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# Elementary Rate Processes in the Dissociative CO for C<sub>2</sub>H<sub>4</sub> Substitution Reactions of Organometallic Complexes in the Gas Phase

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Dissociative substitution mechanisms abound in organometallic chemistry. For certain systems, such processes can be isolated in the gas phase, where, as sequences of elementary unimolecular and bimolecular reactions, their kinetics can convey information on fundamental energetics and dynamics of metal-centered chemical transformations. Methods of competitive kinetics, using time-resolved infrared absorption spectrometry, provide relative and absolute rate constants for comparatively fast reactions. Work yielding unimolecular decay and relative bimolecular production rate constants for selected *bis*- and *tris*-ethylene complexes of iron and chromium carbonyls is summarized together with a report of new work on the CO-for-C<sub>2</sub>H<sub>4</sub> substitution kinetics of (C<sub>2</sub>H<sub>4</sub>)Cr(CO)<sub>5</sub>.

**KEY WORDS:** Dissociative substitution reactions; organometallic complexes; transient ir spectroscopy.

## I. INTRODUCTION

The study of chemical change is a science of intermediates. Atomic and molecular transients guide the chemistry of complex systems and determine the stereospecific paths of individual reactions. Organometallic chemistry is among the richest of all for its intermediate

structures. Metal-centered transients variously appear and disappear via oxidative addition, insertion, metallocyclization and their reverse reactions.<sup>1</sup> Progress in stoichiometric synthesis as well as catalysis depends on the accurate knowledge of the intermediate forms at work in these and other organometallic transformations.

Despite their importance, organometallic intermediates are among the most rarely observed. They are quite often highly reactive and exist only in infinitesimal concentration in steady state and catalytic sequences. In solution, coordinatively unsaturated species interact significantly with virtually all solvents including, for example, liquified rare gases.<sup>2</sup> Solution-phase characterization of uncomplexed intermediates is therefore beyond the reach of even the fastest spectroscopic methods,<sup>3</sup> leaving transient structures to be determined indirectly from such evidence as stereochemistry and isotope distributions.

Gas phase approaches to the problem of chemical transients do not suffer this limitation. Indeed, gas-phase detection and characterization of reactive intermediates has been a cornerstone of fundamental knowledge in main-group chemical kinetics for more than 50 years.<sup>4</sup> As exemplified by programs in place in our laboratory and elsewhere, a small but growing collection of comparable efforts are now underway which are concerned with the kinetic behavior of gas phase organometallic intermediates.<sup>5</sup>

Some of the earliest of this work on gaseous organometallics extended simple flash photolysis/UV-visible absorption methods that had been extensively developed for solution phase systems.<sup>6</sup> By incorporating laser sources, such techniques achieve excellent sensitivity and time resolution.<sup>7</sup> However, the UV-visible absorption spectra of organometallics are generally too broad and featureless to characterize structures or definitively resolve contributions from spectrally similar compounds.<sup>8</sup>

Infrared spectroscopy of organometallics is more informative. For carbonyl compounds in particular, which exhibit strong CO stretching transitions in the region from 2100 to 1900  $\text{cm}^{-1}$ , the number and relative intensities of the bands observed establish the group symmetry of the CO ligands.<sup>9</sup> Applicability to intermediates is well illustrated by the wealth of information provided by the infrared spectroscopy of organometallic transients captured in matrix isolation.<sup>10</sup> This latter work in particular has spurred the refinement of infrared methods for detection and identification of organometallic fragments. It has also

provided a base of information critical to the assignment of infrared spectroscopic transients observed under other conditions. At present, recent technological advances in infrared sources and detectors have increased both sensitivity and time resolution of gas phase transient infrared experiments. As a result, fundamental data of great importance on the elementary properties of a number of key organometallic systems is now emerging.<sup>5,11,12</sup>

