence [1]. The sequence of steps generally accepted in the reaction is shown in eq. 2–6. There is good evidence for the reversibility [1,3] of steps 3,



4, and 5 but there is no spectroscopic evidence for the tricarbonylcobalt hydride or its olefin complex. While there have been reports of alkylcobalt carbonyls and acylcobalt carbonyls yielding aldehydes under high CO and H<sub>2</sub> pressures (oxo conditions) [4,5], no alkylcobalt carbonyl has as yet been directly observed as an intermediate in the reaction.

The very high vapour pressure of HCo(CO)<sub>4</sub> suggested a study involving matrix isolation techniques to demonstrate the existence of transient species during the stoichiometric hydroformylation reaction. In such studies, the compound of interest is diluted with an inert gas such as Ar, N<sub>2</sub>, or some hydrocarbon vapour, and this mixture is then deposited on a cold (as low as 8 K) infrared window. The reactive molecules are condensed and are essentially isolated from all but the inert matrix species. Although the species of interest to us, HCo(CO)<sub>3</sub> and <sup>5</sup>Co(CO)<sub>4</sub>, would be expected to be highly reactive, it thus might be possible to isolate them in a dilute Ar matrix if they do in fact exist. We report here a set of experiments in which HCo(CO)<sub>4</sub> was examined by IR spectroscopy, both before and after intensive UV irradiation.

## Results and discussion

Although the matrix isolation spectrum of HCo(CO)<sub>4</sub> has been briefly reported previously [6], none of the bands observed were or could be assigned to HCo(CO)<sub>3</sub>. The IR bands observed in our matrix isolation spectrum are listed in Table 1. The major bands correspond quite well with those reported earlier, but additional bands of special significance were also noted. Furthermore, these new bands do not correspond to any assignments reported in the very elegant study of the room temperature vapour phase spectrum of HCo(CO)<sub>4</sub> [7]. We believe that the band at 2018 cm<sup>-1</sup> (Table 1) is associated with HCo(CO)<sub>3</sub> and that the other new bands in the carbonyl region can be ascribed either to <sup>5</sup>Co(CO)<sub>4</sub> or to cobalt cluster carbonyls of undetermined composi-

TABLE 1  
THE INFRARED SPECTRUM OF HCo(CO)<sub>4</sub> IN AN Ar MATRIX <sup>a</sup>

Position (cm <sup>-1</sup> )	OD	Assignment
485 <sup>b</sup>	—	HCo(CO) <sub>3</sub>
549 <sup>c, d</sup>	0.39	HCo(CO) <sub>4</sub>
676	0.15	Impurity
708 <sup>c</sup>	0.31	HCo(CO) <sub>4</sub>
1969	0.04	HCo(CO) <sub>4</sub>
1999 <sup>c</sup>	0.14	HCo(CO) <sub>3</sub> <sup>13</sup> (CO) and/or impurity
2018 <sup>b</sup>	0.02	HCo(CO) <sub>3</sub>
2025 <sup>b</sup>	—	HCo(CO) <sub>3</sub>
2037 <sup>c</sup>	>>1	HCo(CO) <sub>4</sub>
2048	0.03	Impurity
2059 <sup>d</sup>	>1	HCo(CO) <sub>4</sub>
2123	0.16	HCo(CO) <sub>4</sub>
2140	0.09	CO

<sup>a</sup> Deposition tube packed in dry ice. <sup>b</sup> Intensifies significantly upon irradiation. <sup>c</sup> Major component of a site split peak. <sup>d</sup> In DCo(CO)<sub>4</sub>, the 2059 cm<sup>-1</sup> band shifts to 2054 cm<sup>-1</sup> and the 549 cm<sup>-1</sup> band shifts to 547 cm<sup>-1</sup>.

tion. The evidence which leads to these conclusions follows.

The bands reported in Table 1 were observed when the stainless steel deposition tube leading from the  $\text{HCo}(\text{CO})_4$  reservoir to the cold cell was packed in dry ice. When the deposition tube was held at room temperature a greater concentration of impurities appeared in the spectrum of the matrix.

