# Kinetics of Reduction of Cinnamaldehyde by Means of Hydrido- and Deuteridocobalt Tetracarbonyl

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Received 25 July 1996; accepted 14 November 1996

ABSTRACT: The reaction of  $HCo(CO)_4$  (**HT**) or  $DCo(CO)_4$  (**DT**) with excess cinnamaldehyde (**CA**) in methylcyclohexane (**RH**) at 22.2° and under 1 atm of CO follows pseudo-first-order kinetics in **HT** or **DT** with an inverse isotopic effect of 0.54. Identified products of the reaction are hydrocinnamaldehyde (**HCA**) and styrene (**STY**). The **STY** is believed to be an artifact of the thermal decomposition of the true product PhCH<sub>2</sub>CH<sub>2</sub>C( = O)Co(CO)<sub>4</sub> (**X**) or its isomer. Reduction of the carbon-carbon double bond in **CA** is effected by hydrogen from both the cobalt compound and **RH**. It is proposed that the reaction involves a free-radical chain mechanism in which the rate of the slow step is proportional to  $|CA|_0^n$ , the initial molar concentration of **CA** raised to a power of 1.5-1.8. Additionally the rate of conversion of **CA** to **HCA** and **X** meets the criteria of a homocompetitive reaction with |CA|, |HCA|, and |STY| simple functions of  $t^{0.5}$  (where *t* is reaction time) for use of **DT** or (in a single case) a function of  $(t^{0.5} + t)$  for use of **HT.** ©1997 John Wiley & Sons, Inc. Int J Chem Kinet **29**: 473–481, 1997.

## **INTRODUCTION**

Problems associated with the catalytic hydrogenation of cinnamaldehyde (CA) to form hydrocinnamaldehyde (HCA) rather than cinnamyl alcohol, hydrocinnamyl alcohol, or mixtures of various reduction products have been summarized by Rylander [1]. In contrast, Goetz and Orchin [2] reported that  $HCo(CO)_4$  (HT), used in excess, readily effects reduction of the carbon-carbon double bond of CA in the mixed solvent hexane-benzene at 25° and atmospheric pressure to give HCA in 97% yield. It was assumed that both hydrogen atoms involved in the reactions came from **HT**. The reaction, conveniently followed by titration,



was pseudo-first-order in **HT**, but gave some accompanying evolution of gas, presumably CO from de-

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composition of **HT**. We now report a more elaborate kinetic study of this reaction in unmixed solvents, i.e., mainly in methylcyclohexane at  $22.2 \pm 0.1^{\circ}$  or to a lesser extent in toluene at  $3.2 \pm 0.1^{\circ}$ , in an effort to ascertain the mechanism of the reaction. Also the isotopic effect of using DCo(CO)<sub>4</sub> (**DT**) in place of **HT** is reported.

#### EXPERIMENTAL

Unless otherwise noted, all liquids and solutions were contained in rubber-stoppled flasks and transferred by means of syringes. For each kinetic experiment a series of flasks, flushed with CO at 1 atm pressure, was charged with 20 ml (excess) of standard (0.01 M)NaOH solution each. Also for each experiment a stock solution of HT was prepared as follows. Typically, a mixture of 7.0 g of Co<sub>2</sub>(CO)<sub>8</sub> [3] and 70 ml of reagent-grade solvent (methylcyclohexane or toluene) was stirred magnetically in an atmosphere of CO in a flask bearing an attached gasometer and a stoppled side neck. Twenty ml (excess) of dimethylformamide was added slowly while gas evolution (CO) was monitored. The next day the mixture of two liquid layers was cooled to  $0-5^{\circ}$  and treated dropwise with 30 ml of concentrated HCl (12 M). The blue aqueous layer (CoCl<sub>2</sub>) was removed and the yellow hydrocarbon layer was washed three times in situ with 25-ml portions of ice-cold, CO-purged, distilled water [4]. The gasometer was disconnected and the flask was immersed in a bath of dry ice-EtOH to freeze remaining H<sub>2</sub>O and dry the HT solution. Sufficient HT solution (usually 30 ml) for the experiment was now placed in a clean, dry flask (preflushed with CO) held in a constant temperature bath. After 30 min the equilibrated **HT** stock solution was ready for use. Meanwhile, a measured volume (usually an excess) of standard (ca. 0.7 *M*) freshly distilled **CA** in the appropriate solvent and a CO atmosphere was thermally equilibrated (with stirring) in a reaction flask held in the bath.

