TABLE IX: Comparison of Observed and Calculated Frequencies (cm⁻¹) for FeCO₂ (C_{2v}), CuCO₂ (C_s End On), and OTiCO₂ (C_s End On)^a

complex	MCO ₂		$\Delta \overline{\nu}(^{13}CO_2)$		$\Delta \overline{\nu}(C^{10}O_2)$		
	obsd	calcd	obsd	calcd	obsd	calcd	force constants
FeCO ₂	1565 (v _a)	1559	40	44	25	23	$k_{C=O} = 8.5, k_{FeC} = 4.5, k_{OCO} = 1, k_{FeCO} = 0.85, k_{CO,CO} = 1.85, k_{CO,OCO} = 0.44, k_{CO,FeC} = 0.64$
	$1210 (\nu_s)$	1238	25	21	38	39	
CuCO ₂	1716 (v _{C=0})	1724	44	47	29	29	$k_{C=0} = 10.0, k_{C=0} = 8.5, k_{Cu0} = 1.6, k_{OC0} = 1.07, k_{Cu0C} = 0.35, k_{C0,C0} = 1.3, k_{C0,OC0} = 0.4, k_{C0,Cu0C} = 0.38$
	$1215 (v_{CO})$	1208	10	10	49	52	
	718 (δ_{OCO})	720		14		22	
OTiCO ₂	1730 (v _{C=0})	1745	45	44	30	34	$k_{\text{C}-\text{O}} = 11.6, k_{\text{C}-\text{O}} = 6.0, k_{\text{T}i-\text{O}} = 1.6, k_{\text{T}i-\text{O}} = 6.3, k_{\text{OCO}} = 1.15, k_{\text{T}i\text{OC}} = 0.35, k_{\text{O}-\text{T}i\text{O}} = 0.35, k_{\text{O}-\text{T}i\text{O}} = 0.35, k_{\text{O}-\text{O}} = 1.0, k_{\text{CO},\text{OO}} = -0.35, k_{\text{O}-\text{T}i\text{O}} = 0.4$
	1185 (ν_{CO})	1187	20	20	50	38	
	950 $(v_{Ti=0})$	952	0	0	40	39	
	455 $(\nu_{\rm TiO})$	313	0	0	10	10	

^a Force constants are given in mdyn $Å^{-1}$ for bonds, mdyn Å rad⁻² for angles, and mdyn rad⁻¹ for bond-angle interactions.

laboratory in collaboration with Professors M. Aresta and E. Carmona.

VI. Conclusion

The experimental results of the present work lead us to conclude that the first examples of binary transition-metal-atom-carbon dioxide complexes have been observed and can be formulated as firmly bound $M(CO_2)$ compounds for the following reasons:

UV-visible spectra are consistent with a spontaneous reaction between transition-metal atoms and CO_2 at 15 K.

Characteristic FTIR spectra are observed at 15 K: only one kind of compound is formed in both diluted and pure matrices, except for Ti and Cu atoms.

Data obtained in mixed labeled matrices $({}^{12}C/{}^{13}C \text{ and } {}^{16}O/{}^{18}O)$ suggest that the 1:1 stoichiometry is predominant in all cases.

From infrared data, the Cu complex probably has an end-on C_s geometry whereas FeCO₂ seems to be a C-coordinated C_{2v} compound.

Oxophile metals (Ti, V, Cr) are oxidized by fixation of oxygen atom coming from the cleavage of the first CO_2 coordinated molecule and are bound to a second CO_2 molecule possibly in a side-on or end-on fashion.

Fe and Ni atoms are able to reduce CO_2 to CO when annealing complexes $M(CO_2)$ up to 80 and 106 K, respectively. The corresponding reaction schemes probably involve aggregation processes.

