5. Conclusions

(1) A double-ζ STO fit describes adequately both the 6d and the 5f functions of the actinoids. The 6p functions are well described at the single-ζ level. The diffuse 7s functions are also well described but unimportant in bonding.

(2) Going from single-ζ to double-ζ increases the (5fπ) bonding.

(3) It is suggested, as in ref 3 and 15, that the linearity of the uranyl ion should be attributed to the π_u MO. The energy increases by bending is however now ascribed to increased O-(2pπ)–U(6pπ) antibonding.

(4) As first pointed out by Newman in 1965, *relativistic* 5f functions are necessary for describing the bonding of uranium. The use of the present functions should considerably improve a recent method by Glebov and Nefedov,[12] originally based on nonrelativistic functions.

Registry No. UO_2^{2+}, 16637-16-4; Th, 7440-29-1; Pa, 7440-13-3; U, 7440-61-1; Np, 7439-99-8; Pu, 7440-07-5; Am, 7440-35-9; UF_6, 7783-81-5; oxygen, 7782-44-7.

LETTERS

Infrared-Laser-Induced Gas-Phase Isomerization of Olefins in the Presence of $Fe(CO)_5$

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(Received: May 4, 1984; In Final Form: August 20, 1984)

Irradiation of a mixture of 1-pentene or *trans*-2-pentene and $Fe(CO)_5$ with a pulsed CO_2 TEA laser at low pressures in the vapor phase results in the formation of isomeric mixtures of 1- and 2-pentenes and the consumption of $Fe(CO)_5$. Isomerization occurs due to heating of the $Fe(CO)_5$ caused by collisional deactivation of the excited pentene. This results in decomposition of $Fe(CO)_5$ to yield chemically reactive coordinatively unsaturated iron carbonyls or iron atoms which can effect the cis, trans and positional isomerization of olefins. Both the initial and final pentene isomer ratios differ significantly from those observed in solution phase photochemically or in thermally initiated isomerization of the pentenes by iron carbonyls.

Introduction

The spectroscopy and chemistry of metal carbonyls continues to be an active area of research.[1-3] Much of this interest is due to the ability of coordinatively unsaturated metal carbonyl species to catalyze chemical reactions such as olefin isomerization, hydrogenation, and hydrosilation. While the spectroscopy and photochemistry of $Fe(CO)_5$ have been extensively investigated, its thermal chemistry has received relatively little attention. Attempts to effect positional isomerization of terminal alkenes by thermal activation of $Fe(CO)_5$ resulted in decomposition to yield iron powder without extensive olefin isomerization.[3] These observations are consistent with the recent report of Engelking and Lineberger[2a] that the bond dissociation energy for $Fe(CO)_4$–CO is larger than that for any of the coordinatively unsaturated species $Fe(CO)_n$, $n = 1$–4. Thus thermolysis of $Fe(CO)_5$ should result in more rapid decomposition of the catalytically active species than the inactive precursor. Pulsed heating methods offer a potential advantage over conventional thermolysis in that the initially generated internally energized, coordinatively unsaturated species produced during the heat pulse could be collisionally deactivated and effect catalytic reactions between heat pulses.[4] Pulsed laser heating also minimizes dissociation and deposition of material at the cell walls which occur extensively with conventional heating. We report here the preliminary results of our investigation of pulsed laser-induced infrared multiphoton isomerization of 1-pentene and *trans*-2-pentene in the presence of $Fe(CO)_5$. Among the significant findings of this investigation are (a) laser excitation of an olefin in an olefin–$Fe(CO)_5$ mixture results in the gradual decomposition of $Fe(CO)_5$ and concomitant olefin isomerization and (b) the formation of product olefins with both initial and final product ratios substantially different than those obtained in photochemical reactions of $Fe(CO)_5$[1] or thermal reactions of $Fe_3(CO)_{12}$.[3b]

Experimental Section

The *cis*- and *trans*-2-pentenes were obtained from Chemical Samples Co. and were specified to be of >98% purity. The 1-pentene sample was obtained from Aldrich Chemical Co. and was specified to be at >99% pure. On FID GC analysis, each sample was found to be >99% pure and was not subject to further purification. All reported yields have the initial concentration of other pentene isomers subtracted out. Isomer analysis was carried out with a β,β'-oxydipropionitrile column. Infrared spectra were recorded with a Nicolet series 7000 FTIR spectrometer. Pressure measurements were made with an MKS capacitance manometer. Irradiation of the pentenes was carried out with the collimated unfocused output of a Lumonics K203-2 CO_2 TEA

