$$\frac{d[HIO_2]}{dt} = \frac{1}{2}\frac{d[HOO]}{dt} = \frac{1}{2}k_7[H_2O_2][MnOH^{2+}] = \frac{1}{2}k_6[Mn^{2+}][IO_2] \quad (16)$$

where the last equality results from setting $d[MnOH^{2+}]/dt = 0$. Two limiting cases arise, depending upon the relative sizes of the terms $16k_4k_{-4}[H^+][HIO_2][IO_3^-]$ and $k_6^2[Mn^{2+}]^2$ in eq 15. If step 4 is rate determining so that the latter term is much larger, then we find

$$[IO_2]_{pSS} \approx (2k_4/k_6)[H^+][HIO_2][IO_3^-]/[Mn^{2+}] \quad (17)$$

and, substituting in (16)

$$d[HIO_2]/dt = k_4[H^+][HIO_2][IO_3^-] \quad (18)$$

The sequence then produces HIO_2 autocatalytically in a process also catalyzed by manganous ion. On the other hand if step 6 is ratedetermining, then the pseudo-steady-state value of iodine dioxide is given by eq 19 and 20, where $K_4 = k_4/k_{-4}$. We still

$$[IO_2]_{pSS} \approx (K_4[H^+][HIO_2][IO_3^-])^{1/2} \quad (19)$$

$$d[HIO_2]/dt = \frac{1}{2}k_6K_4^{1/2}[Mn^{2+}]([H^+][HIO_2][IO_3^-])^{1/2} \quad (20)$$

have autocatalysis in HIO_2 but now of a lower order and catalyzed by manganous ion. On examining the values of the rate constants and species concentrations during the course of an oscillation or in the two steady states (see Table I), we observe that the relative magnitudes of the two terms in eq 15 are interchanged as the system switches from the radical to the nonradical regime. Thus neither approximation holds over the entire course of the reaction, and the only permissible "simplification" would be to combine eq 4, 6, and 7 into the single autocatalytic process (14) with a rate law derived from eq 15 and 16.

While the mechanism presented here succeeds in predicting many of the dynamic features of the system over a wide range of constraint values, several major discrepancies remain between theory and experiment in the BR system. Minor quantitative differences could probably be improved by further manipulation of the rate constants, but all the major qualitative disagreements appear to be attributable to a common problem which is unlikely to be resolved by additional refinement of the expendable parameters. A more drastic solution is required.

As we see in Figures 1 and 3, wherever there are large differences between the simulated and experimental dynamics of the system, these discrepancies are associated with an overestimate of the region of stability of SSI; the model makes the nonradical state too stable. This is especially clear in the lower left part of Figure 3.

One way to destablize the nonradical SSI in the calculation is to "push" the system toward the radical state by producing an appropriate chemical species. Although varying certain rate constants (e.g., increasing k_4, decreasing k_5) will serve this purpose, this procedure also changes the system in other ways, destroying the agreement between simulation and experiment at other points. One highly suggestive result is that introducing an input flow of iodous acid ($[HIO_2]_0 = 10^{-6}$ M) into the simulation decreases the range of stability of SSI and increases the iodine minimum in the oscillatory state without noticeably affecting the other calculated results. This observation suggests that augmentation of the mechanism by steps which produce HIO_2 at a sufficient rate without perturbing the rest of the model too greatly might resolve most if not all of the remaining discrepancies between theory and experiment. A possible candidate is

$$H_2O_2 + IO_3^- + H^+ = HIO_2 + H_2O + O_2 \quad (21)$$

though the rate given by Liebhafsky in 1931[32] for this reaction would make it much too slow to produce iodous acid at the appropriate rate. Further experimental investigation of this reaction may be in order.

The validity of a model of such complexity is credible only if *several* major experimental features are reproduced. The fact that the mechanism presented here predicts not only oscillations but also bistability with the observed inverse regulation of iodine and the dependence of the period on malonic acid all suggest that this scheme does indeed account for the kinetic skeleton of the Briggs–Rauscher system. The computational effort involved has been considerable and important gaps remain, but in view of the agreement achieved both with experiment and with other models independently arrived at, it appears that mechanistic understanding of the Briggs–Rauscher reaction has taken a large step forward.

Acknowledgment. This work was supported by National Science Foundation Grant CHE7905911. We are extremely grateful to Professors R. M. Noyes and S. D. Furrow for communicating their results to us prior to publication. We thank Professor Kenneth Kustin for a critical reading of the manuscript.

---

[32] Liebhafsky, H. A. *J. Am. Chem. Soc.* **1931**, *53*, 896–911.