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Registry No. 1, 113220-84-1; **1a**, 113220-85-2; Ti, 7440-32-6; V, 7440-62-2; Cr, 7440-47-3; Fe, 7439-89-6; Co, 7440-48-4; Ni, 7440-02-0; Cu, 7440-50-8; CO₂, 124-38-9; Ti(O), 12137-20-1; CoCO₂, 113220-86-3; FeCO₂, 113220-87-4; CuCO₂, 68868-29-1; Ti(O)(CO₂), 113220-88-5; nickel oxide, 11099-02-8.

Factors Affecting Gas-Phase Continuous Wave Infrared Laser Sensitized Pyrolysis

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A model is developed for predicting temperature profiles in a gas cell containing an absorbing gas when irradiated by a CW laser beam with well-defined parameters. The model takes into account the explicit temperature dependence of heat capacities, thermal conductivities, molar absorptivities, and gas densities. The predicted transmittance of the laser beam as a function of incident power agrees with experimental values. The model is further used to predict rate parameters of a standard homogeneous pyrolysis reaction that is sensitized by the heated gas. The results provide insight into the comparison between the traditional thermal processes and CW laser sensitized pyrolysis.

The use of lasers for inducing chemical reactions is a mature field.¹ One application involves the excitation of gaseous reactants by an infrared laser, with or without a sensitizer. Of interest is the comparison with traditional thermal reactions, since the hot reactants can be generated by a laser away from the walls of the cell, avoiding contributions from hot surfaces. Even though the early work on homogeneous pyrolysis by Shaub and Bauer² is based on a CW infrared laser and a sensitizer, much more work has been done using pulsed infrared lasers.³ The latter approach even allows direct pumping of the reactant in the absence of a sensitizer. While very often the laser-induced reactions are shown to closely parallel thermal reactor or shock tube results,^{2,3} there are also examples of significant differences in rate parameters and branching ratios in these studies.⁴

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To obtain reliable information about the rate parameters, the spatial and temporal distribution of temperature in the cell must be known. The problem is simplified if an internal standard is used, similar to the well-established comparative rate single-pulse shock tube methods.⁵ Then, only rough quantitative models are needed for the temperature distribution.^{4a} For pulsed experiments, it is necessary to consider the gas dynamics involved in the expansion of the heated column to the rest of the cell.^{3b} The model is much simpler for CW experiments, since a steady-state temperature profile can be established in the cell. Such a simulation has been attempted previously,² but the results do not compare well with measured conversion for standard test reactions. Despite the lack of a semiguantitative model, CW laser induced comparative rate studies have been quite successful.²

In this article, we present results from a refined model for establishing the temperature profiles in a cell for CW laser sensitized pyrolysis. No adjustable parameters are used. The results are compared to experimental measurements of transmittance as well as unimolecular decomposition rates in a well-known test system. Transmittance turns out to be a sensitive and independent check of the gas temperature. The various features and experimental conditions that influence the determination of rate parameters can thus be depicted.

Model

Temperature distributions due to heating by a Gaussian beam have been treated before in conjunction with the thermal lens effect.⁶ Those results, however, are not applicable to the present problem because the temperature changes are large. This leads to variations in the absorption coefficient, thermal conductivity, and number density in different regions. Fortunately, it is possible to account for these variations by using data from the literature.

For CW excitation, one can consider the steady-state heat flow through cylindrical segments of the gas of thickness dr from r =0 (center of cell and axis of the laser beam) to r = R' (inside cell wall). Since the highest intensity is at r = 0, only heat flow outward (radially) is important. Within each segment dr, the temperature can be considered to be constant. At the first level of approximation, we assume that the gas density is uniform throughout the cell and that the laser beam is not depleted as it travels along the cell. Initially, we also neglect heat flow in the axial direction. For a Gaussian beam, the amount of heat deposited per second in the cylinder a distance r from the axis is given by

$$Q = \frac{I}{4.184} \left[1 - \exp\left(-2\left(\frac{r}{w}\right)^2\right) \right]$$
(1)

