

Photoassisted Alkane Activation under CO Atmosphere: Observation of Aldehyde, Alkene, and Activated Alkane

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Abstract

Direct observation of carbonylated and dehydrogenated products from cyclohexane was made via *in situ* FTIR monitored reaction of half-sandwich iridium dicarbonyl metal centers under carbon monoxide atmosphere. Variation of pressure in semibatch experiments allows for the detection of aldehydes as well as alkene. Changing atmosphere from carbon monoxide to compressed air resulted in ketone formation. Initial product detection was made via GC-MS and pure component IR spectra of the individual products was made possible through recently developed chemometrics- Band Target Entropy Minimization (BTEM). This also allowed for detection degradation products and previously unobserved metal carbonyl species were observed. BTEM also allowed for previously unobserved unseen details in the pure component spectra of the common activated alkane intermediate. Further confirmation of product identity was provided through spectroscopic comparison (IR and NMR) and gas chromatographic (GC-FID) comparison of samples obtained through experiment and those commercially available. It can be concluded that iridium half-sandwich complexes can be used to promote carbonylation of saturated alkanes under photoirradiation.

1.0 Introduction

Alkanes make up a significant portion of the world's carbon reserves. However, their relative inertness requires activation- often through thermal cracking which requires elevated temperatures, usually higher than 800°C.^{1,2} The resulting olefins then undergo further reaction to other products. A direct, room temperature route from alkanes to the corresponding aldehydes and alkenes was described by Tanaka and Sakakura in the late 1980's.³ This route was made possible through UV-irradiation of rhodium-based catalysts with slight carbon monoxide pressures. The limitations of iridium based complexes for this particular activity were noted. However, alkane activation has been noted for many half-sandwich iridium complexes.^{4,5} This seemed to warrant further consideration to the possibility. Understanding of this particular carbonylation chemistry has so far been limited by the analytical techniques involved in characterizing the products, as well as the equipment (glassware) utilized in the experiments. In the present contribution, *in situ* techniques were utilized to investigate the effect of higher pressures (up to 15 barg) on the formation of product, as well as the formation of potentially catalytically active species.

In-situ infrared techniques have proven remarkable in determining the reaction topologies⁶- as well as discovering new chemical species.⁷ This is particularly important when short-lived intermediates are involved.[8] When combined with chemometrics, the analytical strength of *in-situ* techniques is greatly improved.⁸ Similarly time-resolved *in-situ* studies have been done for half-sandwich Rh complexes as well.⁹[9] Based on the stability of the complexes formed, it may be possible to infer much of the reaction topography from examining the product mixture after the reaction has been concluded. Likewise, previous studies of photoassisted reactions of iridium-half sandwich complexes usually employ post reaction characterization based on isolation, with the characterization technique being spectroscopic (IR, NMR, MS, etc.) or gas chromatographic.^{4,5,10} These techniques are quite reliable when testing stable compounds. However, they require isolatable amounts of the species of interest to be of use.

Presently, the alkane route to aldehydes is not well understood- though it is highly attractive to have another functionalization route for alkanes. While iridium complexes- as well as oxygenated hydrocarbons- are stable enough for normal characterization, it stands to reason that the use of *in-situ*

techniques combined with chemometrics may be able to detect low concentrations of active species under the conditions used. Carbonyl insertion is expected to be promoted by high pressure carbon monoxide because of the increased amount of dissolved carbon monoxide.

2.0 Results and Discussion

Two iridium half-sandwich complexes- (η^5 pentamethylcyclopentadienyl)dicarbonyliridium (I) and (η^5 -1-(2-(dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl)dicarbonyliridium(II)- were irradiated with a simple UV-radiation source (Ace Glass, Vineland, New Jersey) under two different types of experiments (denoted “a” and “b” in Table 1). In experiments of type “a”, a stirred quartz reactor was filled with a solution of one of the complexes dissolved in freshly distilled cyclohexane. The reaction mixture was circulated to a ZnSe cell of 0.2 mm. The atmosphere of the reaction mixture was changed between Ar and CO. Temperature was allowed to fluctuate and it was noted that the solution was noticeably warmed after irradiation.

In type “b”, experiments, a 100-mL stainless steel thermostatted autoclave type reactor was charged with various amounts of the metal complex and the reaction solution was pumped to a thermostatted high pressure IR cell (constructed of AMTIR) of 0.5 mm pathlength. In these experiments, irradiation was provided by circulating the mixture through an industrial sapphire tube (Almaz Optics, Marlton, New Jersey) of inner diameter 0.7mm in the presence of the same irradiation source. All data was collected in 0.2 cm^{-1} increments. Temperature was controlled via cryostats to be 20°C at all times.

Species/Expt	Number of Spectra	Wavenumber Range	Atmosphere
(I)/(a)	232	[2250,1650]	1 atm Ar/CO
(II)/(a)	105	[2250,1650]	1 atmAr/CO
(I)/(b)	209	[2200,1600]	5/10/15 bar CO
(II)/(b)	103	[2200,1600]	5/10/15 bar CO

After experiment type “a” was concluded, chemometric numerical techniques were used to analyze the data. Iterative Band Target Entropy Minimization (iBTEM) numerical analysis was done on the resulting spectral ranges. The presence of cyclohexanecarboxaldehyde, as well as dicyclohexyl ketone, was detected and confirmed by GC-MS analysis of a sample of the resulting reaction mixture. After experiments of type “b” were concluded, a similar workup was performed with the exception that the

strong C=O stretching vibration of the aldehyde in the IR spectrum did not require confirmation via GC-MS.

From experiments of type “a”, the presence of a metal carbonyl with an “organic” CO vibration was detected suggesting similar chemistry to that of the well-known hydroformylation reaction. Since it is known for rhodium that higher pressures are needed to stabilize intermediates, the type “b” experiments were carried out. These saw increased amounts of aldehyde, as well as formation of cyclohexene for (I) but not (II). Addition of compressed air at the end of the (II)/b experiments indicates the role of oxygen in the formation of dicyclohexyl ketone, as the aldehyde present was seen to change into the latter. Pure component spectra of activated alkane (II/a, II/b), aldehyde (II/a, IIb) and alkene (IIa) were recovered via chemometric techniques.

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