Our laboratory has had a role in this progress. We have developed specialized kinetic and spectroscopic approaches, which we have extensively applied to studies of the chemical relaxation behavior of gas phase systems of pulsed laser prepared organometallic intermediates. We have focussed thus far on a class of reactions that occupies a place of central importance in homolytic organometallic chemistry, dissociative substitution:



This general scheme is representative of the broad class of organometallic reaction processes in which a stable substitution product forms by displacement of an abundant weakly bound ligand. For instance, a minimal mechanism in solution-phase photosubstitution necessarily includes the steps above with solvent coordinating and decoordinating as  $\text{L}'$ . To have efficient turnover, substrates in catalytic processes must not be too strongly bound, and thus the engineering of reversible coordination steps are key to sustaining catalytic activity.<sup>13</sup>

Work in our laboratory on the kinetics of gas phase organometallic substitution<sup>14-17</sup> and homogeneous catalysis<sup>13</sup> extends the important place of weakly bound intermediates and dissociative substitution mechanisms to the elementary sequence of events in the conversion of *isolated* substrates and metal complexes. In the iron carbonyl catalyzed hydrogenation of ethylene, for example, the metastable complex  $(\text{C}_2\text{H}_4)_2\text{Fe}(\text{CO})_3$  serves as a reservoir for the active catalyst,  $(\text{C}_2\text{H}_4)\text{Fe}(\text{CO})_3$ .<sup>13,17</sup> The dissociative properties of this reservoir complex determine the overall rate of catalysis, while competing CO substitution regulates turnover numbers. A time-resolved FTIR examination of its dissociative substitution kinetics, isolated,<sup>17</sup> and in the presence of substrate  $\text{H}_2$ ,<sup>13</sup> has given us our most critical insights on the elementary mechanism and rate properties of the gas phase catalytic hydrogenation cycle.

In other work, we have shown that photogenerated chromium carbonyl olefin complexes are also effective hydrogenation catalysts in gas phase systems.<sup>18</sup> Here again it is suspected that *bis*-olefin metastables serve as reservoirs that release coordinatively unsaturated catalytic intermediates for which substrates compete. Catalytic efficiency in chromium mediated hydrogenation is in general much lower than that found for iron complexes. This can, of course, be at least in part attributed to differences in electron density on  $d^6$  chromium centers vs.  $d^8$  iron, with accompanying differences in reactivity toward  $H_2$ .

However, it is also the case, as shown by transient infrared absorption studies in our laboratory,<sup>15,16</sup> that *bis*-olefin complexes of chromium, typified by  $(C_2H_4)_2Cr(CO)_4$ , are less stable and intrinsically shorter lived with respect to dissociative substitution. Recognition of these differences underlines the means by which, through the understanding and accurate modeling of key elementary processes, we might design novel and kinetically optimized catalytic systems.

Studies of dissociative substitution chemistry also convey important fundamental information about the energetics of organometallic bond-forming and rearrangement reactions. For example, in the chromium *bis*-ethylene system, we observe infrared spectroscopic evidence for the presence only of the metastable *cis* isomer, *cis*- $(C_2H_4)_2Cr(CO)_4$ . This spectral evidence persists despite the many gas-phase detachment and recombination cycles which occur over the course of relaxation of a typical complex, coupled with the fact that the rearranged isomer *trans*- $(C_2H_4)_2Cr(CO)_4$  is stable under our conditions.<sup>19</sup> These results tell us: (1) that the recombination of  $C_2H_4$  with unsaturated  $(C_2H_4)Cr(CO)_4$  is stereoselective, and (2) that the energy released in the *isolated* gas-phase molecule by the formation of the second  $(C_2H_4)$ -Cr bond is insufficient to overcome the barrier for isomerization:



## II. EXPERIMENTAL APPROACH TO THE STUDY OF THE ELEMENTARY KINETICS OF DISSOCIATIVE SUBSTITUTION IN THE GAS PHASE

We extract rate information on the elementary reactions involved in dissociative substitution by transient infrared absorption spectrometry. The particular technique required depends upon the timescale of

the process under investigation, which, given a specific system, depends on conditions: It is a convenient virtue of dissociative substitution that, within limits, one can tune the characteristic time for chemical relaxation from  $ML'$  to  $ML$  by varying partial pressures of  $L$  and  $L'$ . This in particular, permits highly accurate, robust spectroscopic techniques such as FTIR to be brought to bear on transient compounds associated with reactions which are intrinsically rather fast. The way in which this is realized is perhaps best seen by a brief examination of the dissociative substitution mechanism and its associated kinetics. The reactions again are:



Steady-state analysis of the decay gives an overall rate law:

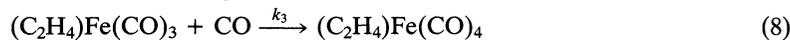
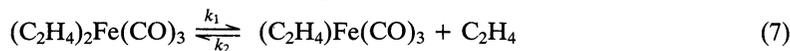
$$\frac{-d[ML']}{dt} = \frac{d[ML]}{dt} = \frac{k_1 k_3 [ML'] [L]}{k_2 [L'] + k_3 [L]}, \quad (5)$$

which, under pseudo first-order conditions in  $L$  and  $L'$ , has the form

$$\frac{-d[ML']}{dt} = k_{\text{obsd}} [ML'] \quad (6)$$

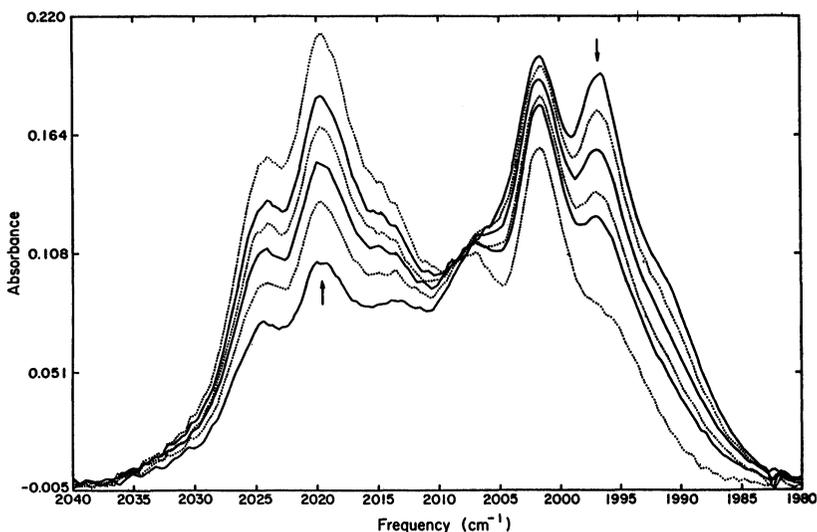
in which  $k_{\text{obsd}}$  is a phenomenological decay constant, which has a magnitude that depends inversely on  $[L']$ . Thus, overall kinetics can be slowed, and unstable  $ML'$  complexes can be preserved for spectroscopic study by high  $L'$  pressures. This puts reactions with even relatively large rate constants within reach of faster FTIR methods.

We have had good success with this approach in the case, for example, of  $(C_2H_4)_2Fe(CO)_3$ .<sup>17</sup> Time-resolved spectra of a system decaying by the reaction sequence:



are shown in Figure 1.

In these experiments metastable  $(C_2H_4)_2Fe(CO)_3$  is prepared by excimer (351 nm) laser irradiation of  $(C_2H_4)Fe(CO)_4$  in the presence of ethylene. The subsequent acquisition of series of transient infrared spectra, such as those shown in Figure 1, provide time dependent concentrations of reactant and product, from which phenomenologi-



**Figure 1** IR spectral changes as  $(\text{C}_2\text{H}_4)_2\text{Fe}(\text{CO})_3$  reacts with CO to form  $(\text{C}_2\text{H}_4)\text{Fe}(\text{CO})_4$ . The time between the first and last spectrum is 79 min. Pressures of reagents are  $(\text{C}_2\text{H}_4)\text{Fe}(\text{CO})_4$  0.050 torr ethylene 200 torr, and 1.50 torr CO 1.5 torr.