where w is the laser beam radius, I is the absorbed laser intensity per unit length in watts, and Q is in calories. Naturally, one can measure the exact distribution of the laser intensity and consider heat flow in infinitesimal cylinders if the distribution is irregular. Finally, if the light beam is attenuated significantly as it passes along the cell, one can repeat these calculations for each part of the path length by allowing I to vary in eq 1. The temperature difference between two consecutive cylinders is then

$$\Delta T = T_2 - T_1 = Q_1 \, \mathrm{d}r / \lambda A \tag{2}$$

where A is the area of the boundary between cylinders in cm^2 , and λ is the thermal conductivity of the gas in cal/(cm s). The latter can be calculated in the hard-sphere approximation (zeroth order) as⁷

$$\lambda = (1.9891 \times 10^{-4}) \frac{(T/M)^{1/2}}{\sigma^2} \left(\frac{4}{15} \frac{C_{\nu}}{R} + \frac{3}{5} \right)$$
(3)

where M is the molecular weight, σ is the molecular radius, C_{μ} is the heat capacity at constant volume, and R is the universal gas constant. We can also use the first approximation, i.e., divide by $\Omega^{(2,2)*}(T^*)$ according to Hirschfelder et al.⁷ C_v can be derived from standard tables⁸ for the temperature of interest via $C_v = C_p$ -R.

As the temperature increases significantly above room temperature $T_{\rm R}$, the gas density $\rho(T)$ can no longer be assumed to be uniform across the cell. The lower gas density at the center of the cell plus a lower absorption coefficient ϵ results in a lower amount of heat deposited. So, eq 1 has to be modified by a factor $T_{\rm R}/T$ for each cylinder. So

$$Q(T) = Q(T_{\rm R})[T_{\rm R}/T][\epsilon(T)/\epsilon(T_{\rm R})]$$
(4)

Values for $\epsilon(T)$ have been reported in the literature.⁹ We note that even though there is a density gradient in the cell, there is not enough refractive index change to create a thermal lens that will change w in eq 1.

Actual temperature calculations can be done numerically. The cylindrical zones can be treated consecutively starting at the cell wall at $T_{\rm R}$. For a unit length of the gas, the area A is simply given by $2\pi r$. So, eq 1 through 3 can be used to calculated the temperature of the next inner zone by using the constants $(C_v, \lambda, \epsilon(T),$ gas density) associated with the present zone. If the zones are thin enough, as in the present case, the temperature differences are small between zones, and the errors are negligible.

Finally, if the light beam is attenuated significantly as it passes along the cell, one can repeat these calculations for each part of the path length Δx by allowing I to vary in eq 1. The amount of light passing onto the next segment (Δx) can be treated exactly since the amount of light absorbed in the previous segment is governed by the temperature, and thus defining $\epsilon(T)$ and $\rho(T)$. It can be seen that the beam does not remain Gaussian as it propagates through the gas. Also, there is a second boundary condition at the cell windows (entrance and exit of the laser) that requires the temperature to be at $T = T_R$. Rather than to treat the axial heat flow exactly, an approximation can be made by considering a "buffer" zone near the windows. We therefore treat the middle 3.6 cm of the cell as being free from conduction to the windows. The buffer zones at both ends then follow a linear temperature drop to $T_{\rm R}$ over 0.1 cm to the windows. As can be seen below, the exact details of the buffer zone do not influence the determination of activation energies much, since most of the reaction occurs in the small region where T is the largest.

Experimental Section

The laser used is a grating-tuned CO_2 laser (Molectron C250). By proper tuning, it is possible to produce a homogeneous beam about 1.5 mm in diameter. Occasionally, there appear stray modes that are well-separated from the main beam. These are removed completely by a diaphragm without truncating the main beam. The beam size and shape are then measured by translating a 50- μ m pinhole across the beam on a stage (Aerotech) and measuring the power (Coherent 210). The laser wavelength is determined by a spectrum analyzer (Optical Engineering).

