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Carbonyliron–Olefin Photochemistry: Quantum Yields for the Sequential Substitution of Two CO Groups in Pentacarbonyliron by (*E*)-Cyclooctene. Synthesis of the First Stable (η^2-Olefin)$_3$Fe(CO)$_2$ Complex[†]

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Abstract: Multiple photosubstitution of CO groups in pentacarbonyliron by an olefin has been investigated by using (*E*)-cyclooctene as a model olefin exhibiting exceptional coordination properties. The quantum yields Φ_1 and Φ_2 for sequential conversion of Fe(CO)$_5$ into (η^2-(*E*)-C$_8$H$_{14}$)Fe(CO)$_4$ (**1**) and (η^2-(*E*)-C$_8$H$_{14}$)$_2$Fe(CO)$_3$ (**2**), respectively, when evaluated using the appropriate formalism for internal light filter corrections (presented in detail in the Appendix), are found to be constant up to high conversion: $\Phi_1 = 0.80$ at 302 nm and 0.77 at 254 nm, $\Phi_2 = 0.59$ at 302 nm and 0.82 at 254 nm. The wavelength dependence of Φ_2 is interpreted in terms of two different ligand field excited states of **1**, providing for varying CO vs olefin photodetachment. The overall quantum yield for the generation of **2** from Fe(CO)$_5$ (ca. 0.20 at 60% conversion of pentacarbonyliron) is discussed in the context of carbonyliron photocatalyzed olefin isomerization, which is known to involve (labile) (η^2-olefin)$_2$Fe(CO)$_3$ as the active catalyst. The synthesis of (η^2-(*E*)-C$_8$H$_{14}$)$_3$Fe(CO)$_2$ (**3**), which is the first isolated representative of this type of complex, is achieved by irradiation of **2** in the presence of excess (*E*)-cyclooctene, whereby liberated CO is required to be rigorously removed by an inert-gas stream.

Carbonyliron photochemistry has a long tradition[1] and has received considerable attention[2] with regard to synthetic applications, catalytic processes, and mechanistic aspects. Irradiation of pentacarbonyliron with highly efficient[3] formation of Fe$_2$(CO)$_9$ represents the first reported photoreaction of a carbonylmetal complex.[1] Photogenerated Fe(CO)$_{5-n}$ fragments have been characterized in low-temperature matrices,[4,5] in the gas phase[5,6] and in solution.[7,8] Photolysis of Fe(CO)$_5$ in the presence of suitable ligands (L) provides convenient access to a large variety of substituted L$_n$Fe(CO)$_{5-n}$ derivatives.[2]

With olefin ligands much of the interest has focused on photocatalytic processes[9-12] such as olefin isomerization, hydrogenation, and hydrosilation. Considerable effort was made in identifying the species involved in those reactions. Beyond the initial formation of (η^2-olefin)Fe(CO)$_4$ further CO photodissociation has been considered to be an essential step in the generation of the catalytically active species. This has recently been substantiated by using photochemically synthesized (η^2-(*Z*)-C$_8$H$_{14}$)$_2$Fe(CO)$_3$[13] and (η^2-C$_2$H$_4$)$_2$Fe(CO)$_3$[9] as a source of the Fe(CO)$_3$ unit, which was demonstrated to carry the catalytic cycle in the isomerization of 1-pentene. Because of their lability and rapid decomposition (η^2-olefin)$_2$Fe(CO)$_3$ complexes[9,13-15] in general are difficult to characterize. Consequently, quantitative studies on the multiple-photosubstitution reactions of Fe(CO)$_5$ with olefins are severely hampered. Up to now there are no quantum yield data available in the literature, not even for the formation of the monosubstituted (η^2-olefin)Fe(CO)$_4$ complexes, which has been utilized for preparative purposes since more than 20 years.[16]

Taking advantage of the exceptional coordination properties of (*E*)-cyclooctene,[17,18] we have recently prepared and fully characterized the first stable bis(olefin)tricarbonyliron complex, (η^2-(*E*)-C$_8$H$_{14}$)$_2$Fe(CO)$_3$.[19] This compound is accessible by two different routes, either thermally by olefin exchange from labile (η^2-(*Z*)-C$_8$H$_{14}$)$_2$Fe(CO)$_3$ or photochemically from Fe(CO)$_5$ and (*E*)-cyclooctene. Owing to the stability of the complexes involved, the latter process provides a unique opportunity to investigate the photosubstitution of CO groups in Fe(CO)$_5$ by an olefin on a quantitative level.

Higher substitution products of Fe(CO)$_5$ with monoolefins are presumably even more labile than (η^2-olefin)$_2$Fe(CO)$_3$. Indeed, such compounds were not known until recently when the generation of (η^2-C$_2$H$_4$)$_3$Fe(CO)$_2$ and (η^2-C$_2$H$_4$)$_4$Fe(CO) in low-temperature 2-methylpentane glass was reported.[9] Using (*E*)-cyclooctene, we have been able to isolate the first stable (η^2-olefin)$_3$Fe(CO)$_2$ complex, the synthesis and characterization of which is reported in this paper.