cal decay constants can be obtained. From analysis of such data under conditions of systematically varying  $\text{C}_2\text{H}_4$  and CO partial pressures, we obtain an intrinsic room temperature unimolecular decay rate for  $(\text{C}_2\text{H}_4)_2\text{Fe}(\text{CO})_3$  of  $k_1 = 2.9 \times 10^{-3} \text{ sec}^{-1}$ . We additionally find that competition between CO and  $\text{C}_2\text{H}_4$  for unsaturated  $(\text{C}_2\text{H}_4)\text{Fe}(\text{CO})_3$  favors CO by a factor  $k_3/k_2 = 35$ .

For reactions too fast to follow by FTIR, we have used a fast transient absorption apparatus which features a Nernst Glower source, 0.3M monochromator, and a fast InSb photovoltaic detector. Though limited both in spectral resolution and sensitivity, this set-up has allowed us to obtain elementary rate information on systems with overall decay timescales in the range from tens of microseconds to tens of milliseconds.<sup>14-16</sup> Kinetic parameters obtained in our laboratory by time-resolved FTIR and dispersed absorption methods are summarized in Table I.

The most recent addition to this table is  $(\text{C}_2\text{H}_4)\text{Cr}(\text{CO})_5$ . In the following section we present new experimental results on the dissociative substitution kinetics of this compound. Kinetic analysis gives the

**Table I** Comparison of rate constants derived from studies of dissociative substitution in the gas phase.

Parent compound <sup>a</sup>	Parent unimolecular decay constant ( $s^{-1}$ )	CO vs. C <sub>2</sub> H <sub>4</sub> recombination branching ratio ( $k_3/k_2$ )	Ref.
(C <sub>2</sub> H <sub>4</sub> )Cr(CO) <sub>5</sub>	$6 \pm 3 \times 10^{-3}$	$3.3 \pm 0.9$	this work
<i>c</i> -(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> Cr(CO) <sub>4</sub>	$6 \pm 2 \times 10^{+4}$	$0.7 \pm 0.2$	15, 16
(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> Fe(CO) <sub>3</sub>	$2.9 \pm 0.3 \times 10^{-3}$	$35 \pm 5$	17
<i>t</i> -(C <sub>2</sub> H <sub>4</sub> ) <sub>3</sub> Fe(CO) <sub>2</sub>	$1.2 \pm 0.4 \times 10^{+3}$	$480 \pm 220$	14
<i>c</i> -(C <sub>2</sub> H <sub>4</sub> ) <sub>3</sub> Fe(CO) <sub>2</sub>	$3.6 \pm 0.9 \times 10^{+3}$	$370 \pm 130$	14

<sup>a</sup> Values determined from the dissociative substitution reaction for this species.

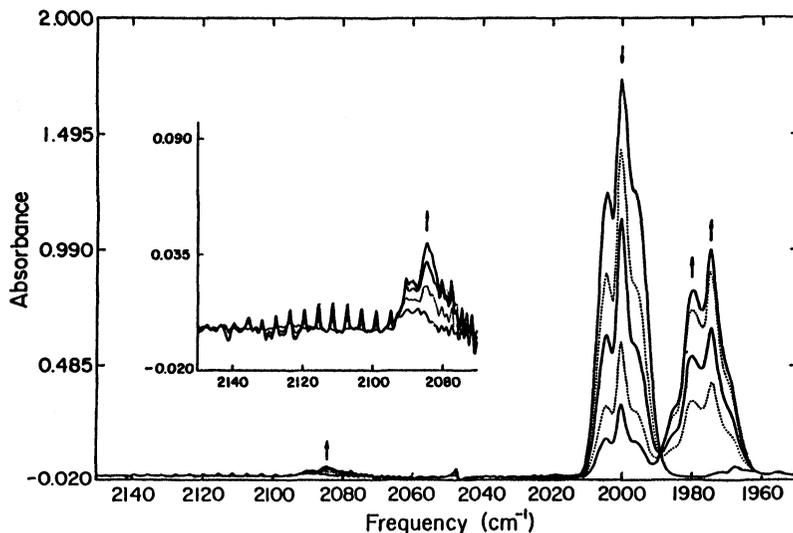
room temperature rate constant for unimolecular Cr—C<sub>2</sub>H<sub>4</sub> bond scission, and, by use of data available on the rate of CO recombination with Cr(CO)<sub>5</sub>, the absolute rate constant for reaction of Cr(CO)<sub>5</sub> with C<sub>2</sub>H<sub>4</sub>.