At time t = 0 the reaction was started by injecting a measured volume of stock solution **HT** into the reaction flask containing **CA**. Periodically a sample (usually 1.00 ml) of the reaction mixture was transferred to one of the NaOH samples at elapsed time t. As time permitted each basic sample mixture was back-titrated with standard (0.01 *M*) HCl to determine the amount of **HT** used. The data were corrected for spontaneous decomposition of **HT**, as measured by means of an occasional sample withdrawn from the stock solution and titrated in the same way.

A stock solution of **DT** was obtained by mixing 90 ml of the **HT** stock solution successively with 10, 5, and 5 ml of 99.8 atom %  $D_2O$  followed by the aforementioned freezing and drying procedure. A mass spectrum of the stock solution showed it was 97.2% isomerically pure **DT**. Kinetic experiments with **DT** were conducted in an identical manner to those with **HT**. No correction was made for the presence of **HT** in the **DT** solution.

Typical pseudo-first-order plots for **HT** and **DT** reactions are shown in Figure 1 and data for all of the experiments are presented in Table I. These plots were made of  $\log[(V_{\infty} - V_t)/V_{\infty}]$  vs. *t*, where *t* is the reaction time in minutes and  $V_t$  and  $V_{\infty}$  are volumes of standard HCl (in ml) used for back titration at times *t* and "infinity," respectively, [5], by means of a Mathcad computer program [6] which determines the least-squares linear fit of the data and calculates the slope k' and the correlation coefficient (0.995 to 0.999) for it. For most experiments, linear log plots were obtained over 2.4–4.4 half lives. However, the three slowest reactions (Expts. 1, 10, 11) were followed for only 300–500 min.

In Expts. 4 (with HT) and 7-9 (with DT) the or-



**Figure 1** Typical pseudo-first-order plots of  $\log[(V_{\infty} - V_t)/V_{\infty}]$  vs. reaction time *t* (in minutes) for disappearance of HCo(CO)<sub>4</sub> in Expts. 2 (Fig. a) and 5 (Fig. b) and of DCo(CO)<sub>4</sub> in Expt. 9 (Fig. c).  $V_{\infty} = 17.98$ , 15.9, and 18.14 ml, respectively.

Reaction Conditions			Initial Molar Concentrations					
Expt. no.ª	solvent, <sup>b</sup> temp.	Cobalt reagent used	[ <b>HT</b> ] <sub>0</sub> or [ <b>DT</b> ] <sub>0</sub> <sup>c</sup>	[ <b>CA</b> ] <sub>0</sub> <sup>d</sup>	No. of data points	First-order rate constant $k'$ $(10^4 \text{ min}^{-1})^{\text{e}}$	Half-life of HT or DT (min)	Corrected <sup>f</sup> rate constant, k
1	MeC, 22.2°	НТ	0.152	0.0965	19	35.8	194.	0.218
2	ditto	HT	0.129	0.181	18	93.7	74.0	0.189
3	ditto	HT	0.140	0.239	11	125.3	55.3	$(0.155)^{g}$
4	ditto	HT	0.133	0.245	13	189.3	36.6	0.224
5	ditto	HT	0.151	0.322	12	294.0	23.6	0.216
6	ditto	HT	0.116	0.358	8	393.3	17.6	0.239
7	ditto	DT	0.118	0.160	9	244.5	28.3	0.398
8	ditto	DT	0.123	0.229	12	426.4	16.3	0.403
9	ditto	DT	0.141	0.283	10	579.1	12.0	0.396
10	T, 3.2°	HT	0.184	0.190	15	8.4	825.	0.013
11	ditto	HT	0.150	0.570	16	50.5	137.	0.013

**Table I** Experimental Data for the Kinetics of Reaction of  $HCo(CO)_4$  (**HT**) and  $DCo(CO)_4$  (**DT**) with Cinnamaldehyde (**CA**)

<sup>a</sup> Listed in order of increasing  $[CA]_0$  for each subset of conditions and reagents, as given in columns 2 and 3. Not listed in chronological order.

<sup>b</sup> MeC is methylcyclohexane; T is toluene.