Experimental Section

All reactions and manipulations were carried out under argon and in argon-saturated solvents. The following materials were prepared ac-

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[†] Dedicated to Prof. Günther O. Schenck at the occasion of his 75th birthday.

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Table I. Determination of Φ_1 from the Irradiation of Pentacarbonyliron and Excess (*E*)-Cyclooctene in *n*-Hexane Solution

$\tau \times$	$\bar{c} \times 100^{b,c}$				
100^a	$Fe(CO)_5$	**1**	**2**	conditions^d	$\Phi_1{}^e$
8.4	93.9 (93.5)	5.6 (6.3)	f (0.2)	A	0.748
16.8	87.6 (87.5)	12.3 (11.9)	1.8 (0.6)	A	0.788
19.0	84.7 (85.9)	12.6 (13.3)	3.0 (0.8)	B	0.875
33.6	76.9 (76.5)	22.2 (21.2)	4.1 (2.3)	A	0.787
38.1	74.1 (73.8)	20.8 (23.3)	5.5 (2.9)	B	0.791
57.1	63.1 (63.4)	28.3 (30.6)	10.0 (6.0)	B	0.810
76.2	55.1 (54.6)	32.0 (35.7)	13.9 (9.8)	B	0.788
134.2	35.0 (34.5)	39.9 (42.0)	27.7 (23.5)	A	0.790
				Φ_1(mean) = 0.80 at 302 nm	
				$\Phi_1{}^g$ = 0.80 (±0.01)	
78.3	51.1 (53.1)	34.0 (35.8)	14.9 (11.1)	C	0.815
89.5	48.7 (48.4)	36.1 (37.8)	19.3 (13.9)	C	0.754
111.9	40.8 (40.2)	39.1 (40.1)	23.9 (19.7)	C	0.750
167.8	26.8 (25.4)	38.5 (39.9)	32.8 (34.7)	C	0.736
				Φ_1(mean) = 0.76 at 254 nm	
				$\Phi_1{}^g$ = 0.77 (±0.02)	

[a] $\tau = Q_{abs}t/c_{Fe(CO)_5}{}^0$, i.e., light absorbed (einstein L^{-1}) divided by the initial concentration of $Fe(CO)_5$. [b] $\bar{c} = c/c_{Fe(CO)_5}{}^0$, i.e., concentration of the particular complexes divided by the initial concentration of $Fe(CO)_5$. [c] Values in parentheses are calculated on the basis of eq A-4a and A-4b and A-3a and A-3b given in the Appendix. [d] (A) $c_{Fe(CO)_5}{}^0$ = 1.378 mM, 22-fold excess of olefin, λ = 302 nm; (B) $c_{Fe(CO)_5}{}^0$ = 1.214 mM, 38-fold excess of olefin, λ = 302 nm; (C) $c_{Fe(CO)_5}{}^0$ = 0.522 mM, 117-fold excess of olefin, λ = 254 nm. [e] Quantum yield for disappearance of $Fe(CO)_5$, evaluated with correction for internal light filtering (cf. text). [f] Not detected. [g] Least-squares procedure; standard deviation in parentheses.

cording to literature procedures: (*E*)-cyclooctene[20] (modified procedure on larger scale), $(\eta^2\text{-}(E)\text{-}C_8H_{14})Fe(CO)_4$,[17b] $(\eta^2\text{-}(E)\text{-}C_8H_{14})_2Fe(CO)_3$.[19] $Fe(CO)_5$ (BASF, Ludwigshafen) was distilled under vacuum prior to use. Analytical grade solvents (Merck) were used as received. Microanalysis was performed by Dornis and Kolbe, Mülheim a.d. Ruhr. Spectra were recorded using the following instruments: NMR, Bruker AM 400; IR, Perkin-Elmer 580 in combination with Data Station 3600; UV-vis, Perkin-Elmer 320.

Quantum Yield Determinations. Light absorption was measured by means of a modified version of an electronically integrating actinometer,[21] compensating for incomplete absorption of light in the sample cell, which was calibrated by ferrioxalate actinometry.[22] Irradiations of 3.0-mL aliquots of stock solutions of $Fe(CO)_5$ and complex **1**, respectively, in hexane containing excess (*E*)-cyclooctene were carried out at 25 ± 1 °C in quartz cuvettes (*d* = 1 cm), using a Hanovia 1000-W Hg-Xe lamp in connection with a Schoeffel Instruments GM 252 grating monochromator. Light intensities at 254 and 302 nm were on the order of 10^{-6}–10^{-7} einstein min^{-1} absorbed by the 3.0-mL sample.