Olefin Rearrangement Resulting from the Gas-Phase KrF Laser Photolysis of $Cr(CO)_6$

William Tumas, Barbara Gitlin, Alan M. Rosan, and James T. Yardley*

Contribution from Corporate Research and Development, Allied Corporation,
Morristown, New Jersey 07960. Received January 16, 1981

Abstract: We have found that irradiation of $Cr(CO)_6$–1-butene mixtures in the gas phase with a KrF laser (248 nm) results in the efficient (yield ~0.2) isomerization of 1-butene to 2-butene, in marked contrast to results in solution. The primary photochemical yield is independent of 1-butene pressure and of $Cr(CO)_6$ pressure over wide pressure ranges. Secondary photochemical processes are also found, the importance of which depends upon 1-butene pressure. We also report yields of species $Cr(CO)_m(PF_3)_{6-m}$ resulting from irradiation of $Cr(CO)_6$–PF_3 mixtures at 248 nm. At high dilution [$Cr(CO)_6$:PF_3 = 2×10^{-3}], we find relative yields of 0.10, 0.14, 0.73, and 0.03 for $Cr(CO)_2(PF_3)_4$, $Cr(CO)_3(PF_3)_3$, $Cr(CO)_4(PF_3)_2$, and $Cr(CO)_5PF_3$, respectively. These results suggest a high degree of fragmentation following optical excitation at 248 nm. We present a reasonable kinetic model to explain the observed isomerization of butene in which a primary photofragment, probably $Cr(CO)_3$ or $Cr(CO)_2$, is the active species.

I. Introduction

It has long been recognized that the photoexcitation of metal carbonyl compounds may result in species which are active for photocatalytic or photoassisted processes.[1-3] For species of the form $M(CO)_n$, where M is a transition metal, it has generally been accepted that the primary photochemical process involves the

---

[1] M. S. Wrighton, *Chem. Rev.*, **74**, 401 (1974).

scission of a single metal–CO bond to generate the reactive intermediate $M(CO)_{n-1}$.[2-4] Upon subsequent reactions with olefins, for example, this fragment may complex with the olefin to generate a relatively stable compound $M(CO)_{n-1}$(olefin). Additional thermal or photochemical processes may be required to generate a coordinatively unsaturated compound $M(CO)_{n-2}$(olefin) which has the potential for direct olefin isomerization or through interaction with hydrogen, olefin hydrogenation. In the case of isomerization, the transformation may proceed through a π-allylic intermediate. Such a mechanism has been suggested by Wrighton, Hammond, and Gray[5] to explain the isomerization of olefins resulting from the photolysis of $W(CO)_6$, $Mo(CO)_6$, and $Cr(CO)_6$ in solution. In particular, these workers noted that photolysis of $Cr(CO)_6$ is inefficient in promoting the isomerization of simple olefins. Similar mechanisms have been invoked for processes involving $Fe(CO)_5$ and other metal carbonyls in solution.[6]

We have recently presented evidence that the *gas-phase* photolysis of iron pentacarbonyl[7,8] may result in the direct generation of highly unsaturated fragments: $M(CO)_n \rightarrow M(CO)_{n-m} + m(CO)$ for $m \geq 2$. These unique fragments can provide the basis for entirely new reaction pathways in organometallic photochemistry. For example, through π-allylic intermediates, certain of these fragments should be able to isomerize olefins *directly* without the necessity of additional thermal or photochemical steps. It may be noted that mechanisms involving such species have been proposed for several thermal catalytic processes in metal carbonyl systems,[9,10] although a number of mechanistic questions remain.[11,12]

We report here the isomerization of 1-butene to *cis*- and *trans*-2-butene with relatively high quantum efficiency as the result of gas-phase excitation of 1-butene–chromium hexacarbonyl mixtures with a pulsed KrF laser. We have studied the product yield as a function of 1-butene and $Cr(CO)_6$ partial pressure as well as laser fluence and laser exposure. In addition, we have examined products $Cr(CO)_m(PF_3)_{6-m}$ resulting from pulsed laser photolysis of $Cr(CO)_6$-PF_3 gas mixtures as a function of the ratio $[Cr(CO)_6]/[PF_3]$. Our observations are consistent with a simple kinetic model in which a primary photofragment, probably $Cr(CO)_3$ or $Cr(CO)_2$, interacts with 1-butene to generate a species bound to the fragment which ultimately yields 2-butene.

II. Experimental Section

Experiments involving photolysis of $Cr(CO)_6$–PF_3 mixtures were carried out using a procedure employed previously in studies of $Fe(CO)_5$ laser photofragmentation.[7,8] Briefly, gaseous mixtures of $Cr(CO)_6$ (Strem Chemical Co.), previously rigorously outgassed, and PF_3 (Columbia, Pennwalt), equilibrated for 30 min (there is no thermal chemistry under these conditions), were irradiated in a stainless steel reactor cell with the output of a commercial KrF excimer laser (Tachisto Model TAC II). Operating parameters were 248-nm wavelength, 0.5-nm bandwidth, 10-ns pulse duration, and peak pulse energy of 10–30 mJ in an unfocused area of approximately 1.3 cm^2. Standard vacuum-line procedures were employed for cell filling and product collection and analysis. Product analyses were performed on a HP Model 5840A GC and HP Model 5990A GC/MS using a 0.32-cm o.d. ss 10% SP2100/100-200 Supelcoport column.