Among the bands which could not be attributed to  $\text{HCo}(\text{CO})_4$  was a very weak band at  $2018\text{ cm}^{-1}$ . This absorption was present in what were otherwise very clean spectra of very pure  $\text{HCo}(\text{CO})_4$ , as well as in spectra showing considerably more impurities, but its intensity relative to  $\text{HCo}(\text{CO})_4$  bands was fairly constant. Results [8] from a kinetic study of  $\text{HCo}(\text{CO})_4$  decomposition indicate that  $\text{HCo}(\text{CO})_4$  is about 2% dissociated to  $\text{HCo}(\text{CO})_3$  at room temperature, indicating that a small amount of  $\text{HCo}(\text{CO})_3$  might be anticipated.

Irradiation of the matrix in the expectation of achieving decarbonylation led to a rapid growth of the  $2018\text{ cm}^{-1}$  band, and to the appearance of new bands at  $2025$  and  $485\text{ cm}^{-1}$ . These three bands maintained an approximately constant intensity ratio with respect to one another in the various experiments in which they were observed, indicating that they can all be ascribed to the same species. The expanded scale spectra of several experiments before and after irradiation are shown in Fig. 1 and 2.

When CO was present in the Ar matrix in concentration greater than that of  $\text{HCo}(\text{CO})_4$ , the three bands associated with the new species failed to appear, even after irradiation. Furthermore, the presence of ethylene or propylene in the matrix inhibits the growth of the set of bands, presumably by reacting with the new species.

In a detailed study of the wavelength dependence on the appearance of the new set of bands, it was found that irradiation only with light of wavelength

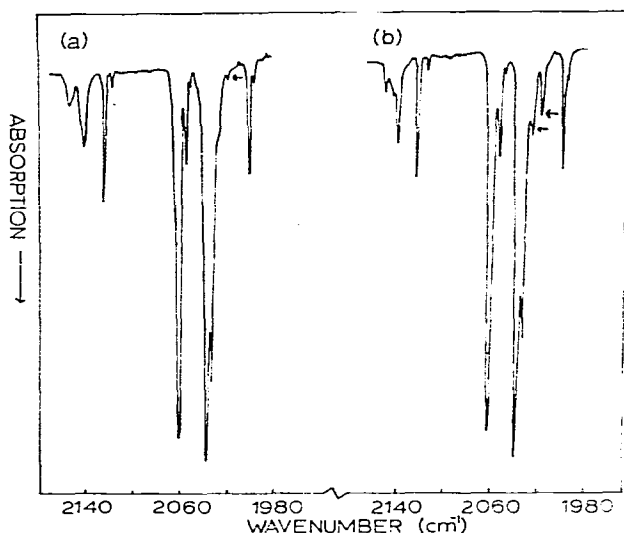


Fig. 1. Infrared spectra over the spectral region  $1980\text{--}2180\text{ cm}^{-1}$  of samples of argon matrix isolated  $\text{HCo}(\text{CO})_4$ . In each of these traces, an arrow denotes the  $2018$  and  $2025\text{ cm}^{-1}$  bands of  $\text{HCo}(\text{CO})_3$ . Trace (a) shows a dilute sample of  $\text{Ar}/\text{HCo}(\text{CO})_4$  before photolysis, while trace (b) shows a spectrum of the same sample after 28 min mercury arc irradiation.

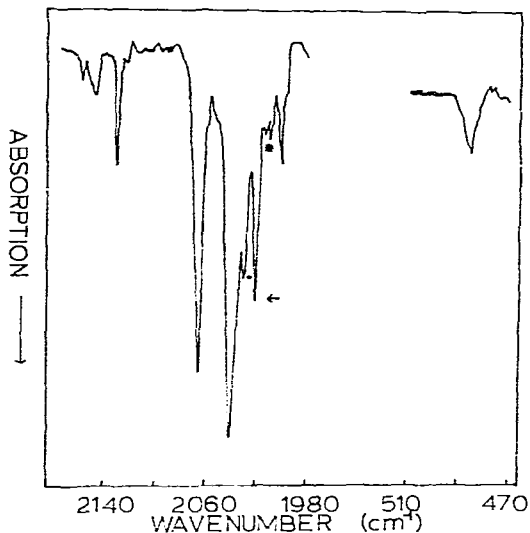


Fig. 2. Spectrum of a more concentrated Ar/HCo(CO)<sub>4</sub> sample over the spectral regions 1980–2160 and 470–510 cm<sup>-1</sup> after 408 min photolysis period. The weak set of band marked by \* is due to Co(CO)<sub>4</sub> also present before irradiation.