<sup>c</sup> Obtained from the relationship  $[\mathbf{HT}]_0 = \mathbf{V}_0 M$ , where *M* is the titrated molarity of the standard HCl used and  $\mathbf{V}_0$  is the volume (in ml) obtained by extrapolation of the plot for log  $(\mathbf{V}_{\infty} - \mathbf{V}_t)$  to t = 0. Likewise for  $[\mathbf{DT}]_0$ .

<sup>d</sup> Concentration of prepared standard solution used, adjusted for the volume of HT (or DT) solution added.

<sup>e</sup> From the slope of the Mathcad plot noted before.

<sup>f</sup> For experiments 1–6,  $k = k'/[CA]_0^{1.758}$ ; for experiments 7–9,  $k = k'/[CA]_0^{1.523}$ ; for experiments 10–11,  $k = k'/[CA]_0^{1.63}$ .

<sup>g</sup> Omitted in calculation of average, i.e., k = 0.217, for experiments 1–6.

ganic layer from each neutralized kinetic sample was analyzed by gas chromatography using disk integration and a column packed with Ucon Polar held at 180°. Three main components, viz. recovered **CA**, **HCA**, and styrene (**STY**), were identified by comparison of retention times with those of authentic samples. Time-dependent analytical data for the organic product composition from Expts. 4 and 8 are presented in Tables II and III and plotted in Figures 2 and 3.

## **RESULTS AND DISCUSSION**

Examination of Table I and Figure I shows three general relationships, which occur, viz. (1) the disappearance of either **HT** or **DT** follows first-order kinetics closely, (2) the rate of reaction with **DT** is larger than with **HT**, i.e., there is an inverse isotopic effect, and (3) with either **HT** or **DT** the rate constant k' increases monotonically with the increasing initial concentration of **CA** used. A fourth pertinent relationship is found in the stoichiometry of the reaction, as exemplified by the data in Tables II and III. This result is considered later.

It was assumed that the apparent first-order rate constant k' (Table I) can be represented by the relationship  $k' = k[\mathbf{CA}]_0^n$ , where k is a corrected first-order rate constant. The numerical values of n for Expts. 1–6 (with **HT**) and for Expts. 7–9 (with **DT**) are obtained from Figures 4 and 5. There log k' is plotted vs. log [**CA**]\_0 to give values for n of 1.758 and 1.523, respectively. From these n values one obtains an average rate constant for  $k_{\rm H}$  of 0.217 and for  $k_{\rm D}$  of 0.399, i.e., an isotopic effect of  $k_{\rm H}/k_{\rm D} = 0.54$ . This value compares favorably with that of 0.45 reported for reaction of styrene with **HT** [7,8]. Although only two experiments (10 and 11) were conducted with **HT** in toluene at 3.2°, one obtains values for n of 1.63 and  $k_{\rm H}$  of 0.013 for them.

The occurrence of nonintegral values for n in kinetic expressions has been noted by Shoemaker et al. [9], who suggest that two or more simultaneous mechanisms may be in competition or that no single reaction step is effectively rate controlling. More specifically, nonintegral (especially 1/2 or 3/2) values for n are associated with radical chain reactions [10]. These generalizations are considered in our mechanistic proposals. Also, we adopt the concept of transition state theory that the activated complex involves

Time <i>t</i>	HCl used	<b>ՈНТ</b> ] թ	Molar Concentrations in Organic Product Mixture <sup>c</sup>			
(min)	$V_t (ml)^a$	M	$[\mathbf{CA}]_t$	$[\mathbf{HCA}]_t$	<b>[STY]</b> <sub>t</sub>	
0	(3.7) <sup>d</sup>	0.133	0.245 <sup>e</sup>	$(0.000)^{\rm f}$	(0.000) <sup>f</sup>	
3.26	4.76	0.122	0.232	0.009	0.004	
8.65	5.71	0.112	0.227	0.011	0.006	
14.63	6.70	0.102	0.212	0.021	0.013	
28.53	8.75	0.080	0.210 <sup>g</sup>	$0.024^{g}$	$0.009^{g}$	
			0.218 <sup>g</sup>	$0.020^{g}$	$0.008^{g}$	
36.40	9.75	0.071	0.214	0.028	0.003	
46.29	10.71	0.061	0.190	0.043	0.011	
56.18	11.94	0.048	0.159 <sup>g</sup>	$0.062^{g}$	$0.022^{g}$	
			0.162 <sup>g</sup>	$0.059^{g}$	0.022 <sup>g</sup>	
66.57	12.44	0.043	0.160	0.061	0.025	
77.68	13.34	0.034	0.153	0.060	0.033	
88.15	14.27	0.024	0.141	0.076	0.028	
122.33	15.27	0.014	0.129	0.083	0.033	
144.36		0.009	0.121	0.088	0.035	
$(\infty)^{h}$	(16.60) <sup>i</sup>	$(0.000)^{\rm f}$				