Concentrations of the carbonyliron complexes were determined by means of quantitative IR spectroscopy (PE 580 spectrometer operating with 4A slit program; IR cell with CaF_2 windows, d = 495 μm), cf. Figure 2, using the following molar absorbance data. $Fe(CO)_5$: ε = 10 100 L mol^{-1} cm^{-1} at 2022 cm^{-1}. **1**: ε = 2745 L mol^{-1} cm^{-1} at 2079 cm^{-1}. **2** (C_s/C_2 isomers ca. 1:1): ε = 1420 L mol^{-1} cm^{-1} at 2046 cm^{-1}. The following UV-vis data were used for internal light filter corrections. $Fe(CO)_5$: ε = 9760 L mol^{-1} cm^{-1} at 254 nm and 1840 L mol^{-1} cm^{-1} at 302 nm. **1**: ε = 7370 L mol^{-1} cm^{-1} at 254 nm and 1880 L mol^{-1} cm^{-1} at 302 nm. **2**: ε = 11 060 L mol^{-1} cm^{-1} at 254 nm and 1890 L mol^{-1} cm^{-1} at 302 nm. The results of the individual runs are listed in Table I (Φ_1) and Table II (Φ_2).

Synthesis of $(\eta^2\text{-}(E)\text{-Cyclooctene})_3Fe(CO)_2$ (3). A solution of **2** (0.062 g, 0.17 mmol) and (*E*)-cyclooctene (1.0 g, 9 mmol) in *n*-hexane (100 mL) was irradiated at −60 °C using an immersion lamp vessel (solidex glass, λ > 280 nm) and a Philips HPK 125-W mercury lamp. During the irradiation a vigorous stream of argon was passed through the solution. After 20 min the concentration of **3** reached an optimum, as monitored by IR spectroscopy. The solution was combined with a second run and passed through a 20-cm silica column in order to remove decomposition products. Complex **3** and unreacted **2** were eluted from the column with *n*-hexane. After evaporation to dryness residual **2** was removed by repetitive washing with small portions of cold *n*-hexane to yield pure **3**, 0.035 g (23%), off-white crystals, ca. 130 °C dec without melting: IR ν(CO) 1930.5 cm^{-1} (ε = 11 100 L mol^{-1} cm^{-1}, in *n*-hexane): UV-vis λ_{max} 271 nm (in *n*-hexane); $^{13}C\{^1H\}$ NMR δ 69.2 (−CH=CH−), 40.7/37.9/30.0 ($-CH_2-$), 208.7 (CO), in methylcyclohexane-d_{14} at 273 K. Anal. Calcd for $C_{26}H_{42}FeO_2$: C, 70.58; H, 9.57; Fe, 12.62. Found: C, 70.48; H, 9.53; Fe, 12.68.

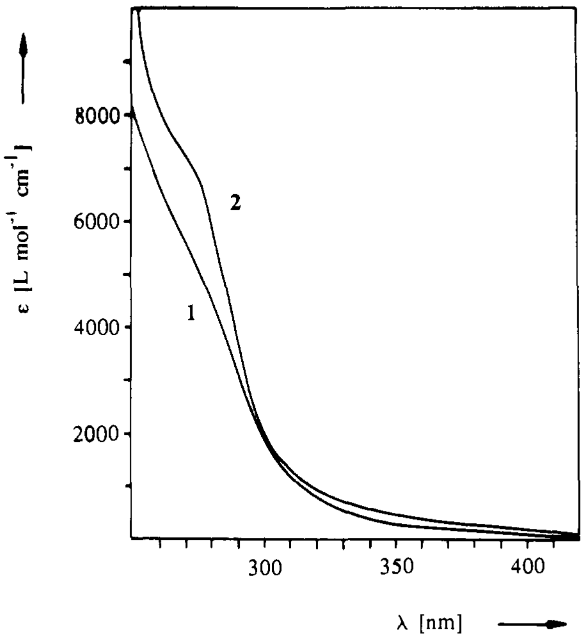

Figure 1. UV–vis absorption spectra of $(\eta^2\text{-}(E)\text{-}C_8H_{14})Fe(CO)_4$ (**1**) and $(\eta^2\text{-}(E)\text{-}C_8H_{14})_2Fe(CO)_3$ (**2**) in *n*-hexane.

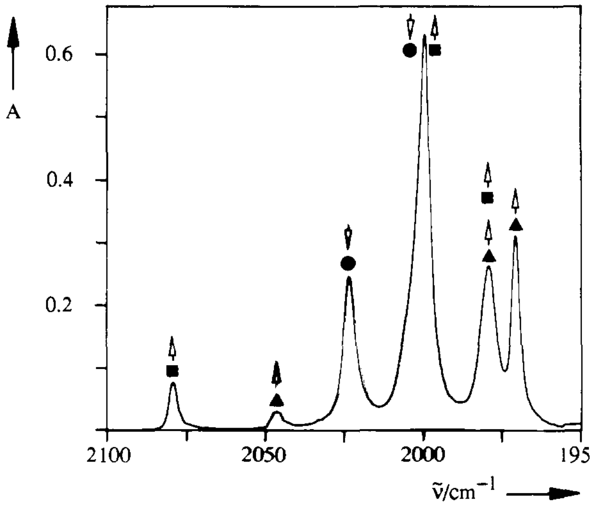

Figure 2. Infrared spectrum obtained after irradiation (λ = 302 nm) of $Fe(CO)_5$ (●) in the presence of excess (*E*)-cyclooctene in *n*-hexane yielding **1** (■) and **2** (▲). The spectrum represents the data in Table I, line 8 (τ = 1.342).

