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Time-Resolved Infrared Observation of a Long-Lived Transient in the Photo-Decarboxylation of Mn(CO)₅C(O)CH₃: Potential Relevance to the CO Migratory Insertion Mechanism

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Abstract: Flash photolysis experiments have been carried out at ambient temperature to probe potential reaction intermediates in the carboxylation of the methylnanese complex CH₃Mn(CO)₅(M) to give the acyl product CH₃C(O)Mn(CO)₅(A). Photo-decarboxylation of A gives a long-lived transient C, whose time-resolved infrared spectrum shows only modest sensitivity to the coordinating ability of the solvent such as cyclohexane, perfluoromethylcyclohexane, tetrahydrofuran, and 2,5-dimethyl-THF. Notably, C has an unexpectedly long lifetime (exceeding milliseconds) in each of the solvents investigated. Kinetics studies in cyclohexane show the competing trapping by CO to reform A and isomerization to M occurs with the respective rate constants $k_{CO} = 3.8 \times 10^{10} \text{M}^{-1} \text{s}^{-1}$ and $10^2 \text{s}^{-1}$. The former value is 3 orders of magnitude less than expected for a solvent complex under these conditions. Thus, it is concluded that TRIR spectra and reactivity patterns of C reflect stabilization of this intermediate by $\pi^2$-coordination of the acyl group.

Migratory insertion of carbon monoxide into metal alkyl bonds is a key step in mechanisms proposed for catalytic carboxylation of organic substrates and is of fundamental interest in organometallic chemistry. A prototype for migratory insertion is the carboxylation of methylnanese carbonyl CH₃Mn(CO)₅(M) to form the acyl analog CH₃C(O)Mn(CO)₅(A) (eq 1). Various thermochemical studies have concluded that this reaction proceeds via the migration of CH₃ from the Mn to an adjacent CO followed by trapping of the resulting intermediate I with CO or another ligand. The nature of I has been the subject of various experimental and theoretical studies, however, direct observation of intermediates in fluid solution has proved elusive, except in very strongly coordinating media such as dimethyl sulfoxide. Described here are laser flash photolysis experiments with time-resolved infrared (TRIR) detection designed to prepare I and to interrogate its spectrum and kinetics. These experiments demonstrate that the putative intermediate is surprisingly stable and suggest that it may have an $\pi^2$-acyl structure in weakly coordinating solvents such as alkanes and perfluoroalkanes.

Pulse laser excitation (308 nm) of A in 295 K cyclohexane or methycyclohexane gave a TRIR difference spectrum (Figure 1) showing disappearance of the CO bands for A and the formation of a long-lived transient C with CO bands at 990, 1952, and 1607 (w, br) cm⁻¹. Disappea-

Figure 1. TRIR spectrum of C in cyclohexane formed by 308-nm flash excitation of CH₃C(O)Mn(CO)₅. Data points represent the absorbance change measured 100 µs after the laser flash at individual monitoring frequencies. Conditions: [A] = 1 × 10⁻⁴ M; P_CO = 1.0 atm; T = 22 °C. Inset: spectral changes in acyl stretching region from analogous experiment with [A] = 3 × 10⁻⁵ M.


(11) In alkane and PFMCO solutions (but not in THF), a low yield of A was observed to form promptly (< 100 ns) along with C. The same result was seen when the reaction is investigated in a methycyclohexane glass at 77 K. This is believed to be the result of reaction from an electronic or vibrational excited state of A manifesting itself as a CO-independent component in the formation of M. A similar result was obtained when the photolysis was carried out in a solid inert-gas matrix; see ref 6.

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of A and formation of C occurred within the rise time of the detection apparatus (~100 ns). Subsequently, C reacted to give M, but under CO, trapping of C by CO to re-form A proved competitive with the methyl migration step (i.e., eq 2). Even under CO (1 atm), C displayed remarkably long lifetimes (several seconds), significantly longer than the ~1 ms upper limit for direct observation by the TRIR apparatus. Comparably long lifetimes extended to every solvent for which TRIR spectra were recorded (Table I). The relatively unreactive nature of C made it convenient to carry out photolyses at a lower temperature (200 K), where the transient spectra were recorded with an FTIR spectrometer. At this T, 308-nm irradiation (XeCl laser pulses) of A gave transient C with a lifetime of hours in each solvent. In methylcyclohexane, the FTIR spectrum recorded within a few minutes displayed νCO bands (2080 (w), 1988 (s), 1941 (s), 1607 (w, br) cm⁻¹), similar to the TRIR spectra in cyclohexane and methylcyclohexane. Furthermore, the spectra of C under these conditions are similar to that reported for the species generated by photolysis of A in frozen methane (12 K) (νCO: 2084 (w), 1992 (s), 1948 (s), 1610 (w, w) cm⁻¹). Thus, it is likely that the species formed in the varied alkane media are structurally analogous.