### III. KINETICS OF THE DISSOCIATIVE SUBSTITUTION OF CO FOR C<sub>2</sub>H<sub>4</sub> IN (C<sub>2</sub>H<sub>4</sub>)Cr(CO)<sub>5</sub>

(C<sub>2</sub>H<sub>4</sub>)Cr(CO)<sub>5</sub> is prepared for kinetic study *in situ* by low-power pulsed XeCl excimer laser irradiation of gas phase samples, containing 120 m torr Cr(CO)<sub>6</sub> in combination with measured partial pressures of CO and C<sub>2</sub>H<sub>4</sub> ranging from 3 to 120 torr and 500 to 1000 torr respectively. Progress of the photoconversion from Cr(CO)<sub>6</sub> to (C<sub>2</sub>H<sub>4</sub>)Cr(CO)<sub>5</sub> is followed by FTIR. Figure 2 shows a succession of spectra taken under typical photopreparation conditions.

After sufficient (C<sub>2</sub>H<sub>4</sub>)Cr(CO)<sub>5</sub> is produced, its decay by thermal reaction back to Cr(CO)<sub>6</sub> is followed in time by successive FTIR scans. For concentrations of CO and C<sub>2</sub>H<sub>4</sub> given above this process is slow, requiring intervals of observation ranging from 30 minutes to 2 hours. Loss of (C<sub>2</sub>H<sub>4</sub>)Cr(CO)<sub>5</sub> proceeds at the same rate as recovery of Cr(CO)<sub>6</sub>, exhibiting simple exponential behavior in time.

Time constants for this relaxation by CO-for-C<sub>2</sub>H<sub>4</sub> substitution are found to depend on both CO and C<sub>2</sub>H<sub>4</sub> concentrations, the overall rate of reaction increasing to saturation with increasing [CO] and decreasing with increasing [C<sub>2</sub>H<sub>4</sub>]. Figure 3 shows a plot of  $k_{\text{obsd}}$  vs. [CO] at a constant C<sub>2</sub>H<sub>4</sub> pressure of 600 torr.