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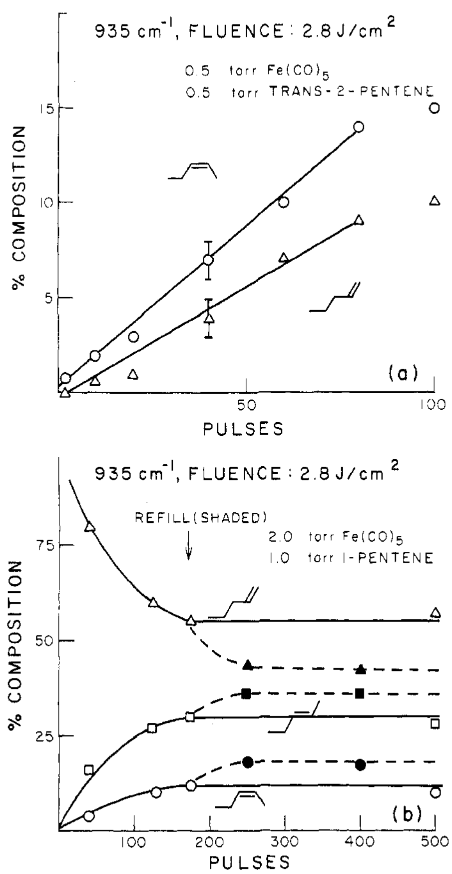

Figure 1. (a) Formation of *cis*-2-pentene (○) and 1-pentene (△) upon laser irradiation (935 cm^{-1}, 2.8 J/cm^2) of *trans*-2-pentene (0.5 torr) and Fe(CO)$_5$ (0.5 torr). (b) Formation of *trans*-2-pentene (□) and *cis*-2-pentene (○) and disappearance of 1-pentene (△) upon laser irradiation (935 cm^{-1}, 2.8 J/cm^2) of 1-pentene (1.0 torr) and Fe(CO)$_5$ (2.0 torr). Filled symbols and dashed lines are for data obtained after refilling cell with Fe(CO)$_5$ after 175 laser pulses.

laser. Irradiation was with the P(30) 10.6-μm transition (935 cm^{-1}) with laser lines determined with an Optical Engineering CO$_2$ laser spectrum analyzer and energies with a Scientech calorimeter. Irradiation was performed in a 1-dm path length Pyrex cell with NaCl windows. Visible emission from the cell was observed with a JY320 monochromator and a IP28 phototube. The monochromator was calibrated with a He:Ne laser and Hg lamp emission lines.

Results

We previously reported[5] that irradiation of *trans*-2-pentene (0.1 torr) with the unfocused output of a Lumonics K203-2 CO$_2$ TEA laser can effect clean trans → cis isomerization to a steady-state isomer mixture of 10% *trans*- and 90% *cis*-2-pentene. Irradiation of either *trans*-2-pentene or 1-pentene at higher laser fluence results in fragmentation but still no appreciable positional isomerization. Irradiation (935 cm^{-1}) of either *trans*-2-pentene or 1-pentene and Fe(CO)$_5$, at a fluence (2.8 J/cm^2) below the threshold for trans → cis isomerization in the absence of Fe(CO)$_5$, results in the formation of a mixture of 1-pentene and *trans*- and *cis*-2-pentene and the decomposition of Fe(CO)$_5$. When other isomers are not present, no isomerization of *cis*-2-pentene is obtained under these reaction conditions as a consequence of the low single-photon absorption cross section of this isomer. However, when a 1:1 mixture of *cis*-2-pentene and 1-pentene is irradiated in the presence of Fe(CO)$_5$ both isomers are converted to *trans*-2-pentene at comparable rates. Fe(CO)$_5$ does not absorb at the frequency of irradiation and is inert under reaction conditions in the absence of *trans*-2-pentene or 1-pentene.[6]