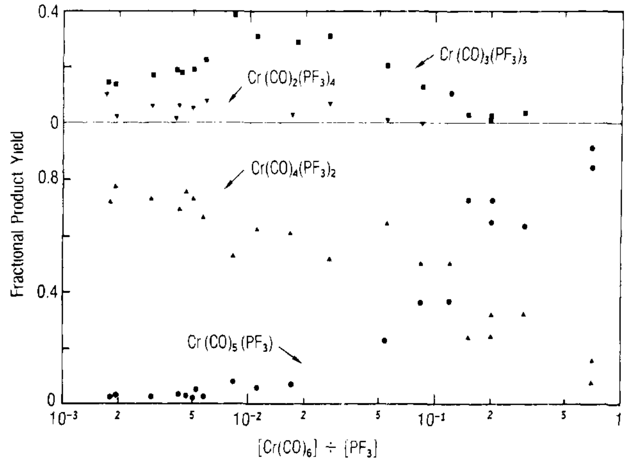


Figure 1. Relative fractional yields of photosubstitution products $Cr(CO)_m(PF_3)_{6-m}$ as a function of reagent ratio $[Cr(CO)_6]/[PF_3]$ for a fixed PF_3 pressure of 0.16 Torr (21.2 Pa). Five pulses from a KrF laser (248 nm) were employed in these experiments.

For olefin isomerization experiments, mixtures of 1-butene and $Cr(CO)_6$ were placed in a cell at room temperature and irradiated with a pulsed KrF laser. The absorbance at 248 nm and the partial pressure of *cis*- and *trans*-2 butene products were monitored as a function of laser exposure. The reaction cells were stainless steel cylinders (3.7-cm i.d. by 10-cm length) fitted with Spectrosil B windows. The windows were periodically removed and cleaned.

The energy output of the laser was continuously monitored by using a quartz window (Spectrosil A) to reflect a fraction of the beam into an energy detector (Gen-Tec) interfaced to a computer which reported both individual laser pulse energy and integrated incident laser energy. In several experiments where low pulse energy (ca. 3 mJ/pulse) was desired, the cell and the detector were interchanged.

Chromium hexacarbonyl (Alfa) was used without further purification. The $Cr(CO)_6$ sample was thoroughly degassed prior to use each time by pumping on the white solid for brief intervals at room temperature. 1-Butene (Matheson Research Grade, 99.9%) was found to contain no measurable 2-butenes and 0.1% of two unidentified impurities. Argon (Matheson Research Grade, 99.995%) was used without further purification. Samples were allowed to mix for at least 0.5 h before and after each irradiation.

All UV spectra were obtained with a Perkin-Elmer Model 330 spectrophotometer. This spectrophotometer was used to monitor the apparent disappearance of $Cr(CO)_6$ during a reaction by recording the absorbance at 248 nm. In one experiment an entire spectrum was run after each irradiation. Gas chromatographic analyses were obtained with a Hewlett-Packard Model 5880A gas chromatograph using flame ionization for detection. Samples were introduced in the vapor phase by direct injection from the reaction cells through a minimum-volume gas inlet system.

III. Results

Following irradiation of $Cr(CO)_6$–PF_3 mixtures with 1 to 50 pulses from an unfocussed KrF laser (248 nm, approximately 10 mJ/pulse, 10 ns/pulse) for $Cr(CO)_6/PF_3$ ratios of $X \sim 5 \times 10^{-3}$ at a $Cr(CO)_6$ pressure of 0.16 Torr (21.2 Pa), six distinct product peaks are observed with gas chromatography. The four principal peaks may be identified with considerable certainty through gas chromatography/mass spectrometry. Peak A corresponds to $Cr(CO)_5PF_3$; peaks B and B′ are isomers of $Cr(CO)_4(PF_3)_2$; peak C is $Cr(CO)_3(PF_3)_3$; and peak D is $Cr(CO)_2(PF_3)_4$. Two low-intensity peaks, designated E and F, are observed at retention times which are reasonable for isomers of $Cr(CO)_2(PF_3)_4$ or $Cr(CO)_3(PF_3)_3$, or which could represent $Cr(CO)(PF_3)_5$. Since peaks D, E, and F are not well resolved under all of our conditions and since D is generally the dominant peak, we will lump these three peaks together and associate the net yield primarily with $Cr(CO)_2(PF_3)_4$. We have found experimentally that under our conditions secondary photochemistry is unimportant for exposures of five or fewer laser pulses. This would be expected since the laser beam area (1.3 cm^2) is a factor of 15 smaller than the cell

---

(2) G. L. Geoffrey and M. S. Wrighton, "Organometallic Photochemistry", Academic Press, New York, 1979.

(3) E. A. von Gustorf, L. H. G. Leeders, I. Fischler, and R. Perutz, *Adv. Inorg. Chem. Radiochem.*, **19**, 65 (1976).

(4) M. S. Wrighton, D. S. Genley, M. A. Schroeder, and D. L. Morse, *Pure Appl. Chem.*, **41**, 671 (1975).

(5) M. S. Wrighton, G. S. Hammond, and H. B. Gray, *J. Organomet. Chem.*, **70**, 283 (1974).

(6) M. A. Schroeder and M. S. Wrighton, *J. Am. Chem. Soc.*, **98**, 551 (1976).