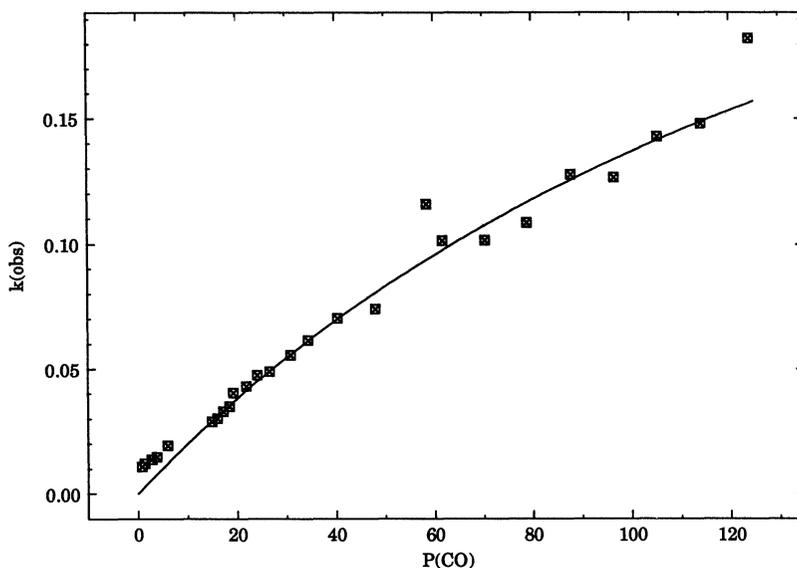


**Figure 2** IR spectra of a mixture of  $\text{Cr}(\text{CO})_6$  (0.12 Torr) and  $\text{C}_2\text{H}_4$  (750 Torr) photo-lyzed at 337 nm. The arrows mark the change in bands with increased irradiation time. The resolution is  $1\text{ cm}^{-1}$ , and the small features in the region from 2075 to 2020  $\text{cm}^{-1}$  are artifacts due to incomplete subtraction of strong  $\text{C}_2\text{H}_4$  absorptions. The inset is a 10-fold absorbance scale expansion which shows the new weak band at 2085  $\text{cm}^{-1}$  and the growth of lines for gaseous CO.

Such rate behavior parallels entirely that found for other gas phase CO for olefin substitution reactions found in our laboratory.<sup>13-17</sup> In those cases, as with this, it is easily shown that rate saturation in  $[\text{CO}]$ , coupled with an inverse dependence on  $[\text{C}_2\text{H}_4]$  signifies the mechanism of dissociative substitution:



With reference to the generalized rate expression Eq. (5), it can be seen that the relative CO pressure at which saturation is achieved is a good physical indicator of the comparative magnitudes of the recombination rate constants  $k_2$  and  $k_3$ . Thus, comparing our present figure with previous CO saturation curves for  $(\text{C}_2\text{H}_4)_2\text{Cr}(\text{CO})_4$ ,  $(\text{C}_2\text{H}_4)_2\text{Fe}(\text{CO})_3$  and  $(\text{C}_2\text{H}_4)_3\text{Fe}(\text{CO})_2$  (Figure 2 of reference 15, Figure 4 of reference 17, and Figure 5 of reference 14), we see immediately that overall decay, as measured by  $k_{\text{obsd}}$ , behaves com-



**Figure 3** CO dependence of  $k_{\text{obsd}}$  at constant  $\text{C}_2\text{H}_4$  pressure (600 Torr). The curved line is plotted according to the form for  $k_{\text{obsd}}$  as contained in Eq. (11) with parameters taken from the linear fit to the data plotted in Figure 4.

parably to the bis chromium complex, becoming limited by the rate of unimolecular decay at a higher CO pressure than for any of the iron systems. This simple, physical observation qualitatively places the relative rate constant for CO vs.  $\text{C}_2\text{H}_4$  recombination,  $k_3/k_2$ , for  $\text{Cr}(\text{CO})_5$  at a number close to one.

A more quantitative assessment can be made by considering the explicit steady-state rate law for the present system:

$$-\frac{d[(\text{C}_2\text{H}_4)\text{Cr}(\text{CO})_5]}{dt} = \frac{k_1 k_3 [(\text{C}_2\text{H}_4)\text{Cr}(\text{CO})_5][\text{CO}]}{k_2 [\text{C}_2\text{H}_4] + k_3 [\text{CO}]}, \quad (11)$$