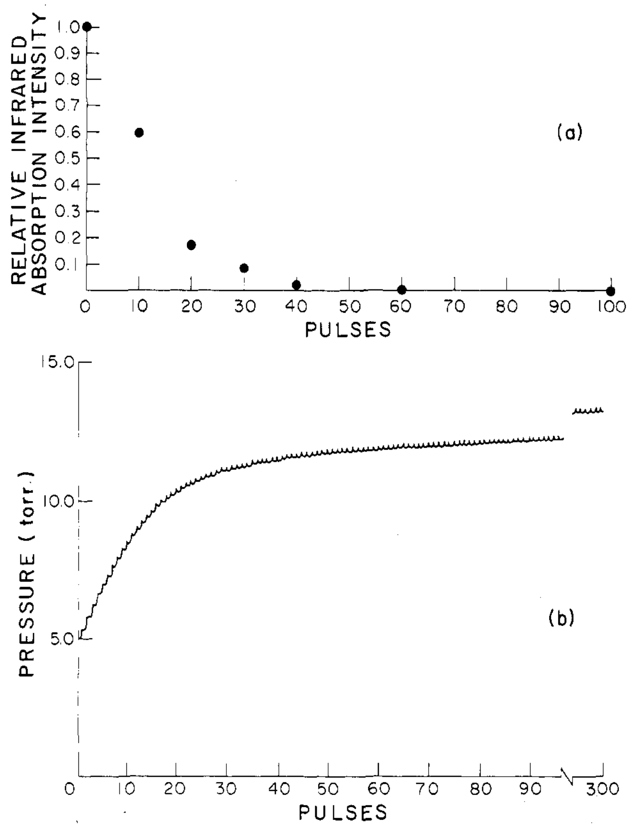

Figure 2. (a) Relative intensity of the infrared absorption of Fe(CO)$_5$ at 2012 cm^{-1} vs. the number of laser pulses. The initial sample contained 2 torr of 1-pentene and 3 torr of Fe(CO)$_5$. It was irradiated at a fluence of 2.8 J/cm^2 on the 935-cm^{-1} laser line. (b) Cell pressure vs. number of laser pulses. Irradiation and sample parameters were as in Figure 2a. The spiked appearance of the curve is due to the transient pressure rise following the absorption of each laser pulse.

The variation in the pentene isomer content vs. the number of laser pulses for *trans*-2-pentene and 1-pentene parents is shown in Figure 1 a and b. Irradiation of *trans*-2-pentene for ~100 laser pulses yields an isomer mixture consisting of 75% *trans*-2-pentene, 15% *cis*-2-pentene, and 10% 1-pentene. The composition of this mixture does not change appreciably upon continued irradiation or when fresh Fe(CO)$_5$ is added to the reaction vessel after condensation of the olefins and evacuation to remove CO generated via Fe(CO)$_5$ decomposition. The same mixture is obtained by irradiation of a mixture of 75% *trans*-2-pentene and 25% 1-pentene with 100 laser pulses. When 1-pentene is irradiated for a few hundred pulses (Figure 1b), isomerization proceeds to a mixture of 1-pentene (60%), *trans*-2-pentene (27%), and *cis*-2-pentene (13%). Addition of fresh Fe(CO)$_5$ to the reaction vessel and subsequent irradiation alters the isomer ratio slowly in the direction of the mixture obtained from *trans*-2-pentene irradiation. The stepped appearance of Figure 1b following addition of fresh Fe(CO)$_5$ reflects both the consumption of Fe(CO)$_5$ and inhibition of reaction due to pressure rise from the liberation of CO.

The IR absorption of Fe(CO)$_5$ at 2012 cm^{-1} is observed to decrease approximately exponentially and the cell pressure correspondingly increase with the number of laser pulses (Figure 2). After 100 pulses ≥95% of the Fe(CO)$_5$ is consumed, involatile material deposits on the cell walls, and the pressure increases to a value consistent with the liberation of ~4 CO molecules per dissociated Fe(CO)$_5$. After a few pulses, a pale pink luminescence (λ_{max} = 356.5 and 381.1 nm, corresponding to iron atom emission[7]) can be detected within the irradiated volume of the cell during the laser pulse. This luminescence persists until all the Fe(CO)$_5$

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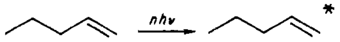
has been consumed as judged by infrared intensity measurements of the $Fe(CO)_5$ concentration.

Discussion

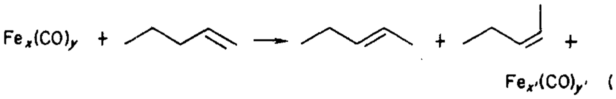
These results establish that pulsed excitation of $Fe(CO)_5$–olefin mixtures can effect olefin isomerization. While turnover numbers are modest compared to those obtained in the solution phase photochemistry of $Fe(CO)_5$ or in the solution phase thermally initiated reaction of $Fe_3(CO)_{12}$,[1-3] these results establish that homogeneous pulsed heating of $Fe(CO)_5$ can effect clean olefin isomerization, whereas, conventional thermolysis of $Fe(CO)_5$ in olefin solution results in decomposition of $Fe(CO)_5$, without isomerization.