shorter than 310 nm produced these bands. Attempts were made to destroy the new species by irradiation for 2 h with visible light (Corning filter No. 5260) and with infrared irradiation (full light of the Nernst Glowler) for 12 h but no decrease (photobleaching) in the intensities of the three bands was observed.

Although there is no direct evidence for the decarbonylation of HCo(CO)<sub>4</sub>, photochemical decarbonylation of matrix isolated Co<sub>2</sub>(CO)<sub>8</sub> has been reported [9], and we have observed the formation of Co(CO)<sub>x</sub> ( $x = 1, 2, 3$ ) upon irradiation of a matrix containing Co(CO)<sub>4</sub>. Photodecarbonylation of transition metal carbonyl compounds is well established [10,11], and hence it seems reasonable to assume that HCo(CO)<sub>4</sub> would behave similarly. On this basis, we assign the bands at 2018, 2025 and 485 cm<sup>-1</sup> to HCo(CO)<sub>3</sub>. Irradiation of HCo(CO)<sub>4</sub> in a N<sub>2</sub> matrix resulted initially in a doublet at 2018 and 2012 cm<sup>-1</sup>, while on prolonged photolysis this doublet coalesced to a band at roughly 2013 cm<sup>-1</sup> with a shoulder at 2017 cm<sup>-1</sup>. Based on C<sub>3v</sub> symmetry, one would expect one doubly degenerate and one singly degenerate band in the carbonyl region. The singly degenerate band should be very weak and near 2100 cm<sup>-1</sup>, analogous to HCo(CO)<sub>4</sub>. Site splitting or matrix perturbations of the doubly degenerate band would account for the 2018, 2025 cm<sup>-1</sup> doublet in argon.

These results suggest that HCo(CO)<sub>3</sub> is in gas phase equilibrium with HCo(CO)<sub>4</sub>, and that photolysis simply enhances the yield of this species. However, one must consider the possibility that the 2018 cm<sup>-1</sup> band observed before irradiation is associated with an unknown species with an absorption degenerate with the tricarbonyl. This possibility seems unlikely for the following reasons: no simple mononuclear or binuclear cobalt carbonyls with only a single major absorption near 2018 cm<sup>-1</sup> have been reported; annealing a matrix with various HCo(CO)<sub>x</sub> and Co(CO)<sub>x</sub> species present did not yield an increase in this band;

annealing an  $\text{HCo}(\text{CO})_4/\text{Ar}$  matrix did not enlarge this band; also,  $\text{HCo}(\text{CO})_x$  ( $x = 1, 2$ ) is unlikely to exist in the absence of  $\text{HCo}(\text{CO})_3$  in even greater concentration.

No firm conclusions can be made as yet with respect to the relative concentration of  $\text{HCo}(\text{CO})_4$  and  $\text{HCo}(\text{CO})_3$  in the argon matrix because of uncertainties in peak intensities and extinction coefficients. However, by using the crude assumption of equal extinction coefficients for  $\text{HCo}(\text{CO})_4$  and  $\text{HCo}(\text{CO})_3$ , we estimate that approximately 0.2% of  $\text{HCo}(\text{CO})_4$  is dissociated under the conditions of the experiment. Extrapolation to relative gas phase concentrations is even more difficult due to catalytic wall effects.

