Alkane Carbonylation Photocatalyzed by Aromatic Ketones Under High CO Pressure

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Abstract: Aromatic ketones photocatalyze the carbonylation of alkanes to the corresponding aldehydes at room temperature under high CO pressures (20 - 80 atm). In the presence of CCl_4 , cyclohexanecarbonylchloride is formed from cyclohexane; this reaction was used to determine the rate of addition of cyclohexyl radical to CO.

The functionalization of saturated hydrocarbons is a topic of considerable current interest. Although photoexcited ketones have long been known to cleave alkane C-H bonds,¹ to our knowledge this reaction has never been incorporated into a catalytic functionalization.² During the course of our studies of transition metal catalyzed carbonylation,³ we have discovered that irradiation of alkane solutions of aromatic ketones under CO pressure can result in highly photoefficient alkane carbonylation, eq 1.

RH + CO aromatic ketone > RCHO (1)
hv (
$$\lambda = 366$$
 nm)

From *n*-pentane in the presence of $(p-CF_3C_6H_4)C(O)CH_3$ (1), 2-ethylbutanal and 2-methylpentanal are formed in a 1:2 molar ratio (1:1 per C-H bond); no linear aldehyde is detected, in accord with the expected selectivity for hydrogen abstraction.⁴ Quantum yields for the carbonylation of cyclohexane in the presence of several exemplary ketones are given in Table 1.

We propose, in accord with observations discussed below, that reaction 1 proceeds via the following pathway.

$$CyH + ArR'C=O \xrightarrow{hv} Cy + ArR'C(OH) \quad (Cy = c-C_6H_{11})$$
(2)

$$Cy + CO \iff CyC(O)$$
 (3)

$$CyC(O) + ArR'C(OH) \rightarrow CyC(O)H + ArR'C=O$$
(4)

In addition to aldehydes, other products resulting from the carbonylation of cyclohexyl radicals are observed including Cy₂CO, $[Cy_2C(O)]_2$, and CyCHR'(OR')⁵ (R' = CyC(O)) (Table 1).

Pinacol formation severely limits the catalytic efficiency of reaction 1 with most ketones. In the case of acetophenone and 1, approximately one equivalent of ketone is lost, mostly as pinacol, per equivalent of aldehyde formed. $(o-CF_3C_6H_4)C(O)Ph$ (2), however, yields several equivalents of aldehyde. An experiment with 0.010 M 2 in cyclohexane yielded 0.016 M cyclohexanecarboxaldehyde (3) while 0.007 M 2 remained after 420 min irradiation.

| ketone (concentration) | Φ^{a} | product distribution (%) | | | |
|--|--------------------|--------------------------|-------------------------|-----------|--------------|
| | (CyCHO production) | CvCHO | <u>Cv₂CO</u> | [CyC(0)]2 | CyCHR'(OR')b |
| acetophenone (0.20 M) | 0.061 | 48 | 5 | 25 | 22 |
| (p-CF ₃ C ₆ H ₄)C(O)CH ₃ (1; 0.035 M) | 0.129 | 67 | 6 | 7 | 20 |
| benzophenone (0.012 M) | 0.084 | 53 | - | 19 | 28 |
| (o-CF ₃ C ₆ H ₄)C(O)Ph (2; 0.010 M) | 0.258 | 91 | - | 2 | 7 |

Table 1. Cyclohexane carbonylation (1200 psi CO) with various ketones.

a) Conditions: cyclohexane solvent, 25° C, 30 min irradiation time, $\lambda = 366$ nm, 1 cm path length cell (quantum yields corrected for optical density of solution at 366 nm). b) R' = CyC(O).

Ketone 2 also affords a particularly high selectivity for aldehydes versus other acyl and alkyl radical coupling products (see Table 1). This higher selectivity is consistent with the lower pinacol formation noted above since pinacol formation must be accompanied by the formation of non-aldehyde products such as dialkyldione and dialkylketone. Presumably, the increased efficiency of 2 is due to the bulkiness of its corresponding ketyl radical, which results in slow pinacol formation (ketyl dimerization), and the fact that that 2 contains no C-H bonds that are susceptible to radical abstraction.

Consistent with high chemical yields and selectivity, quantum yields with 2 were found to be particularly high, especially in relation to the respective primary quantum yields for H-abstraction. The latter were determined by trapping the cyclohexyl radical with benzotrichloride in the absence of CO; observed yields of cyclohexyl chloride were independent of benzotrichloride concentration (0.05 - 0.30 M) and thus the trapping is assumed to be virtually complete. In this way, Φ for cyclohexyl radical formation with 1 (0.035 M) was found to be 0.46, whereas the quantum yield for aldehyde formation in this system (1200 psi CO) is 0.13. With 2 (0.010 M), the quantum yield for cyclohexyl formation was found to be 0.31, while the quantum yield for aldehyde formation is 0.26.