Results

Quantum Yields for Mono- and Disubstitution of $Fe(CO)_5$ by (*E*)-Cyclooctene. The photoreaction of pentacarbonyliron with (*E*)-cyclooctene involves initial formation of $(\eta^2\text{-}(E)\text{-}C_8H_{14})Fe(CO)_4$ (**1**), which upon further irradiation is converted into the disubstituted product $(\eta^2\text{-}(E)\text{-}C_8H_{14})_2Fe(CO)_3$ (**2**)[19] (eq 1). With racemic (*E*)-cyclooctene, complex **2** is obtained as a nearly equimolar mixture of two isomers, **2a** and **2b**, with C_2 and C_s symmetry, respectively, which can be separated by repetitive fractional crystallization.[19] The two isomers are clearly distinguishable by NMR spectroscopy but exhibit quite similar CO stretching vibrational patterns.[19] Nevertheless, for the sake of accuracy in quantitative infrared (and UV-vis) spectroscopic measurements, the original equimolar mixture (rather than one of the pure isomers) is used for calibration and determination of

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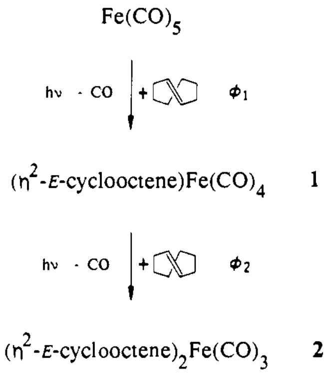

(1)

ε values. Due to substantial overlap of the UV–vis absorptions of $Fe(CO)_5$[23] and of complexes **1** and **2** (Figure 1), this spectral region is not suitable for monitoring the progress of the reaction (eq 1) with sufficient accuracy. Therefore, quantitative infrared spectroscopy in the CO stretching vibrational region is employed for this purpose (Figure 2).

The disappearance of $Fe(CO)_5$, with concomitant formation of **1** and **2**, upon extended irradiation in the presence of excess (*E*)-cyclooctene in *n*-hexane at ambient temperature is displayed in Figure 3. Under these experimental conditions and up to 65% conversion of $Fe(CO)_5$, there is no indication of further substitution yielding the $(olefin)_3Fe(CO)_2$ complex (vide infra). The evaluation of quantum yields indispensably requires corrections for internal light filter effects, because of the above-mentioned overlap of the electronic absorption spectra of the complexes involved. This is manifested in the deviation from linearity of the plot of $Fe(CO)_5$ concentration vs τ shown in Figure 3.

For a simple one-step photoreaction (eq 2), internal light filtering caused by the product is taken into account by using eq 3.[24] In case of two consecutive photoreactions (eq 4), the above

$$A \xrightarrow{\Phi} B \tag{2}$$

$$\Phi = \frac{[(\epsilon_A - \epsilon_B)(c_A{}^0 - c_A) + \epsilon_B c_A{}^0 \ln (c_A{}^0/c_A)]}{\epsilon_A Q_{abs} t} \tag{3}$$

$$A \xrightarrow{\Phi_1} B \xrightarrow{\Phi_2} C \tag{4}$$

formula may be used for the evaluation of Φ_1, provided that the molar absorbances of the two photoproducts B and C are equal. Fortuitously, this applies to complexes **1** and **2** in the 300-nm region of the UV–vis spectra (Figure 1). Therefore, the general treatment[25,26] appropriate for eq 4 (cf. Appendix, eq A-4a and A-4b; evaluation of Φ_1 from $\bar{c}_A = c_A/c_A{}^0$ at $\tau = Q_{abs}t/c_A{}^0$, ϵ_A, ϵ_B, ϵ_C, and Φ_2) is not necessary in the particular case of the stepwise conversion of $Fe(CO)_5$ into **1** and **2** upon irradiation at 302 nm.