(7) G. Nathanson, B. Gitlin, A. M. Rosan, and J. T. Yardley, *J. Chem. Phys.*, **74**, 361 (1981).

(8) J. T. Yardley, B. Gitlin, G. Nathanson, and A. M. Rosan, *J. Chem. Phys.*, **74**, 370 (1981).

(9) M. A. Schroeder and M. S. Wrighton, *J. Organomet. Chem.*, **128**, 345 (1977).

(10) (a) M. Cais and G. Yagupsky, *Inorg. Chim. Acta*, **12**, 127 (1975); (b) M. Cais and A. Rejoan, *ibid.*, **4**, 509 (1970); E. N. Frankel, E. Selke, and C. A. Glass, *J. Am. Chem. Soc.*, **90**, 2446 (1968); (c) E. N. Frankel and R. O. Butterfield, *J. Org. Chem.*, **34**, 3930 (1969); (d) E. N. Frankel and R. O. Butterfield, *ibid.*, **34**, 3936 (1969); (e) M. S. Wrighton and M. A. Schroeder, *J. Am. Chem. Soc.*, **95**, 5764 (1973).

(11) W. P. Cullen and M. Williams, *J. Fluorine Chem.*, **14**, 429 (1979).

(12) (a) G. L. Swartz and R. J. Clark, *Inorg. Chem.*, **19**, 3191 (1980); (b) R. Bonneau and J. M. Kelly, *J. Am. Chem. Soc.*, **102**, 1220 (1980).

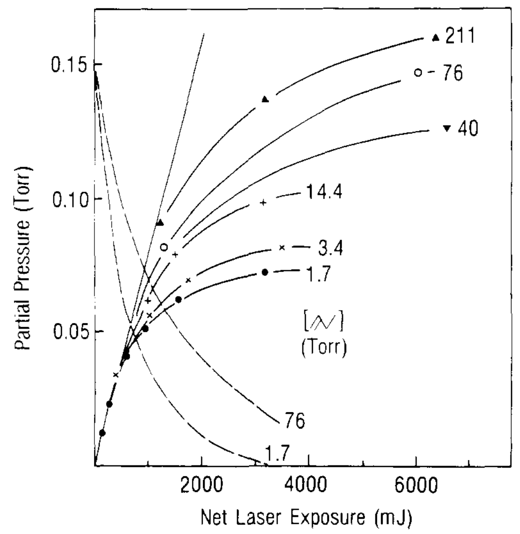


Figure 2. Dashed lines give measured absorbance expressed in terms of equivalent $Cr(CO)_6$ pressure (see text) as a function of integrated laser exposure for 0.15 Torr of $Cr(CO)_6$ in 1.7 and 76 Torr of 1-butene. Also shown is the yield of 2-butene product as a function of integrated laser exposure for 0.15 Torr of $Cr(CO)_6$ in various pressures (in Torr) of 1-butene: ●, 1.7 Torr; ×, 3.4 Torr; +, 14.4 Torr; ▼, 40 Torr; ○, 76 Torr; and ▲, 211 Torr.

area and ample time (5 min) is generally allowed between pulses for gas mixing. For all of the data presented, five laser pulses were used.

The relative yields of products were unchanged within experimental error over a laser fluence (energy per unit area) range of 1 to 10 mJ/cm^2. The net yields are roughly proportional to laser fluence. This provides reasonable assurance that the observed products result from simple one-photon absorption processes under our conditions.

Figure 1 shows the relative yields for $Cr(CO)_m(PF_3)_{6-m}$ as a function of $Cr(CO)_6/PF_3$ ratio, X. These data were obtained for 0.16 Torr (21.2 Pa) of $Cr(CO)_6$ with varying amounts of PF_3. Although vapor pressure and detectability limitations precluded a systematic examination of the yields as a function of total pressure for fixed X, previous experience with $Fe(CO)_5$ suggests that the relative yields should be independent of total pressure, at least below 200 Torr (2.7×10^4 Pa). For $X \leq 5 \times 10^{-3}$, it may be that some of peaks C, D, E, and F are lost in the base line of the chromatogram, thus possibly providing for some systematic error.

Within experimental error the ratio of signal for peak B to the signal for peak B′, both of which are associated with isomers of $Cr(CO)_4(PF_3)_2$, is independent of the reagent ratio X, of the laser fluence, and of the number of laser pulses used. This ratio is 4.8 ± 1.2. Some systematic error, perhaps as much as 20–30%, may be present owing to slight overlap of the peaks in the gas chromatograms.