TRIR (295 K) and FTIR (200 K) spectra in various solvents ranging from perfluoromethylcyclohexane (PFMC) to the differently methylated tetrahydrofurans are summarized in Table I. These are qualitatively similar to those described above for the alkanes and are consistent with labilization of a CO adjacent to the acetyl ligand to give a tetracarbonyl intermediate such as proposed in thermal carboxylation. The bands shift modestly to lower frequency on going from poorly coordinating perfluoroalkane to the stronger donor THF, an effect which one might attribute to solvent molecule coordination at the site previously occupied by the photodissociated CO. However, the relative languor of C in reacting with CO, even in alkane and perfluoroalkane media, clearly points to a different explanation (see below). Furthermore, transient spectra recorded in tetrahydrofuran, 2-methyl-THF, and 2,5-dimethyl-THF each gave identical νCO band frequencies for C despite differences in the coordinating abilities of these solvents. If C were the solvent complex CH₃C(O)Mn(CO)₄S (S = solvent), νCO would be expected to shift to higher energy on going from THF to the bulkier 2,5-dimethyl-THF. Prospective structures for C are illustrated in Figure 2. The solvento species 1 and the coordinatively unsaturated pentacoordinate species CH₃C(O)Mn(CO)₄ proposed in the matrix studies can also be excluded given the sluggishness of the reactions of C. As noted above, C did not undergo measurable reaction with CO in cyclohexane at pCO = 1 atm within the 1-ms time window of the TRIR detection device. If one conservatively assumes a 10% loss of signal would have been detected, upper limits of k₂ < 2 × 10⁴ M⁻¹ s⁻¹ for trapping C by CO and of k₁ < 2 × 10⁴ s⁻¹ for unimolecular methyl migration to M can be calculated for eq 2. Notably, C proved to be surprisingly unreactive in each of the solvents investigated, including PFMC. More accurate rate constant values were determined in cyclohexane by carrying out kinetic flash photolysis studies of A using optical detection (which allowed for observing longer lived species). These gave the respective rate constants k₁ = 10 s⁻¹ and k₂ = 3.8 × 10⁴ M⁻¹ s⁻¹ under the same conditions.

Table I. Carbonyl Bands (νCO Values in cm⁻¹) for Intermediate C Formed by 308-nm Excitation of A* in Various Solvents at Ambient Temperature and at ~78 °C As Measured by TRIR and FTIR, Respectively

<table>
<thead>
<tr>
<th>solvent</th>
<th>νCO data at room temp</th>
<th>νCO data at ~78 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>2080 (w), 1988, 1941, 1607 (w)</td>
<td>1977, 1928, 1602 (w)</td>
</tr>
<tr>
<td>methylcyclohexane</td>
<td>2077 (w), 1977, 1928, 1600 (w)</td>
<td>1977, 1939, 1603 (w)</td>
</tr>
<tr>
<td>dichloromethane</td>
<td>2077 (w), 1977, 1928, 1600 (w)</td>
<td>1977, 1939, 1603 (w)</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>2077 (w), 1977, 1928, 1600 (w)</td>
<td>1977, 1939, 1603 (w)</td>
</tr>
</tbody>
</table>

* The CO stretching frequencies for A are 2110, 2051, 2012, and 1661 cm⁻¹ and are independent of solvent. All solvents were dried and redistilled before use. Room-temperature data taken from TRIR spectra 100 μs after 308-nm flash excitation. Low-T data recorded on a Bio-Rad FTS-60 FTIR spectrometer immediately after 308-nm excitation with one pulse from an XeCl excimer laser.

Figure 2. Prospective structures for C.
s⁻¹ in alkane solution but is 4 orders of magnitude slower (1.4 × 10² M⁻¹ s⁻¹) in THF. Similarly, flash photolysis of Cr(CO)₆ leads to formation of the solvento complex Cr-(CO)₅S, which reacts with CO at k₂ values of 3 × 10⁶ M⁻¹ s⁻¹ and ~3 × 10⁹ M⁻¹ s⁻¹ in cyclohexane and perfluoroalkanes, respectively.¹⁷ The acyl intermediate C is orders of magnitude less reactive than are the above solvento complexes in the latter solvents, thus, C’s extraordinary stability must be due to some type of intramolecular stabilization such as chelation by the acyl ligand as shown in structures 2 and 3. Of these, agostic coordination of the methyl group as in 3 has the appeal of appearing to be closer to the transition state expected for the methyl migration pathway. However, ab initio calculations⁵⁶ have concluded that isomer 2 should be the much more stable of these two. Thus, the unusual longevity of C appears to be the result of its stabilization by ƞ²-coordination of the acyl.¹⁸

The acyl νCO band (1607 cm⁻¹) recorded for C in cyclohexane is significantly shifted to lower frequency from A and falls within the range (1470–1625 cm⁻¹) observed for stable ƞ²-(C=O) coordinated acyl complexes.¹⁸ However, this is not as convincing evidence for such coordination as is kinetic properties, since parameters such as

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