The data for this reaction are compiled in Table I. Each line in this table refers to an individual run in which a fresh aliquot of a stock solution of $Fe(CO)_5$ and excess (*E*)-cyclooctene in *n*-hexane was irradiated for a certain period of time. Depending on the duration of irradiation, the extent of conversion of $Fe(CO)_5$ varies from one experiment to another, ranging up to 65%. The summation of the concentrations of complexes $(\eta^2\text{-}(E)\text{-}C_8H_{14})_nFe(CO)_{5-n}$ (n = 0–2) reveals a satisfactory material balance in each experiment, thus confirming the accuracy of the quantitative infrared spectroscopic analyses and indicating that any side reactions are negligible. The values for the quantum yield Φ_1, evaluated using eq 3, are scattering around the mean value ($\Phi_1 = 0.80$) and do not show any dependence on the extent of conversion. This reasonably justifies the simplified treatment of the system according to eq 3. From measurements with irradiation at 254 nm, the quantum yield $\Phi_1 = 0.77$ is obtained as the average result of four runs with ca. 50–75% conversion of $Fe(CO)_5$ (Table I). This data was evaluated by using the general treatment, eq A-4a and A-4b. At 254 nm the molar absorbance of **2** is somewhat larger than that of **1**. Therefore, the correction for internal light filter effects using eq 3 is not quite appropriate and yields Φ_1 values marginally smaller (av. 0.76) than those obtained from the full treatment (eq A-4a), which accounts for the individual light absorption properties of the two products **1** and **2**. However, it should be noted that this requires prior knowledge of Φ_2.

Table II. Determination of Φ_2 from Irradiation of $(\eta^2\text{-}(E)\text{-}C_8H_{14})Fe(CO)_4$ (**1**) and Excess (*E*)-Cyclooctene in *n*-Hexane Solution

$\tau \times 100$[a]	$\bar{c} \times 100$[b] **1**	$\bar{c} \times 100$[b] **2**	conditions[c]	Φ_2[d]
20.3	89.7	10.5	A	0.537
20.5	89.4	13.4	B	0.547
24.6	85.7	15.6	B	0.627
30.7	84.2	18.8	B	0.561
30.4	83.9	17.7	A	0.578
41.0	76.9	23.8	B	0.641
60.8	68.2	30.8	A	0.630
101.4	53.4	46.0	A	0.620
141.9	42.8	56.6	A	0.600
			Φ_2(mean) = 0.59 at 302 nm	
23.9	82.7	11.8	C	0.830
27.4	79.9	15.9	C	0.858
34.2	78.1	19.6	C	0.764
41.1	73.4	23.1	C	0.805
51.3	67.5	28.6	C	0.833
			Φ_2(mean) = 0.82 at 254 nm	

[a] $\tau = Q_{abs}t/c_1{}^0$, i.e., light absorbed (einstein L^{-1}) divided by the initial concentration of complex **1**. [b] $\bar{c} = c/c_1{}^0$, i.e., concentration of the particular complexes divided by the initial concentration of complex **1**. [c] (A) $c_1{}^0$ = 2.281 mM, 40-fold excess of olefin, λ = 302 nm; (B) $c_1{}^0$ = 2.256 mM, 27-fold excess of olefin, λ = 302 nm; (C) $c_1{}^0$ = 1.707 mM, 36-fold excess of olefin, λ = 254 nm. [d] Quantum yield for disappearance of **1**, evaluated with correction for internal light filtering (cf. text).

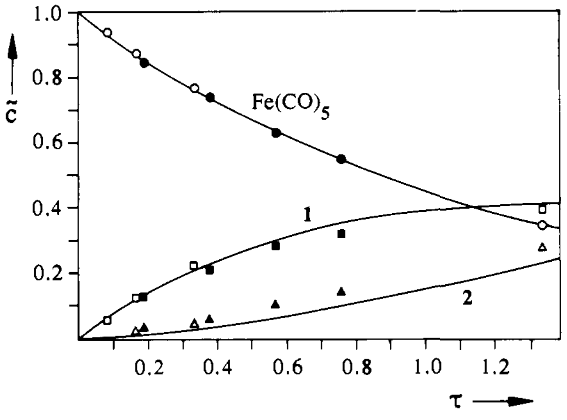

Figure 3. Photochemical formation of **1** and **2** upon irradiation of $Fe(CO)_5$ in the presence of excess (*E*)-cyclooctene in *n*-hexane at λ = 302 nm (note that the reduced quantities $\bar{c} = c/c_{Fe(CO)_5}{}^0$ and $\tau = Q_{abs}t/c_{Fe(CO)_5}{}^0$ are displayed). Open and filled symbols represent the experimental data (Table I; conditions A and B, respectively). The solid curves represent the course of the reaction computed on the basis of $\Phi_1 = 0.80$ and $\Phi_2 = 0.59$ by means of eq A-4a and A-3a (cf. Appendix).

The quantum yield Φ_2 for the second step in eq 1 is obtained from experiments starting directly with $(\eta^2\text{-}(E)\text{-}C_8H_{14})Fe(CO)_4$ (**1**), which is irradiated in the presence of excess (*E*)-cyclooctene at two different wavelengths, 302 and 254 nm. The data for the conversion of **1** into the disubstituted product **2** are compiled in Table II. Material balances prove to be satisfactory throughout. Quantum yields, evaluated using eq 3, are scattering around mean values $\Phi_2 = 0.59$ at 302 nm and $\Phi_2 = 0.82$ at 254 nm.