**Table II** Measured Data for Kinetic Experiment Number 4. Reaction Conditions: Solvent Methylcyclohexane, Temperature 22.2°. Reaction of  $HCo(CO)_4$  (**HT**) with Cinnamaldehyde (**CA**) to give Hydrocinnamaldehyde (**HCA**) plus Styrene (**STY**)

<sup>a</sup> Corrected for spontaneous decomposition of **HT**.

<sup>b</sup> [HT]<sub>t</sub> =  $M(V_{m} - V_{t})/1000$ . See text of experimental part.

<sup>c</sup> Based on the assumption that  $[CA]_t + [HCA]_t + [STY]_t = [CA]_0$  throughout the experiment and that molarities are proportional to the integrated chromatographic areas found in each sample.

<sup>d</sup> Obtained from extrapolation of the first-order kinetic plot to t = 0.

<sup>e</sup> See footnote d, Table I.

<sup>f</sup> Not measured experimentally.

<sup>g</sup> Duplicate chromatographic data from the same neutralized sample.

<sup>h</sup> Hypothetical infinity.

<sup>i</sup> From extrapolation of log plot.

1 molecule of **HT** or **DT** plus 1.75 or 1.5 (respectively) molecules of **CA** [11].

Meanwhile, the data in Tables II and III show that the stoichiometry of our reaction with either HT or DT does not conform to a simple 2:1 molar ratio of Co reagent to CA, as had been suggested earlier [2]. In fact, this discrepancy was also noted by Terapane [12]. In particular, our data show that the solvent methylcyclohexane (shown here as RH) is not chemically inert. Rather, it furnishes some of the hydrogen atoms involved in the transformation CA-HCA. Thus, for Expt. 4 (Table II) a change in [HT] from 0.133 *M* to 0.009 *M* (i.e.,  $\Delta M = -0.124$ ) is accompanied by a change in [CA] from 0.245 M to 0.121 M (i.e., also  $\Delta M = -0.124$ , instead of -0.062 expected if two HT molecules had reacted with one CA molecule). Over the same reaction period, the concentrations of HCA and STY changed from 0 M to 0.088 and 0.035, respectively. Consistent with the conservation of phenyl groups, one has 0.124 M

 $CA \rightarrow 0.088 + 0.035 = 0.123 M$  phenyl groups in products. One can, therefore, propose balanced eq. (2) for Expt. 4, where the styrene found is believed to be a decomposition product of  $\mathbf{X}$  and/or its isomer  $\mathbf{X}'$ [4] (vide infra). It seems likely that styrene is accompanied by ethylbenzene due to hydrogenolysis of X or  $\mathbf{X}'$ , but we did not measure PhEt independently. Formation of  $Co_2(CO)_8$  has been established by others [2, 7, 13-16] and R-R is a simplified representation of expected hydrocarbon byproducts (including likely ones from disproportionation) from the interaction of R free radicals. No attempt was made to isolate or identify these byproducts. Compounds X and X' were proposed as products from hydroformylation of styrene with HT and CO [4,7]. However, in our reaction we propose that X and X' form from CA rather than from styrene. Since an equilibrium should exist between X and X' in the reaction mixture we confine further discussion only to X [4]. It should be noted that linear acylcobalt tetracarbonyls are well-