Upon KrF laser irradiation of mixtures of 1-butene (1–200 Torr) and $Cr(CO)_6$ (0.05–0.15 Torr) at room temperature, the observed ultraviolet absorbance at 248 nm decreased. In the case of 14.4 Torr of 1-butene and 0.15 Torr of $Cr(CO)_6$ the observed UV spectrum was identical with that of $Cr(CO)_6$ for total exposures less than 1 J. A slight change in the shape of features near 225 nm was evident for exposures in excess of 1.5 J. Following irradiation of one mixture (0.15 Torr of $Cr(CO)_6$ and 20.1 Torr of 1-butene) with an exposure of 0.3 J, no change in the ultraviolet absorption spectrum was observed over a 24-h period. Figure 2 shows records of absorbance at 248 nm as a function of laser exposure for mixtures of 0.15 Torr of $Cr(CO)_6$ with 1.7 and 76 Torr of 1-butene. This absorbance is expressed in units of equivalent or apparent $Cr(CO)_6$ concentration denoted here $[Cr]_{ap}$ and derived from the measured absorbance using Beer's law $I = I_0 \exp(-\alpha L p)$, where the absorption coefficient at 248 nm has been determined to be $\alpha = 1.87\ Torr^{-1}\ cm^{-1}$. For 0.15 Torr of $Cr(CO)_6$, the observed change in apparent $Cr(CO)_6$ concentration per unit laser exposure at small exposures is slightly dependent upon 1-butene pressure, as shown in Figure 3. Our observations are adequately described by $(\partial[Cr]_{ap}/\partial E_{in})_0 = \{-1.6 \times 10^{-4} + 5.0 \times 10^{-7}[\text{1-butene}]\}$ Torr/mJ for 1 Torr < [1-butene] < 100 Torr. For these data, the precision is sufficiently poor that extension outside of the specified pressure range is unwarranted.

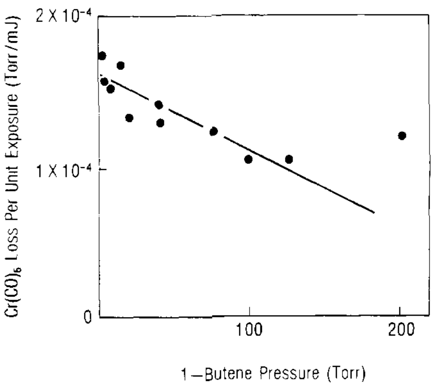


Figure 3. Loss in $Cr(CO)_6$ per unit laser exposure deduced from extrapolated initial slopes of absorbance–exposure curves and plotted against 1-butene pressure.

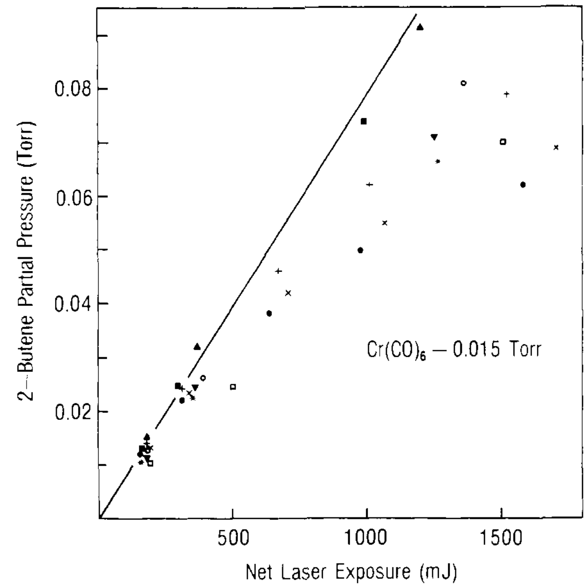


Figure 4. Yield of 2-butene product as a function of integrated laser exposure for 0.15 Torr of $Cr(CO)_6$ and various pressures of 1-butene and for two different laser pulse energies. For 30 mJ/pulse: ●, 1.74 Torr; ×, 3.4 Torr; *, 20.2 Torr; ▼, 40.3 Torr; +, 14.4 Torr; ○, 76.0 Torr; ■, 40.1 Torr; ▲, 211 Torr. For 3 mJ/pulse: □, 20.0 Torr.

The loss of absorbance at 248 nm shown in Figure 2 is accompanied by the production of isomerization products *cis*- and *trans*-2-butene. In all experiments utilizing 30 mJ per pulse excitation energy, the cis/trans ratio was 1.0 ± 0.2. For the few experiments carried out with 3 mJ per pulse excitation, this ratio was 1.8 ± 0.4. Figure 4 shows typical data for the total yield of 2-butene product as a function of laser exposure for single-pulse energies of 30 and 3 mJ. It is seen that the product yield as a function of exposure is relatively independent of laser fluence (energy per area). Figures 2 and 4 give product yield as a function of laser exposure and 1-butene pressure for 0.15 Torr of $Cr(CO)_6$. The product yield per unit of laser exposure at low exposures is within experimental error (30%) independent of [1-butene] over the range 2–200 Torr and is given by $(\partial[\text{2-butene}]/\partial E_{in})_0 = 7.8 \times 10^{-5}$ Torr/mJ. Experiments at 0.05 Torr of $Cr(CO)_6$ showed similar results with $(\partial[\text{2-butene}]/\partial E_{in})_0 = 2.2 \times 10^{-5}$ Torr/mJ. It is also evident from Figure 2 that the product yield in the limit of high laser exposure does increase with increasing 1-butene pressure. However, the ultimate yield even at very high 1-butene pressures (200 Torr) is approximately equal to the initial $Cr(CO)_6$

pressure, giving a net product yield per $Cr(CO)_6$ of approximately unity. The addition of 600 Torr of Ar to a mixture of 0.15 Torr $Cr(CO)_6$ and 20 Torr 1-butene had no effect on the observed dependence of absorbance at 248 nm or of product yield on laser exposure.