A plausible mechanism for 1-pentene isomerization is as follows, where eq 1 is the excitation step which is followed by vibrational relaxation and energy transfer. This results in a rise in cell gas temperature sufficient to effect thermal decomposition of $Fe(CO)_5$ to yield coordinatively unsaturated $Fe(CO)_{5-n}$ (eq 2). A coordinatively unsaturated iron species, generated either directly via decomposition of $Fe(CO)_5$ (eq 2) or via reaction of the decomposition products[2] of $Fe(CO)_5$ then activates the parent isomer as shown in eq 3, where $Fe_x(CO)_y$ represents the unknown coordinatively unsaturated iron species discussed above which induces isomerization of the pentenes. The $Fe(CO)_{5-n}$ and/or the $Fe_x(CO)_y$ species can react further to yield iron atoms or involatile iron clusters.[1,2] The lack of isomerization in the period from several minutes to several hours following the laser pulse is also consistent with the active species being a short-lived coordinatively unsaturated iron-containing species.[8] The observation of a cell pressure rise consistent with the liberation of ~4 CO molecules per dissociated $Fe(CO)_5$ indicates that metallic iron is the major final product of $Fe(CO)_5$ decomposition and is consistent with iron atom emission.[9] The material deposited on the cell walls is magnetic and has an atomic absorption spectrum consistent with metallic iron. However, since the rise in cell pressure does not completely account for all the CO from totally dissociated $Fe(CO)_5$, some to as much as 20% of the initial $Fe(CO)_5$ may be involved in the formation of involatile iron species such as $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$.



(1)

$$Fe(CO)_5^{\dagger} \rightarrow Fe(CO)_{5-n} + (CO)_n \qquad (2)$$



(3)

As alluded to, we do not at present know either the precise identity of the $Fe_x(CO)_y$ species which effects olefin isomerization or whether it is regenerated unchanged following the isomerization process, thus the use of $Fe_{x'}(CO)_{y'}$ in eq 3. In the absence of this information, it is not possible to distinguish between a catalytic reaction with low turnover number (resulting from unimolecular decomposition of the catalyst) or a noncatalytic process. In view of the occurrence of both cis, trans and positional isomerization it does appear likely that isomerization is effected by one or more reactive $Fe_x(CO)_y$ species.[1] The observation of an induction period for iron atom luminescence (Figure 2) but not for olefin isomerization indicates that iron atoms are not the dominant reactive species, at least in the early stages of the reaction.

Both the initial and final isomer ratios observed in the present investigation (Figure 1) differ significantly from those observed in $Fe(CO)_5$ UV photoinitiated or $Fe_3(CO)_{12}$ thermally catalyzed isomerization. The initial trans/cis isomer ratio from 1-pentene is ca. 4.0, larger than the values (2.9) obtained for UV or thermally catalyzed reactions,[1,3] or the value expected for thermodynamic equilibrium (e.g., 3.7 at 350 K or 2.5 at 500 K).[3] At higher conversions, this value drops to 2.1, lower than the equilibrium value. The initial cis/1-pentene ratio from *trans*-2-pentene is initially >10 but drops to 1.5, substantially lower than the value expected for thermodynamic equilibrium (e.g., 4.0 at 350 K and 2.6 at 500 K). A high cis/1-pentene ratio (>10) is also observed after 100 laser pulses in the presence of 10 torr argon buffer gas, suggesting that a low-energy trans ⇄ cis isomerization pathway may dominate the positional isomerization pathway at lower conversion/pulse. Since low conversion per pulse is indicative of a lower reaction temperature, this implies that, even in the presence of catalyst, the cis ⇄ trans isomerization barrier is of lower activation energy than the barrier to positional isomerization. The observation of initial and final product ratios which are not compatible with thermodynamic equilibrium indicates that product ratios may be kinetically controlled; in accord with either a noncatalytic process or a catalytic process with a low turnover number. The change from initially high trans/cis (Figure 1b) and cis/1-pentene (Figure 1a) ratios to lower final ratios could result from either a change in the effective reaction temperature or a change in the nature of the catalytic species during the reaction.[10] Efforts to distinguish between these alternatives are in progress.

Acknowledgment. We thank the National Science Foundation for support of this work under grants CHE82-06976 (E.W.) and CHE80-26020 (F.D.L.). The CO_2 laser was purchased with funds provided by National Science Foundation Grant CHE80-09060.

Registry No. $Fe(CO)_5$, 13463-40-6; 1-pentene, 109-67-1; *trans*-2-pentene, 646-04-8.

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