With the knowledge of Φ_1 and Φ_2 it is possible to precalculate the photochemical conversion of $Fe(CO)_5$ into **1** and **2** depicted

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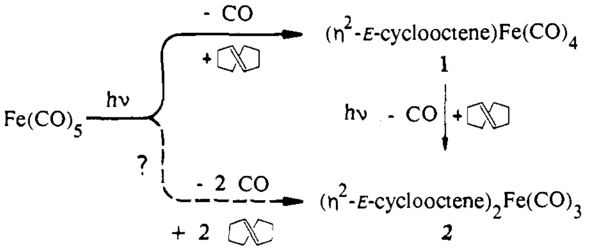
(26) Skibbe, V. Doctoral Dissertation, Universität Duisburg, 1985.

in eq 1 by means of eq A-4a and A-4b and A-3a and A-3b, which are developed for the general case of two consecutive photoreactions (eq 4; cf. Appendix). The computation starts with a given initial concentration of $Fe(CO)_5$ ($\bar{c}_A = 1$) and accounts for the amount of light absorbed by the system ($\tau = Q_{abs}t/c_A{}^0$), Φ_1, and Φ_2 and for the individual light absorption properties of $Fe(CO)_5$ (ϵ_A), **1** (ϵ_B), and **2** (ϵ_C). The results of this computation, presented in parentheses in Table I and in the form of the solid curves in Figure 3 (for λ = 302 nm), are in good agreement with the experimental data, particularly as far as $Fe(CO)_5$ is concerned. With respect to the products **1** and **2**, we note a systematic trend in the deviations such that the computed values for **2** invariably are somewhat smaller than the experimentally determined concentrations, whereas the results for complex **1** exhibit marginal deviations in the opposite direction. A plausible explanation for this could be that a minor fraction of the pentacarbonyliron is directly converted into the disubstituted product **2** (eq 5). Such



(5)

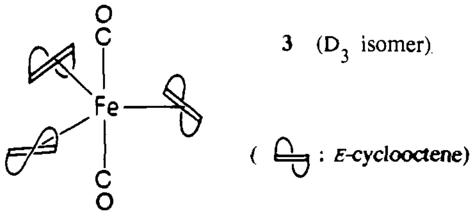
a process is well established for the substitution of $Fe(CO)_5$ with a phosphorus ligand[10] but appears not to have been observed so far with an olefinic substrate. Certainly, this aspect requires further investigation. However, as long as this parallel process remains of minor importance, it will not cause any significant changes in the evaluation of the quantum yield Φ_1.[27] Moreover, the quantum yield Φ_2 will not be subject to any changes, as it has been determined separately starting with complex **1**.

Synthesis of (η^2-(E)-C_8H_{14})$_3$Fe(CO)$_2$. Under the conditions of the quantum yield measurements (η^2-(E)-C_8H_{14})$_2$Fe(CO)$_3$ (**2**) appears to be the ultimate product. However, when irradiating complex **2** in the presence of excess (E)-cyclooctene with continuous bubbling of argon through the solution, we note the appearance of a CO stretching vibrational band at 1930.5 cm^{-1}. This single band is assignable to the trisubstituted complex, (η^2-(E)-C_8H_{14})$_3$Fe(CO)$_2$ (**3**), with a *trans*-Fe(CO)$_2$ subunit and the three olefinic ligands lying in the equatorial plane of the trigonal-bipyramidal geometry. The conversion of **2** into **3** (eq 6) seems

$$\begin{array}{cc} (\eta^2\text{-}E\text{-cyclooctene})_2\text{Fe(CO)}_3 & \mathbf{2} \\ + & \\ E\text{-cyclooctene} & \\ h\nu \Big\uparrow\Big\downarrow h\nu & \\ (\eta^2\text{-}E\text{-cyclooctene})_3\text{Fe(CO)}_2 & \mathbf{3} \\ + & \\ \text{CO} & \end{array} \qquad (6)$$

to be photoreversible, leading to a photostationary state strongly dependent on the concentrations of (E)-cyclooctene and carbon monoxide. At ambient temperature and under a slow stream of argon the IR band of **3** remains a less prominent feature, even after extended photolysis of **2** in the presence of a 20–40-fold excess of (E)-cyclooctene. Nearly complete conversion of **2** can be achieved by removing the liberated carbon monoxide with an extremely vigorous stream of inert gas. Addition of carbon monoxide to such a solution under continuous irradiation results in effective reconversion of **3** into **2**. The synthesis of **3** on preparative scale requires prolonged irradiation, which in turn is accompanied by substantial isomerization of (E)-cyclooctene into (Z)-cyclooctene and, consequently, decomposition of **3**. For this reason and in view of the limited availability of (E)-cylooctene, the preparation of **3** is restricted to small batches. Moreover, it proved favorable to lower the temperature to ca. −60 °C in order to improve the yield of **3**.