In these experiments, we have not directly monitored the number of photons absorbed. In the absence of saturation effects, this quantity may be calculated from Beer's law. This should be correct if the saturation parameter R is less than unity.[7] In our case we have $R \sim 2$ for pulse energies of 30 mJ and $R \sim 0.2$ for 3 mJ pulse energies. Thus some saturation may be present in our experiments. Using Beer's law and the measured values for $(\partial[\text{2-butene}]/\partial E_{\text{in}})_0$, we may determine a primary quantum yield of 0.21 for 0.15 Torr of $Cr(CO)_6$ and 0.15 for 0.05 Torr of $Cr(CO)_6$. If saturation is present, these numbers give lower limits. We point out that the agreement of the data for 3 mJ/pulse and 30 mJ/pulse as well as that for 0.15 Torr and for 0.05 Torr of $Cr(CO)_6$ suggests that 0.2 is close to the actual primary yield. These data give values for the apparent loss of $Cr(CO)_6$ (as measured by absorption at 248 nm) per absorbed photon ranging from 0.44 at 2 Torr of 1-butene to 0.27 at 120 Torr of 1-butene.

IV. Photofragmentation of Chromium Hexacarbonyl

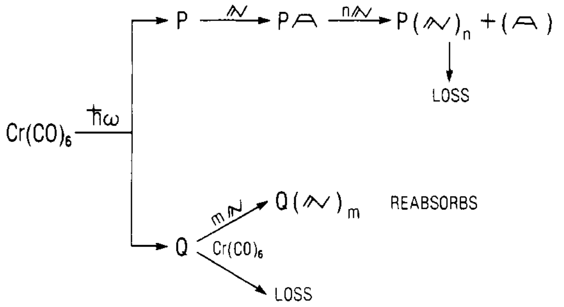
In our investigation of photodissociation in $Fe(CO)_5/PF_3$ mixtures, we have suggested[7,8] that the kinetics of the system may be described by a scheme in which primary photochemical events produce fragments $Fe(CO)_4$, $Fe(CO)_3$, and $Fe(CO)_2$. These fragments and subsequent intermediates may undergo *trapping* reactions with PF_3 such as $Fe(CO)_2 + PF_3 \rightarrow Fe(CO)_2(PF_3)$. Reactions of this type ultimately generate the observed stable products. We also proposed that the primary fragments and subsequent intermediates may undergo reaction with $Fe(CO)_5$ resulting in *mixing* of the products. An example of such a reaction is $Fe(CO)_2 + Fe(CO)_5 \rightarrow Fe(CO)_3 + Fe(CO)_4$. We have postulated that *quenching* reactions of the type $Fe(CO)_4 + Fe(CO)_5 \rightarrow Fe_2(CO)_9$ are important. Finally we presented argument that *exchange* reactions of the type $Fe(CO)_4 + PF_3 \rightarrow Fe(CO)_3PF_3 + CO$ are not important under our conditions. Under these assumptions, it may readily be seen that in the limit of a large excess of PF_3, the yields of products $Fe(CO)_m(PF_3)_{5-m}$ give directly the primary yields of the photofragments $Fe(CO)_m$. Our data for $Cr(CO)_6$–PF_3 mixtures are not nearly so extensive as our previous work with $Fe(CO)_5$. If the same arguments apply, then we may interpret the yields of $Cr(CO)_m(PF_3)_{6-m}$ for $Cr(CO)_6/PF_3$ ratios $\sim 2 \times 10^{-3}$ to give primary photofragmentation yields for $Cr(CO)_6$ at 248 nm as follows: 0.03 ± 0.03, 0.73 ± 0.16, 0.14 ± 0.05, and 0.10 ± 0.06 for $Cr(CO)_5$, $Cr(CO)_4$, $Cr(CO)_3$, and $Cr(CO)_2$, respectively. In the absence of more definitive results, these conclusions should be taken with caution.

The photochemistry of $Cr(CO)_6$ has been extensively studied in solution and in matrix isolation.[2,13-17] The results have been universally interpreted[1] in terms of single metal–CO bond cleavage following single photon absorption:

$$Cr(CO)_6 + h\nu \rightarrow Cr(CO)_5 + CO$$

Photosubstituion quantum yields of 0.7 or larger have been measured.[14] The condensed-phase results contrast sharply with the high degree of fragmentation observed here for isolated gas-phase molecules. These differences may be rationalized in analogy to $Fe(CO)_5$ as follows.[7,8] The average Cr–CO bond energy[18] is 25.6 kcal/mol (107 kJ/mol). Thus the photon excitation energy of 115 kcal/mol (481 kJ/mol) is sufficient to break four bonds potentially yielding $Cr(CO)_2$. We suggest that the observed fragmentation results from *sequential* loss of CO coupled to a high degree of internal energy retention in the remaining metal carbonyl fragment. In condensed media rapid dissipation of excess energy due to intermolecular interaction prevents additional fragmentation. In an isolated molecule, however, a high degree of internal energy retention must eventually result in considerable fragmentation.