The glass cell used is cylindrical (3.8 cm long and 4-cm i.d.) and is fitted with polished NaCl windows (0.5 cm thick) by epoxy (Eccobond). The cell is connected to a GC sampling septum and then to a grease-free stopcock. The connections only add 2 cm³ to the total volume. Pumping to 10^{-6} Torr is possible on a grease-free vacuum system operated by a turbomolecular pump (Pfeiffer TPU). Pressures are measured on a manometer (MKS 221AHS-F) with 10-Torr full scale. In all experiments, 6 Torr of SF₆ (Matheson) and 1 Torr of C₂H₅Cl (Matheson) are introduced into the cell. After irradiation, a gas-tight syringe (Hamilton) withdraws 1 mL of gas through the septum. Since several minutes elapse between irradiation and withdrawal,

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Figure 1. Radial temperature profile in a disk (0.2 cm thick, 2-cm radius) irradiated by a 2-W laser beam (1.5-mm diameter). $P(SF_6) = 6$ Torr, P(20) CO₂ line.

uniformity of product distribution is assured provided there is no adsorption. The sample is injected into a gas chromatograph (Tracor 550) with an FID detector. Only the C_2H_4 peak is measured as it elutes off the column (packed 60/80 Carbosieve G, Supelco). Reactions at lower incident laser powers are run for longer times to allow better determinations of the conversions. Transmission of the laser beam was determined by measuring the power before and after the cell, which is fixed throughout the series of runs. The evacuated cell was also probed to determine the transmission of the windows, so that a correction to the measured laser power can be made. There is normally a 5% variation of the measured power over the active area of the thermopile. So, the maximum registered power near the center of the sensor was used.

Calculations were done on a microcomputer (Atari 1200 XE) with BASIC programming. Initially, tables of density-weighted absorption coefficients, heat capacities, and thermal conductivities are generated as a function of temperature for SF_6 . The small amount of C₂H₅Cl makes only a minor contribution and is neglected here. This is justified because the measured transmitted intensity (which is a sensitive probe of the temperature, vide infra) was found to be unaffected by this amount of C₂H₅Cl. Then, for a given disk in the cell 0.2 cm thick, 400 radial zones (0.05 mm each) are considered. Temperatures are propagated from the outside (T_R) to the center of the cell by use of eq 1 and 2 based on an estimate of $Q_{\rm R}$, the total heat deposited in this disk by the laser. From the actual incident laser power and the temperature profile calculated, a refined estimate of absorption can then be obtained: A new Q_R is then used for a second iteration. Convergence to a stable temperature profile is obtained in three or fewer iterations. The next disk is then considered given the transmitted laser intensity in each radial zone. For the buffer zones at the beginning and the end of the cell, radial temperature profiles are not determined by eq 1 and 2. Instead, a linear interpolation to $T_{\rm R}$ at the windows for each radial zone is used, starting from the disks at 0.1 and 3.7 cm into the cell. For each temperature zone *i* in the cell, the value $(T_R/T_i) \exp(-E_a/RT_i)$ can be calculated to determine the conversion as a function of laser power and E_a .

Results and Discussion

Temperature Profile. The radial temperature distribution for a disk 0.2 cm thick receiving 2 W of incident laser power (1.5-mm diameter, Gaussian) and insulated longitudinally is shown in Figure 1. Although the general shape resembles the results of previous studies,⁶ the maximum temperature here (1144 K) is much lower than that from the simple model (2260 K). This is because the thermal conductivity increased by a factor of about 4 over this temperature range, the density decreased by a factor of 4, and the molar absorptivity decreased by a factor of 15. The importance of having reliable data on heat capacities (for calculating thermal conductivities via eq 3) and on absorptivities can



Figure 2. Longitudinal temperature profile along the axis of a cell (3.8 cm long, 2-cm radius) irradiated with 2.23 W under the same conditions as in Figure 1. The first and last 1 mm are buffer zones as defined in the text.

be appreciated. The exact model for eq 3, however, is less important. The zeroth-order approximation gives a maximum temperature of 1149 K. This only has a small effect on the calculation of rate parameters. The temperatures are also substantially lower than previous computer models² although a different laser line was involved. Even the P(28) line used there bleaches eventually.⁹ Worse still, no experimental data on ϵ are available in the high-temperature ranges. This may be why previous computer models² have not been successful.