Because of the chiral nature of (E)-cyclooctene two isomers of **3** with D_3 and C_2 symmetry, respectively, can be expected. However, the $^{13}C\{^1H\}$ NMR spectrum of isolated **3** shows only one set of four signals attributable to the (E)-cyclooctene ligand in addition to one signal in the carbonyl region, which unambiguously identify this complex as the D_3 isomer. Nevertheless, we cannot exclude the possibility that the crude product is a mixture of both of the two isomers. In the case of the analogous ruthenium compounds,[18] it was observed that the D_3 isomer is predominant and more stable. Therefore, in view of the general decrease in stability of metal–olefin bonds in going from ruthenium to iron carbonyl complexes, it seems possible that the less stable C_2 isomer of **3** has been decomposed in the course of the workup procedure. This would also account for the relatively small isolated yield.



Comparing the ^{13}C NMR data of the olefinic carbon atoms, we note a significant decrease in the coordination shift $\Delta\delta = \delta(\text{olefin}) - \delta(\text{complex})$ in going from **2** ($\Delta\delta$ = 69.9/72.5 ppm, C_2/C_s isomers)[19] to **3** ($\Delta\delta$ = 64.4 ppm). This parallels the trend observed for the analogous ruthenium compounds[18] and may be interpreted in terms of limited capability of the metal to meet the demand for metal (d_π) $\rightarrow$ olefin (π^*) back-donation as the number of olefin ligands increases. In this context one has to bear in mind that metal (d_π) $\rightarrow$ olefin (π^*) back-donation, unlike metal (d_π) $\rightarrow$ CO (π^*) interaction, is restricted to metal (d_π) orbitals lying in the equatorial plane, because of the single-faced π-acceptor character of the olefin ligands.

Discussion

The high quantum yields (Φ_1 = 0.80 at 302 nm, 0.77 at 254 nm) for the conversion of $Fe(CO)_5$ into (η^2-(E)-C_8H_{14})Fe(CO)$_4$ (**1**) indicate that the primary photolytic dissociation of $Fe(CO)_5$ with generation of the $Fe(CO)_4$ fragment is indeed a very efficient process, in accord with the early reports on the photochemical formation of $Fe_2(CO)_9$ from $Fe(CO)_5$.[3] At first glance the 20% quantum yield deficiency may be attributed to the possible competition between liberated CO and the olefin for the coordination to the $Fe(CO)_4$ species, as illustrated in eq 7. However, taking

$$\begin{array}{c} \text{Fe(CO)}_5 \\ h\nu\ -\text{CO} \Big\downarrow\Big\uparrow +\text{CO} \\ \text{Fe(CO)}_4 \\ \Big\downarrow +\text{olefin} \\ (\eta^2\text{-olefin})\text{Fe(CO)}_4 \end{array} \qquad (7)$$

into account the large excess of olefin together with the respective rate constants ($k_{CO} < k_{olefin}$) obtained from preliminary flash

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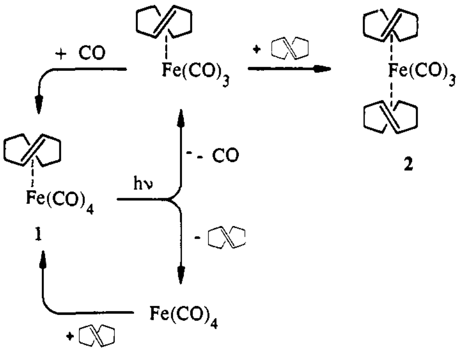
[27] Moderate variation of the ratio of products **1** and **2** will slightly affect the correction accounting for internal light filtering in the evaluation of Φ_1, depending on the difference of the ϵ values of **1** and **2**.

photolysis experiments with time-resolved infrared detection,[7,8,28] we presume that recapturing of $Fe(CO)_4$ by CO should be negligible in this respect. Consequently, the observed quantum yield Φ_1 should reflect the efficiency of the photodetachment of CO from $Fe(CO)_5$. This process has been suggested[29] to occur through an excited triplet state ($^3E'$) of $Fe(CO)_5$, which may be populated by intersystem crossing from its singlet counterpart or from various higher excited states in the singlet manifold. Relaxation to the $^1A_1$ ground state, in competition with intersystem crossing, would reduce the quantum yield of the photolytic process and thus may account for the observed deviation of Φ_1 from unity. Population of the dissociative excited state by intersystem crossing appears to be equally efficient at different wavelengths of excitation, as indicated by the nearly equal quantum yields at 254 and 302 nm.