Scheme I



Assignment of gas chromatograph peaks B′ and B to *trans*- and *cis*-$Cr(CO)_4(PF_3)_2$, respectively, is consistent with the retention times reported for similarly substituted Mo compounds. If this is correct, then the observed cis/trans ratio of 4.8 ± 1.2 is equivalent to the statistical cis/trans ratio of 4.0 within experimental error, suggesting a statistical placement of PF_3 entities on octahedral sites of the precursor $Cr(CO)_4PF_3$.

V. Butene Isomerization

Our experiments demonstrate clearly that 1-butene is isomerized to 2-butene upon the vapor-phase photolysis of $Cr(CO)_6$ with KrF laser radiation at 248 nm. A model for this system must explain the following observations for our experimental geometry.

(1) The primary quantum yield of 2-butene product relative to photon absorption is given by $\Phi \sim 0.2$ relatively independent of $Cr(CO)_6$ pressure (0.05–0.15 Torr) and 1-butene pressure (2–200 Torr).

(2) For low exposures (≤ 1 J) at 0.15 Torr of $Cr(CO)_6$ the apparent loss in $Cr(CO)_6$ molecules relative to the number of absorbed photons decreases with increasing 1-butene pressure from about 0.44 at 2 Torr to about 0.27 at 120 Torr. Thus at high pressures the loss in aborbance more closely approaches the 2-butene product formation.

(3) In the limit of high exposure (≤ 5 J) the yield of 2-butene product relative to initial $Cr(CO)_6$ concentration increases with 1-butene pressure from about 0.5 at 1.7 Torr to about unity at 200 Torr.

(4) Yields of 2-butene product and loss of $Cr(CO)_6$ are unaffected by addition of large excess (30-fold) of Ar.

Scheme I gives a relatively simple model which can qualitatively explain these features. In this model photolysis of $Cr(CO)_6$ generates primary fragments (or groups of fragments) designated P and Q. Fragment P generates isomerized product and is ultimately lost through interaction with either $Cr(CO)_6$ or 1-butene. Fragment Q may complex with 1-butene to generate volatile materials which are available for reabsorption of light and further photochemistry. Interaction of fragment Q with $Cr(CO)_6$ results in loss from the system. This model, then, provides an ultimate primary yield of 2-butene which depends only upon the initial yield of fragment P. Furthermore, for fixed $Cr(CO)_6$ pressure and for high 1-butene pressures, the loss in absorbing species, i.e., $Cr(CO)_6$ and $Q(\text{1-butene})_m$, approaches the amount of 2-butene product, while at lower 1-butene pressures additional loss occurs owing to interaction with $Cr(CO)_6$. The model also provides that in the limit of high 1-butene pressure only one 2-butene product results per initial $Cr(CO)_6$ molecule, while additional losses result at lower 1-butene pressures. Finally, inert gases such as Ar have no effect in this model.

In contrast to previous solution-phase experiments[5] our results clearly demonstrate that the vapor-phase photolysis of $Cr(CO)_6$ in the presence of excess 1-butene yields 2-butene with relatively

---

(13) J. M. Kelly, H. Hermann, and E. K. Von Gustorf, *J. Chem. Soc., Chem. Commun.*, 105 (1973).

(14) J. Nasielski and A. Colas, *J. Organomet. Chem.*, **101**, 215 (1975).

(15) M. A. Graham, R. N. Perutz, M. Poliakoff, and J. J. Turner, *J. Organomet. Chem.*, **34** C34 (1972).

(16) M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc. A*, 2939 (1971).

(17) R. N. Perutz and J. J. Turner, *J. Am. Chem. Soc.*, **97**, 4791 (1975).

(18) G. Pilcher, M. J. Ware, and D. A. Pittam, *J. Less-Common Met.*, **42**, 223 (1975).

(19) J. W. Byrne, H. U. Blaser, and J. A. Osborn, *J. Am. Chem. Soc.*, **97**, 3872 (1975).

high efficiency ($\Phi \sim 0.2$). We believe that this is due to significant differences in photofragmentation patterns. In solution, the dominant photofragment is certainly[2] $Cr(CO)_5$ which becomes coordinatively saturated upon reaction with a simple olefin. Gas-phase photolysis, on the other hand, yields fragments which are more highly unsaturated. Reaction of any of these fragments with an olefin through a simple π complex results in a compound which is still coordinatively unsaturated and which thus is capable of additional unimolecular or bimolecular reaction.

It has recently been suggested[12a] that the photocatalytic isomerization of 1-pentene in the presence of $Fe(CO)_5$ may be a consequence of the formation of bridged dimers since no catalysis is observed for $Fe(PF_3)_5$ which cannot form such species. It has also been observed that $Cr(CO)_5$ is rapidly scavenged by $Cr(CO)_6$ in perfluoromethylcyclohexane and an intermediate $Cr_2(CO)_{11}$ has been proposed.[12b] Since we observe no dependence of 2-butene primary yield on $Cr(CO)_6$ partial pressure, we conclude that species containing more than one Cr atom are not directly involved in the isomerization.