The longitudinal temperature profile is shown in Figure 2. As discussed previously, exact radial temperatures were determined only for the central 3.6 cm, and the buffer zones at either end were interpolated from the boundary conditions. The effect of the entrance buffer zone is to lower the maximum temperature due to preabsorption and heat conduction to the windows. For example, for 2 W to reach the central zones, one needs to send 2.23 W into the cell. Without the buffer zone, the same power would have created a maximum temperature of 1166 K instead. The effect of the exit buffer zone can be neglected, since most of the reaction (vide infra) occurs toward the front of the cell. It can be observed from Figure 2 that the temperature drops roughly linearly in the central region, and only by a small amount. This is again a result of increased thermal conductivity, decreased density, and decreased ϵ , at higher temperatures.

The effect of the details of the cross-sectional laser intensity distribution on the temperature profile can also be examined. From Figure 1, most of the temperature rise from T_R to T_{max} is from the region outside the laser beam. So, the details of the laser beam are not very important in determining T_{max} . Equation 1 is more a convenience in defining a diameter than a critical assumption. On doubling the beam half-width (same total power), we obtain a maximum temperature of 1106 K. Even though uneven absorption causes the laser beam to deviate from a Gaussian shape as it propagates, an effect that is fully accounted for in our calculations, there is little loss in accuracy if a Gaussian shape is assumed throughout the cell because the size of the beam hardly changes.

Finally, it should be noted that no part of the cell, including the windows, feels warm to touch even after lengthy exposures. The boundary conditions are justified. This is not necessarily true for higher laser powers or for smaller diameter cells. For example, at 10 W, the windows start to feel warm, indicating that the boundary conditions are no longer correct. Such conditions probably existed in earlier work² to make comparisons with models difficult.

Transmission. Figure 3 shows the laser power (integrated over its cross section) as the beam propagates through the cell. The details in the buffer zones naturally depend on the interpolation procedure, but the effects are not large. In the central zone, the laser power decreases roughly linearly and not exponentially. This is from bleaching due to ρ and ϵ . We note that, at low powers,



Figure 3. Integrated laser power along the longitudinal axis of the cell in Figure 2.



Figure 4. Calculated (solid lines) and experimental (points) transmittance through the cell at various incident laser powers: (a) parameters as in Figure 2, (b) buffer zones absent, and (c) for a beam with twice the Gaussian beam waist.

6 Torr of SF_6 will absorb 99% of the light in a path length of 1.5 cm.

A real test of the model is the comparison between calculated and measured transmittance through the cell. This is shown in Figure 4. Considering the lack of any adjustable parameters except for the choice of the buffer zones, the agreement is good. To evaluate the contributions from the choice of the buffer zones, we also present the results when the zones are absent. The fit becomes worse. Buffer zones have to exist because the windows are cold. Our interpolation procedure seems to be a reasonable one. Figure 4 depends greatly on the laser beam parameters, since ϵ changes rapidly in this temperature range.⁹ Also plotted are calculated transmittance for a beam twice the diameter but at the same power. This shows the best agreement with experiment. Our laser beam is multimode and falls off slower than a Gaussian shape. The improved fit is not unexpected. In fact, transmittance measurements for well-characterized laser beams may prove to be a good probe of gas temperatures. Naturally, the probe will have to be at low powers to avoid contributions to the local temperature. These results also imply that caution must be taken in interpreting laser transmittance measurements for determining gaseous concentrations whenever the absorption per unit length is high.