The bands which we observe at 2005, 2011, and 2028  $\text{cm}^{-1}$  in an Ar matrix correlate fairly well with the values reported for  $^*\text{Co}(\text{CO})_4$  [12]. The small difference from the reported values [12] is not unreasonable in view of the very different matrices involved. Irradiation of our sample in a  $\text{N}_2$  matrix resulted in a sharp decrease in these bands and the appearance of bands which are assignable to  $\text{Co}(\text{CO})$ ,  $\text{Co}(\text{CO})_2$  and  $\text{Co}(\text{CO})_3$ . Annealing of the Ar matrix of  $\text{Co}(\text{CO})_4$  causes the site split 2005 and 2011  $\text{cm}^{-1}$  bands to coalesce to a single band at 2008  $\text{cm}^{-1}$ . In an  $\text{N}_2$  matrix, the 2005–2011  $\text{cm}^{-1}$  doublet is observed as a very slightly site split ( $<2 \text{ cm}^{-1}$ ) singlet at 2006  $\text{cm}^{-1}$  in contrast to the reported singlet at 2014  $\text{cm}^{-1}$  in Ar. Associated with these bands we also observe two previously unreported bands at 619 and 648  $\text{cm}^{-1}$ . These  $^*\text{Co}(\text{CO})_4$  bands appeared to some extent in almost all spectra. Although they did not display any firm temperature dependence, it was observed that cooling the deposition tube with dry ice decreased  $^*\text{Co}(\text{CO})_4$  formation and heating the deposition tube either decomposed all cobalt carbonyls or led to increased  $^*\text{Co}(\text{CO})_4$ , depending on the condition of the deposition tube. The  $^*\text{Co}(\text{CO})_4$  appears to be formed from some surface catalysed reaction in the deposition tube which depends on the Co containing species absorbed on the inside of the deposition tube. More importantly, no additional  $^*\text{Co}(\text{CO})_4$  was observed after irradiation of  $\text{HCo}(\text{CO})_4$ , which is significant in view of the suggestion that such species are involved in the hydrogenation of aromatic compounds under hydroformylation conditions [13].

The remaining weak impurities appear to be cobalt cluster carbonyls of undetermined structure resulting from the decomposition of  $\text{HCo}(\text{CO})_x$  in the deposition line, and subsequent desorption from the walls of the deposition tube into the argon stream.

## Experimental

These studies were carried out on a conventional matrix isolation apparatus, employing a closed cycle refrigerator, standard gas handling equipment and a high vacuum system, all of which has been described previously [14]. Cobalt tetracarbonyl hydride and deuteride were synthesized following standard procedures [15], and the carbonyl was trapped in a 1/4" diameter stainless steel U-tube immersed in a pentane slush bath ( $\sim -131^\circ\text{C}$ ). The U-tube was then immersed in liquid nitrogen, sealed in the vacuum system, and evacuated. When sample deposition was desired, the U-tube was immersed in a constant temperature bath of appropriate temperature (between  $-95^\circ\text{C}$  and  $-78^\circ\text{C}$ ) and the

$\text{HCo}(\text{CO})_4$  was sublimed directly into the Ar or  $\text{N}_2$  stream, which had a flow rate of roughly 3 mmol/h. The gas mixture was then passed through a 1/4" diameter stainless steel deposition tube before entering the cold cell, where it was directed at a cold (14 K) CsI window. The temperature of the deposition line could be regulated by packing it in dry ice or by wrapping it in heating tape. The cold cell was held at roughly  $10^{-7}$  Torr.

Irradiation of the matrix was performed through the outer CsI windows, using a 200 W high pressure mercury arc lamp focused on the cold window. A several degree rise in window temperature was observed during the irradiation period; however, this temperature rise was not sufficient to cause annealing of the matrix sample.

Photolysis experiments were conducted using a series of Corning filters (No. 3480, 3486, 5120, 5860, 5970, 9863) and a 10 cm water filter in the attempts to achieve photobleaching.

Spectra were recorded on a Beckman IR12 spectrophotometer at intervals during sample deposition. After deposition was complete, a survey scan from 200 to  $4000\text{ cm}^{-1}$  was taken, as well as expanded scale scans of regions of interest. When the matrix was annealed or photolyzed this operation was carried out after the survey and high resolution scans, which were then repeated. Annealing temperatures as high as 40 K were used and these led to a pressure rise to  $10^{-5}$  Torr in the cold cell.

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