Our kinetic model suggests that 1-butene isomerization is a direct consequence of the production of a photofragment designated P in approximate 20% yield. Since our experiments with $Cr(CO)_6$–PF_3 mixtures suggest that $Cr(CO)_2$ and $Cr(CO)_3$ are produced with 10 and 14% yield, respectively, we speculate that the active species is likely to be $Cr(CO)_3$, $Cr(CO)_2$, or both. One attractive mechanism for this isomerization involves a π-allylic complex intermediate. An example reaction is:

$$Cr(CO)_3 + \text{1-butene} \rightarrow HCr(CO)_3\text{-}\eta^3\text{-}C_4H_7 \rightarrow Cr(CO)_3(\text{2-butene})$$

The model suggests that the 2-butene product remains bound to the Cr on a time scale longer than that required to coordinatively saturate the molecule by additional reaction with olefin. In principle, the fragment $Cr(CO)_4$ may also react with 1-butene to generate a hydrido π-allylic complex.

$$Cr(CO)_4 + \text{1-butene} \rightarrow HCr(CO)_4\text{-}\eta^3\text{-}C_4H_7$$

However, although formally an 18-electron species, intramolecular ligand repulsions would probably severely destabilize such a system. In addition, since an η^3-allyl ligand requires two coordination sites, such a species is a seven-coordinate complex, a bonding situation accessible to related second[19] and third-row group 6 complexes but far less likely for chromium. It should also be noted that the generation of cis olefin from a π-allyl hydride intermediate suggests the (transient) formation of an *anti*-1-methallyl complex. Furthermore, a π-allylic intermediate may well be geometrically constrained so that hydrogen transfer to the olefin can only give back the initial 1-butene reactant. Complexes based on $Cr(CO)_3$ or $Cr(CO)_2$ should be stereochemically nonrigid, allowing for conversion to the energetically stable 2-butene.

Alternative mechanistic possibilities exist within the confines of our kinetic scheme. Oxidative addition at C-2, production of a vinyl chromium hydride with subsequent β-hydrogen elimination, and readdition would provide both *cis*- and *trans*-2-butene. Precedent for such oxidative processes is available in the photoreactivity of π complexes of activated olefins.[20] The reactivity expected of highly deligandated d^6 chromium$(CO)_n$ may well be manifested by such processes which are related to the reactivity recently noted for low-valent naked metal atoms.[21]

The observed cis–trans ratio of 1.0 ± 0.2 at 30 mJ/pulse and 1.8 ± 0.4 at 3 mJ/pulse for the 2-butene product shows considerable propensity to generate the cis isomer since the equilibrium ratio is[22] approximately 0.33. The variation in cis–trans ratio with intensity may be indicative of some variation in photofragment yield with laser fluence (energy per area), particularly at 30 mJ/pulse which corresponds to somewhat greater fluence than used in our photofragmentation studies.

The effectiveness of π-triene, arene, or naphthalene $Cr(CO)_3$[10a] complexes for the catalytic regioselective 1,4-hydrogenation of dienes to monoenes has been ascribed to intermediates involving the $Cr(CO)_3$ unit. In particular, the cis stereochemistry attendant to such processes is readily accounted for through syn hydrogen transfer[10e] following partial arene slippage[10b] or total dissociation.[10c] On occasion the diene substrate has been observed to isomerize by a formal 1,5 hydrogen shift, but these catalysts do not promote cis–trans isomerization of the product monoenes.[10d] The photoreduction of dienes catalyzed by $Cr(CO)_6$ in the presence of H_2 is also proposed to occur via a cisoid diene complex. In this case also subsequent cis–trans isomerization of ene products does not occur.[10e]

For 1-butene, we were not able to obtain a catalytic cycle either in terms of number of photons absorbed or in terms of available $Cr(CO)_6$ molecules. These facts are reflected in our kinetic model through a *binding* of the isomerized olefin to the chromium fragment which remains on a time scale long enough for chemical saturation to occur through additional reaction with olefin. This effectively removes the fragment from a catalytic cycle. Thus, catalytic reactions can only be expected in this system if the product is rapidly released. This could be the case for a reaction which is more exothermic or one for which the binding energy is dramatically reduced.

Acknowledgment. We are extremely grateful for the assistance of Ms. Suzanne Kowalski in the chemical analysis and for that of Mr. Stuart Steinhauser in the computer-based data acquisition. We acknowledge helpful discussions with Dr. George Hammond, Professor H. Kaesz, and Professor J. E. Leonard.

Registry No. 1-Butene, 106-98-9; $Cr(CO)_6$, 13007-92-6; PF_3, 7783-55-3.

---

(20) F. W. Grevels and E. K. Von Gustorf, *Justus Liebigs Ann. Chem.*, 547 (1975).

(21) W. E. Billups, M. M. Konarski, R. H. Hauge, and J. L. Margrave, *J. Am. Chem. Soc.*, **102**, 7394 (1980).

(22) E. F. Meyer and D. G. Stroz, *J. Am. Chem. Soc.*, **94**, 6344 (1972).