Kinetic Parameters. One of the major incentives for predicting temperature profiles is to compare laser-induced pyrolysis with thermal experiments. Some success has been reported for pulsed excitation.^{3b} However, the steady-state temperature distribution of CW excitation requires fewer assumptions and should make predictions easier. For excitation periods longer than 1 s, such a steady-state condition will be achieved.⁶ The relative fraction converted per unit volume per unit time, i.e., (T_R/T_i) exp. $(-E_a/RT_i)$, is plotted in Figure 5 as a function of radial distances



Figure 5. Relative conversion in the disk in Figure 1: (a) fractional conversion per second per unit volume, and (b) fractional conversion per second in each cylindrical volume element. $E_a = 57.4$ kcal/mol.



Figure 6. Relative conversion along the cell in Figure 2, integrated over each disk. $E_a = 57.4$ kcal/mol.

from the cell axis for the data in Figure 1. Since this has a logarithmic ordinate, contributions outside the laser beam are essentially negligible. Also plotted in Figure 5 are cumulative yields for each cylindrical zone. The volume-weighted values drop off similarly, but a maximum exists slightly away from the axis. Therefore, most of the reaction occurs near but not at the maximum temperature. The longitudinal distribution of reaction yields is shown in Figure 6. It is clear that 90% of the reaction occurs in the first half of the cell, and increasing the cell length further should not affect the total yield. Another consideration is the effect of the laser beam shape and size. For conditions identical with those in Figure 5, doubling the beam half-width (constant power) only increases the integrated yield in that disk by 30%. Lower temperatures are compensated somewhat by larger volumes in the high-temperature zones. Naturally, this only holds if the laser beam is still small compared to the cell diameter. Otherwise the details of the temperature profile will become important. The increased beam diameter does mean lower transmittance and thus lower powers for the trailing sections of the cell. But since most of the reaction occurs toward the front of the cell (Figure 6), the total yield is affected less, changing by 20% in this case.

The above calculations can be repeated for a series of incident laser powers and a series of E_a values. Two of these calculations of total yields are plotted in Figure 7. A normalization factor was used to allow displaying these on the same scale; i.e., the frequency factor is allowed to vary. The experimental values are also plotted there. The variation of reaction yield as a function of laser power is a result of the differences in temperature in the cell. So, Figure 7 allows us to use C_2H_5Cl as a chemical thermometer to compare with the calculations. Naturally, both the frequency factor and the activation energy contribute to the rates of reaction. The temperature dependence, however, is dominated by the latter. Furthermore, the frequency factor is influenced by



Figure 7. Relative conversions in the entire cell in Figure 2 as a function of incident laser power: (a) $E_a = 57.4 \text{ kcal/mol}$, (b) $E_a = 65 \text{ kcal/mol}$, and (c) experimental points.

activation efficiencies that can cause a falloff from the highpressure limit.¹⁰ Even though it has been shown¹¹ that at these pressures C₂H₅Cl (in traditional thermal experiments) approaches the high-pressure limit, there is no corresponding verification for activation by SF₆. Also, activation at lower temperatures, where literature values for the accepted Arrhenius parameters are obtained, may be quite different than activation at the higher temperatures here.¹² Finally, very low C_2H_4 pressures are formed in these experiments, and standards are difficult to prepare and to sample. Because of these uncertainties, only the relative yields for a series of incident laser powers rather than the absolute yields are determined in these studies.

Although the trends in Figure 7 are nonlinear, an objective way to compare these is to use the slopes of linear regression lines through each data set. The experimental data in Figure 7 do not justify fitting to the very slight curvatures of the lines. Since the frequency factor and the activation energy can be considered as independent parameters, as in conventional Arrhenius plots, it is appropriate to assign these to the intercept and the slope of the linear regression lines, respectively. The measured "slopes" for the experimental data, the theoretical results for $E_a = 65$ kcal/mol, and the theoretical results for $E_a = 57.4$ kcal/mol are 1.432, 1.617, and 1.433, respectively. One can conclude that the best fit is E_a = 57.3 \pm 2 kcal/mol. The agreement (which must be considered fortuitous) with the literature value¹³ of $E_a = 57.4$ kcal/mol is good, especially since the calculations are essentially absolute. The calculations were again repeated for the absence of the buffer zones. The best fit then becomes $E_a = 58.8 \text{ kcal/mol}$. This results from higher temperatures predicted, but still the effect is not a substantial one.