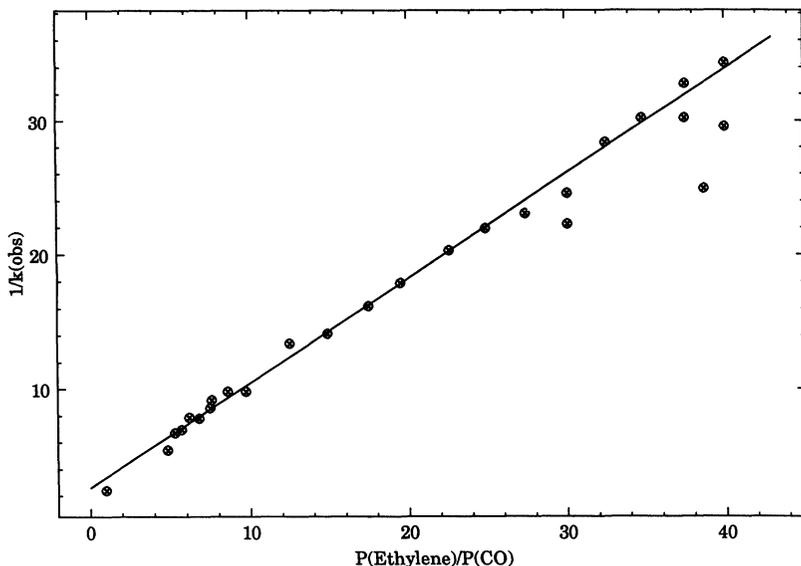
For our conditions of excess  $[\text{C}_2\text{H}_4]$  and  $[\text{CO}]$ , this reduces immediately to the simple pseudo first order form:

$$-\frac{d[(\text{C}_2\text{H}_4)\text{Cr}(\text{CO})_5]}{dt} = k_{\text{obsd}} [(\text{C}_2\text{H}_4)\text{Cr}(\text{CO})_5], \quad (12)$$

where  $k_{\text{obsd}}$  can be conveniently expressed

$$k_{\text{obsd}}^{-1} = \frac{k_1 k_2}{k_3} \frac{[\text{C}_2\text{H}_4]}{[\text{CO}]} + k_1^{-1} \quad (13)$$

Figure 4 shows  $k_{\text{obsd}}$  data plotted according to this linearized form as  $k_{\text{obsd}}^{-1}$  vs.  $[\text{C}_2\text{H}_4]/[\text{CO}]$ . The line is a linear least squares, fit returning  $k_1 = 6 \pm 3 \times 10^{-3} \text{ sec}^{-1}$  and  $k_3/k_2 = 3.3 \pm 0.9$ , as tabulated in Table I. Comparison with other entries shows that at room temperature  $(\text{C}_2\text{H}_4)\text{Cr}(\text{CO})_5$  is intrinsically less stable than  $(\text{C}_2\text{H}_4)_2\text{Fe}(\text{CO})_3$ . Unsaturated  $\text{Cr}(\text{CO})_5$  is shown by our results to be not much more selective than  $(\text{C}_2\text{H}_4)\text{Cr}(\text{CO})_4$  in competitive recombination with CO vs.  $\text{C}_2\text{H}_4$ . In this respect the recombination kinetics of the chromium pentacarbonyl fragment compares reasonably with the behavior of  $\text{Cr}(\text{CO})_4$  as studied by Fletcher and Rosenfeld.<sup>20</sup> Using time resolved infrared laser absorption spectroscopy these workers directly measured  $\text{Cr}(\text{CO})_4$  recombination with CO and with  $\text{C}_2\text{H}_4$ , finding rate constants in the ratio of  $0.8 \pm 0.2$ , with both reactions near the gas kinetic limit. More recently Weitz and coworkers have measured the absolute recombination rate of  $\text{Cr}(\text{CO})_5$  with CO, reporting a value of  $1.5 \times 10^{13} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ . By making use of this result we can



**Figure 4** Plot of  $k_{\text{obsd}}^{-1}$  vs. the ratio of partial pressures,  $[\text{C}_2\text{H}_4]/[\text{CO}]$ . The straight line is a linear least squares fit returning the rate constant  $k_1$  as the inverse of the y intercept, and the rate constant product,  $m = k_2/k_1k_3$ , as the slope.

convert our ratio  $k_3/k_2$  to an absolute estimate of the room temperature recombination rate of  $\text{Cr}(\text{CO})_5$  with  $\text{C}_2\text{H}_4$ , thus finding  $k_2 = 5 \times 10^{12} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ .

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