Aldehyde yields of up to 0.045 M have been obtained (0.100 M 2 in cyclohexane). Yields appear to be limited by the abstraction of aldehydic hydrogen by photoexcited ketone. In this context we note that the aldehydic C-H bond is ca. 8 kcal/mol weaker than the cyclohexane C-H bond.⁷

The quantum yield for formation of 3 was found to be independent of irradiation intensity over a twenty fold range (0.035 M 1; I = 3.9 x 10^{-9} ein/s, $\Phi = 0.138$; I = 8.7 x 10^{-8} ein/s, $\Phi = 0.129$), indicative of a "one-photon" mechanism. Φ is dependent on CO pressure (Fig. 1), consistent with the suggested competition between eq 3 versus side reactions of Cy· and the back reactions of eq 2 and 3. The intermediacy of cyclohexyl and cyclohexanoyl radicals is consistent with results obtained upon addition of CCl₄ to the reaction mixtures; the formation of both CyCl and CyC(O)Cl is observed while aldehyde formation is completely suppressed. Presumably, this may be interpreted in terms of the following mechanism:

$$Cy + CCl_4 \xrightarrow{k_1} CyCl + CCl_3$$
(5)

$$Cy + CO \stackrel{2}{\underset{k_{2}}{\leftarrow}} CyC(O)$$
 (6)

$$CyC(O) + CCl_4 \xrightarrow{k_3} CyC(O)Cl + CCl_3$$
 (7)



Figure 1: Quantum yield for cyclohexanecarboxaldehyde formation; 0.035 M 1, cyclohexane, 25°C.

Figure 2: [CyCl]/CyC(O)Cl], resulting from irradiation of 0.010 M benzophenone/cyclohexane/CCl4 mixtures, 50°C.

Measurement of the rate of attack of Cy on CO. Eq 3 is clearly a key step in the proposed pathways for both aldehyde and CyC(O)Cl formation. To ascertain its viability in these and other potential carbonylation reactions,⁸ we required the corresponding rate constant. Surprisingly, no rate constants are available for the addition of alkyl radicals to CO in organic solvent.^{9,10}

Based on eqs 5 - 7, the ratio of products [CyCl]/[CyC(O)Cl] can be shown to be represented by the following expression:

$$\frac{[CyCl]}{[CyC(O)Cl]} = \frac{k_1[CCl_4]}{k_2[CO]} + \frac{k_1k_2}{k_2k_3[CO]}$$
(8)

A plot of [CyCl]/[CyC(O)Cl] vs. [CCl₄] at constant CO pressure (Fig. 2) yields a straight line whose slope, according to eq 8, is equal to the ratio k_1/k_2 [CO]. Note that addition to CO is competitive with halogen abstraction even at fairly high concentrations of CCl₄, a widely accepted radical trap. Using a previously determined value¹¹ for k_1 , the absolute rate constant for addition of cyclohexyl radical to CO (k_2) is found to be 1.2 x 10⁵ M⁻¹ s⁻¹ at 50° C (1200 psi CO,¹² [CCl₄] = 0.080 - 0.300 M). This value is consistent with addition of CO being very competitive with other potential reactions of cyclohexyl under the carbonylation conditions, e.g. dimerization.

In summary, under high CO pressure, aromatic ketones photocatalyze the carbonylation of alkanes with good photochemical efficiency. More generally, alkyl radical addition to CO apparently is sufficiently fast to compete with fairly rapid side reactions, allowing the addition step to participate in transforming C-H bonds to carbonyl-containing functional groups.

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Experimental:

In a typical experiment, 2.5 mL of a solution of ketone (0.010 - 0.200 M) in dry deaerated cyclohexane was placed in a quartz cuvette fixed inside a Parr high pressure reactor fitted with quartz windows. CO (Matheson Ultra High Purity) was then added and the solution was allowed to equilibrate at 25° C with stirring. Using an Oriel 500 W focussed beam mercury arc lamp, the solution was irradiated through a set of Corning 0-52 and 7-60 glass filters to isolate the 366 nm line. At the end of the reaction the reactor was vented and the solution was analyzed by GC, GC-MS, and ¹H NMR. Cyclohexanecarbonylchloride was quantified by GC as the corresponding methyl ester after treating 1 ml of the solution with 0.075 ml of 1% triethylamine in methanol. Light intensity (366 nm) was measured using the chemical actinometer Aberchrome 540TM.¹³

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