The comparative rate method5 has been very useful for obtaining rate parameters without knowing the actual temperatures. In shock tubes,⁵ one essentially has a single uniform temperature. It is easy to see that the derived slopes and intercepts follow rigorously. If the temperature varies as a function of space and/or time, the comparative rate method leads to errors that are determined by the dissimilarity between the two reactions. The case of having two discrete temperature zones (in space or in time) has been discussed previously.4a A gas dynamic model allowing for continuous temperature variations has been used to determine Zhu and Yeung

Arrhenius parameters for unknown reactions based on an internal standard.³⁵ It is useful to see how well the comparative rate method in the linear equation form⁵ works for a cell with such a large variation in temperatures as here. The theoretical curves in Figure 7 (solid lines) can be used. At each laser power, one can find the relative rates of the two hypothetical reactions with $E_a = 57.4$ and 65 kcal/mol. These relative rates can be treated in a log-log plot following comparative rate methods.⁵ From the slope of that plot, we find that the ratio of the two E_a is 1.118. This is to be compared to the correct ratio of 1.132. The agreement is not bad. Naturally, similar errors will be introduced in the corresponding frequency factors. This shows that even though there is a large variation in local temperatures, only a few zones with the highest temperatures are responsible for most of the reaction yields, so that linear comparative rate methods can be used under these conditions when ΔE_a is small. In other words, the relevant temperature range is actually quite narrow.

The importance of convection under these conditions can be experimentally assessed. From the above, it has already been shown that the transmission of the laser beam provides a sensitive probe for the temperature distributions. We have thus performed parallel transmission measurements at various laser powers for a cell containing 6 Torr of SF_6 , once with the cell placed horizontally and once with the cell placed vertically with the laser beam entering from the top. The former case maximizes convective contributions to heat transfer away from the irradiated central zone, and the latter case minimizes these contributions. From 2- to 9-W input power, we cannot observe any noticeable differences in the transmitted intensities regardless of cell orientation. This confirms that convection can be neglected for the range of conditions used in this study. The fact that the transmitted intensity always reaches a final value after less than 2 s indicates that a steady-state temperature distribution has indeed been achieved for our experiments.

Summary

We have developed a reasonable model for temperature distributions in a cell containing an absorber under irradiation by a CW laser beam. Both the transmitted intensity and the yields in a sensitized pyrolysis reaction compare favorably with experiments. The implication is that the reaction pathway parallels that under thermal excitation. Since the main reaction zone is away from the cell walls, surface effects are minimized. At least for the conditions here, that the surfaces are cold (required by the model) is confirmed experimentally. We find that despite the large variation in temperatures, the traditional (linear) comparative rate method should give reliable predictions. In fact, because of the lack of good data on absorptivities at high temperatures, the comparative rate method with an appropriate internal standard is the method of choice for higher excitation powers (required for studying reactions with larger E_a). Apparently, neglecting convection did not lead to serious errors here, but that may have to be considered for faster reactions (depleting reactants in the high-temperature zone) or for substantially different cell pressures. Finally, the high-pressure limit¹¹ of gas-phase reactions needs to be accounted for to refine similar calculations. For C₂H₅Cl, ref 11 does show that we are at the high-pressure limit, assuming activation by SF_6 is comparable to activation by C_2H_5Cl . The results here admittedly must be used with caution to predict kinetic parameters in the absence of internal standards, but they do offer good insight into the nature of CW laser sensitized gas-phase reactions.

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