Time t	HCl used	[ <b>DT</b> ] <sup>b</sup>	Molar Concentrations in Organic Product Mixture <sup>c</sup>			
(min)	$V_t (ml)^a$	M	$[\mathbf{CA}]_t$	$[\mathbf{HCA}]_t$	<b>[STY]</b> <sub>t</sub>	
0	(6.0) <sup>d</sup>	0.123	0.229 <sup>e</sup>	(0.000) <sup>f</sup>	(0.000) <sup>f</sup>	
3.50	7.20	0.110	0.207	0.013	0.011	
7.45	9.20	0.090	0.193	0.024	0.012	
11.58	10.37	0.078	0.181	0.036	0.013	
15.28	11.27	0.069	0.173	0.039	0.016	
19.73	12.84	0.053	0.161	0.049	0.018	
25.60	13.36	0.047	0.136	0.062	0.031	
30.31	13.96	0.041	0.133	0.070	0.026	
37.32	15.34	0.027	0.121	0.075	0.033	
45.45	15.76	0.022	0.119	0.082	0.028	
55.18	16.68	0.013	0.091	0.096	0.042	
65.37	17.22	0.007	0.084	0.096	0.049	
79.96	17.76	0.002	0.084	0.102	0.044	
103.35 <sup>g</sup>	17.93	0.000	0.086	0.102	0.042	

**Table III** Measured Data for Kinetic Experiment Number 8. Reaction Conditions as in Table II, but with  $DCo(Co)_4$  (**DT**) used instead of **HT** 

<sup>a,b</sup> Same as footnotes in Table II, but for **DT** instead of **HT**.

<sup>c</sup> See footnote c, Table II. Products were not analyzed for deuterium content.

 $^{\rm d-f}$  Same as footnotes in Table II.

<sup>g</sup> Hypothetical infinity.

known compounds, stable in an



atmosphere of CO for hours or days in dilute solution (0.1 M or less) but decomposing in the vapor state [17–21]. Based on the observations of Heck and Breslow for alkyl- and acylcobalt tetracarbonyls, **X** should be converted into styrene upon injection into a gas chromatograph at elevated temperature, as occurs in our work-up [22].

Equation (2) shows that only a 72% yield of **HCA** is produced in Expt. 4. However, in the study by Goetz and Orchin [2], where excess **HT** was used, any **X** formed should react further as in eq. (3) to give potentially a quantitative yield of **HCA** [19,20], perhaps containing isomeric 2-phenylpropanal.



**Figure 2** Plot of the transformation of cinnamaldehyde (circles) into hydrocinnamaldehyde (upper squares) and styrene (lower squares) for Expt. 4, with  $HCo(CO)_4$ . See text for algebraic equations of curves.

While only Expt. 4 of those using **HT** was checked for stoichiometry, all three of those using **DT** (Expts. 7–9) were investigated in this manner. Typically, Expt. 8 shows these correlations for the complete reaction of **DT**:  $\Delta M = -0.123$  for **DT**, -0.143 for **CA**, +0.102 for **HCA**, and +0.042 for **STY**. Again phenyl groups are conserved and one obtains partially balanced eq. (4). We did not ascertain the actual locations of the D atoms in the products. Equation (4) merely illustrates one simple possible distribution.

$$0.86 \text{ DT} + \text{CA} + 0.85 \text{ RH} \longrightarrow$$

$$0.71 \text{ PhCH}_2\text{CHDCH}$$

$$(\text{HCA})$$

$$+ \begin{cases} 0.15 \text{ PhCH}_2\text{CHDCCo(CO)}_4 \\ 0.14 \text{ PhCH}_2\text{CH}_2\text{CCo(CO)}_4 \\ 0 \end{cases} + \dots \quad (4)$$

$$(X)$$

Analogously, partial equations (5) and (6) show the stoichiometries for Expts. 7 and 9, respectively.

$$0.77 \mathbf{DT} + \mathbf{CA} + 0.94 \mathbf{RH} \longrightarrow$$
$$0.71 \mathbf{HCA} + 0.29 \mathbf{X} + \dots \quad (5)$$

$$0.80 \mathbf{DT} + \mathbf{CA} + 0.87 \mathbf{RH} \longrightarrow$$
$$0.67 \mathbf{HCA} + 0.33 \mathbf{X} + \dots \quad (6)$$

Despite the variations in Expts. 4 and 7-9 the yields of **HCA** and **X** (average values of 70% and 30%) remain essentially constant, as based on the **CA** consumed. Of the two g-atoms of H added to the **CA** carbon-carbon double bond only 0.77-1 arises from the Co starting material; 0.72-0.94, from the solvent;



**Figure 3** Same legend as for Figure 2, but for Expt. 8, with  $DCo(CO)_4$ . See text for algebraic equations of curves.



**Figure 4** Plot of log k' vs. log  $[CA]_0$  to obtain values for n and k in the relationship  $k' = k[CA]_0^n$  for Expts. 1–6, with  $HCo(CO)_4$ .

and, presumably, the remainder from the aldehyde group.

In an attempt to clarify the kinetics of the conversion  $CA \rightarrow HCA + X$  (i.e., **STY**) we assumed that the time-dependent concentration of each of these components is given by an expression of the form

$$[\mathbf{Y}]_t = a_0 + bt^{0.5} + ct$$

where  $a_0$  is the initial concentration of mixture component **Y** (i.e., 0 for **Y** is **HCA** or **STY**, cf., Table I for **Y** is **CA**) and *b* and *c* are constants. Moreover, algebraically one should have  $[CA]_t + [HCA]_t + [STY]_t \equiv [CA]_0$ . The data from Tables II and III plus Expts. 7 and 9 were then surveyed for plausibility of fit to these equations by means of a Jandel Table Curve 2-D program [23]. For Expts. 7–9 with **DT**, the data fit well (except for some discrepancy in  $a_0$ ) to the simpler form where c = 0, as given in eqs.



**Figure 5** Plot of log k' vs. log  $[CA]_0$  to obtain values for n and k in the relationship  $k' = k[CA]_0^n$  for Expts. 7–9, with  $DCo(CO)_4$ .

(7)-(15). Conformance of experimental data to the

For Expt. 7:

$$[\mathbf{CA}]_{t} = 0.173 - 0.0140t^{0.5} \tag{7}$$

$$[\mathbf{HCA}]_t = -0.006 + 0.0093t^{0.5} \tag{8}$$

$$[\mathbf{STY}]_t = -0.006 + 0.0047t^{0.5} \tag{9}$$

average  $r^2 = 0.948$ 

For Expt. 8:

$$[\mathbf{CA}]_{t} = 0.238 - 0.0183t^{0.5} \tag{10}$$

$$\left[\mathbf{HCA}\right]_{t} = -0.006 + 0.0128t^{0.5} \tag{11}$$

$$[\mathbf{STY}]_t = -0.003 + 0.0057t^{0.5} \tag{12}$$

average 
$$r^2 = 0.957$$

For Expt. 9:

$$[\mathbf{CA}]_t = 0.287 - 0.0227t^{0.5} \tag{13}$$

$$[\mathbf{HCA}]_{t} = -0.008 + 0.0164t^{0.5} \tag{14}$$

$$[\mathbf{STY}]_t = 0.004 + 0.0063t^{0.5} \tag{15}$$

average  $r^2 = 0.967$ 

equations for Expt. 8 can be seen in Figure 3. A check on these equations for Expt. 8 was also made by obtaining linear plots of concentrations vs.  $t^{0.5}$  by the Mathcad program with corresponding values for intercept, slope, and correlation coefficient r for the three compounds of 0.237, -0.0189, -0.990; -0.006, 0.0129, 0.991; and -0.002, 0.0055, 0.963,respectively. One notes that the conversions of CA into HCA and X (or STY) are homocompetitive [24], i.e., they have identical kinetic equations, except for the constants  $a_0$  and b, and the ratios of b values (e.g., 0.0128/0.0183 = 0.70 and 0.0057/0.0183 = 0.31 in Expt. 8) are consistent with the observed yields of HCA (70%) and STY (30%). The rationale for these relationships is that both HCA and X are derived from an effectively common intermediate (vide infra). Differentiation of eqs. (7)-(15) leads to rate equations of the type (16).

$$d[\mathbf{Y}]/dt = b/2t^{0.5} \tag{16}$$

The chromatographic data for Expt. 4 (Table II) show considerably more scatter than for Expts. 7–9. They do not fit a  $t^{0.5}$  relationship well, but do fit the more extended equations

 $[\mathbf{CA}]_{t} = 0.248 - 0.00657t^{0.5} - 0.00039t,$   $[\mathbf{HCA}]_{t} = -0.003 + 0.00515t^{0.5} + 0.00024t,$  and  $[\mathbf{STY}]_{t} = 0.000 + 0.00138t^{0.5} + 0.00015t;$ average  $r^{2} = 0.914$  (Fig. 2). Rate equations then take the form (17).

$$d[\mathbf{Y}]/dt = b/2t^{0.5} + c \tag{17}$$

We are unable to devise a mechanistic scheme which accounts quantitatively for all of the preceding observations. However, Scheme I, incorporates qualitatively the crucial aspects of such a mechanism for the three experiments with **DT**.

Initiation steps:

$$\mathbf{DT} + 1.5 \mathbf{CA} \longleftrightarrow [\mathbf{DT} - \mathbf{CA}_{1.5}]^{\pm} \xrightarrow{\kappa}_{\text{rate}}_{\text{controlling}}$$

$$O$$

$$[PhCHCHDCH + \mathbf{T} - \mathbf{CA}_{0.5}]$$

$$(\mathbf{A} \cdot) \qquad (\mathbf{Z} \cdot)$$

$$T \cdot + 0.5 \text{ CA} \xleftarrow{\kappa_1} [Z \cdot]^{\pm} \xrightarrow{\kappa_2} O$$

$$0.5[PhCHCH_2CCo(CO)_4] + 0.5 T$$
(B·)

Propagation steps:



In Scheme I brackets indicate assemblages contained in a solvent cage, the symbol  $\pm$  designates an intermediate complex or transition state, and the double hyphen (--) implies association of chemical entities. The formation of the geminate radical pair [A• + Z•] from **DT** and **CA** may be considered to be a modification of a Michaelis–Menten mechanism, but where both **DT** and **CA** are present in appreciable concentrations [25]. Partial dissociation of Z• into T• and **CA** leads to a subsequent caged radical pair  $[A \cdot + B \cdot]$  [26], but not in equimolar amounts for the two components. Disassociated free radical  $\mathbf{T} \cdot$  is shown as located outside of the solvent cage. The rate of formation of caged radical B • is expected to alter the main rate-controlling step. After migration from the cage, A • and B • undergo analogous propagation steps to abstract deuterium from other DT or hydrogen from **RH** to yield corresponding stable products HCA and X, respectively. Termination of the chain mechanism results from dimerization of chain carriers R • and T •, or of hydrogen transfer from A • to B• to form CA plus X. The considerable symmetry of Scheme I and the essentially equivalent chemical natures of A • and B • are consistent with the homocompetition noted previously. Abstraction of an aldehyde hydrogen atom, especially by a free radical (T. here) bearing a metallic element of variable valence, is well known [27-29] and is proposed to occur in the rearrangement of part of Z • to yield B • (rate constant  $k_2$ ). In particular, cinnamaldehyde undergoes such hydrogen abstraction during autoxidation [30].

It should be noted that the complexes  $[DT - CA_{1.5}]$  and  $[Z \cdot]$ , as well as the nonisolated product **X**, are all hypothetical entities which are proposed in order to rationalize the observed kinetics, identified products, and reaction stoichiometry. Unfortunately, time did not permit us to search for these intermediates via direct spectral methods, though such a study would certainly be pertinent.

To accommodate Expt. 4 into the foregoing scheme one merely changes 1.5 **CA** to 1.75 **CA** and changes subscripts and other coefficients for the initiation steps accordingly. Presumably the ratio of rate constants  $k_1$  and  $k_2$  will be altered as well.

## SUMMARY

The reaction of cinnamaldehyde with  $HCo(CO)_4$  or  $DCo(CO)_4$  in methylcyclohexane at 22.2° has been shown to yield hydrocinnamaldehyde and styrene an artifact believed to arise from decomposition of  $PhCH_2CH_2C(=O)Co(CO)_4$ . Kinetic studies indicate that a free-radical chain mechanism is involved, whereby the solvent furnishes much of the hydrogen used to reduce the carbon-carbon double bond of cinnamaldehyde. An inverse isotopic effect is found.

One of us (L.H.K.) wishes to thank the University of Oregon for granting him a sabbatical leave to the University of Cincinnati during the experimental part of this project and to the latter institution for awarding him a Visiting Professorship concurrently. He also acknowledges helpful comments from Professor Paul Engelking of the University of Oregon in interpretation of the experimental results.

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