By contrast, the quantum yield Φ_2 for the conversion of **1** into **2**, involving substitution of a second CO ligand by an olefin, exhibits a marked wavelength dependence, as it amounts to 0.82 at 254 nm and 0.59 at 302 nm. It is evident from these remarkably high values that of the two possible photolytic reactions of **1**, viz., detachment of either the olefin or one of the CO groups, the latter distinctly predominates. The resulting (η^2-olefin)$Fe(CO)_3$ species reacts with excess olefin to form the bis(olefin) complex **2**, whereas olefin dissociation from **1** and subsequent recapturing of $Fe(CO)_4$ would bring about no net reaction, as outlined in eq 8. This is in accord with the photolytic behavior of (η^2-olefin)$Fe(CO)_4$ complexes in low-temperature matrices,[9,30] which shows that olefin loss is a process of minor importance. Concerning the deviation of Φ_2 from unity, one could be tempted to attribute this, at least in part, to recombination of the (η^2-olefin)$Fe(CO)_3$ species with liberated CO, since recent kinetic studies in the gas phase revealed a preference of (η^2-C_2H_4)$Fe(CO)_3$ for reaction with CO over ethene by a factor of 35.[15] However, if so, the continuously increasing concentration of liberated CO with the progress of the reaction should cause a systematic decline of Φ_2, which is not observed (cf. Table II). The observed wavelength dependence of Φ_2 points toward the involvement of two different excited states with differing efficiencies for relaxation to the ground state and/or differing probabilities for CO vs olefin dissociation. Unfortunately, the electronic absorption spectrum of **1** (Figure 1) is rather featureless, apart from a weak shoulder at ca. 280 nm, and does not give any hints in this respect. Pentacarbonyliron exhibits a similar feature in this region, which has been assigned[23] to the ligand field e′ → a₁′ transition, leading to CO detachment (vide supra). Going from $Fe(CO)_5$ to (η^2-olefin)$Fe(CO)_4$, the degeneracy of the ligand field E′ state should be lifted. Two ligand field transitions centered at slightly different energies can be expected, which should affect the metal-olefin and metal-CO bonds to a different extent. The observation of the smaller quantum yield for CO photosubstitution at the longer wavelength seems to indicate that the probability for metal-olefin bond photodissociation is increasing in going to longer wavelength of excitation.



(8)

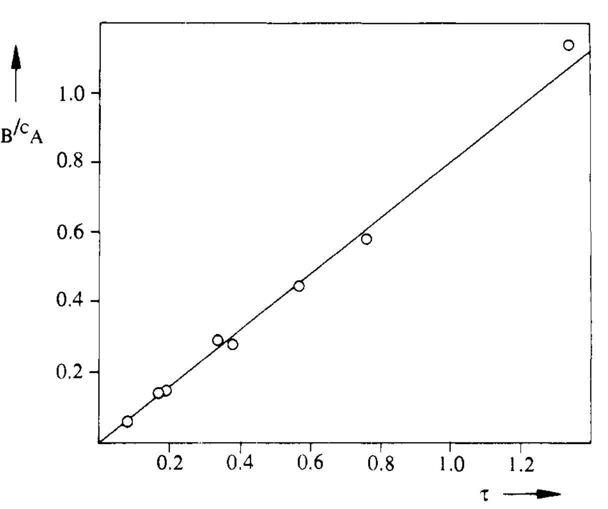


Figure 4. Plot of c_B/c_A vs τ [c_B = concentration of complex **1**; c_A = concentration of $Fe(CO)_5$; $\tau = Q_{abs}t/c_A{}^0$] based on the data in Table I (λ = 302 nm). The slope of the plot yields Φ_1 = 0.80; cf. eq A-6.

As a concluding point it is of interest to discuss the overall quantum efficiency of (η^2-(*E*)-C_8H_{14})$_2Fe(CO)_3$ (**2**) formation with respect to the carbonyliron photocatalyzed isomerization of olefins such as 1-pentene.[9,10,11,13] Mechanistic studies have shown that the catalytic cycle in this process is carried by the $Fe(CO)_3$ unit, which, in those investigations,[9,13] was introduced in the form of the substitutionally labile (η^2-olefin)$_2Fe(CO)_3$ complexes of (*Z*)-cyclooctene and ethene, respectively. Alternatively, photochemical preformation of the active catalyst, (η^2-1-C_5H_{10})$_2Fe(CO)_3$, was achieved by low-temperature photolysis of $Fe(CO)_5$ in the presence of 1-pentene, either in hydrocarbon solution[31] or in a solid matrix,[32] which subsequently was warmed up. Thus, it seems justified to consider the photochemical synthesis of the (η^2-olefin)$_2Fe(CO)_3$ complex **2** (eq 1) as a model reaction for the induction period of the photocatalytic olefin isomerization with $Fe(CO)_5$. An effective overall quantum yield Φ_{eff} for the formation of **2** from $Fe(CO)_5$ can be taken from Figure 3 by dividing the reduced concentration $\bar{c}$ of **2** by the corresponding value of τ. Naturally, Φ_{eff} increases as the conversion of $Fe(CO)_5$ proceeds, but, of course, it remains below 0.5 since the formation of **2** is the result of two photochemical steps. At 60% conversion of $Fe(CO)_5$ the value of Φ_{eff} amounts to ca. 0.20. Assuming that the photochemical formation of the labile, catalytically active (η^2-1-C_5H_{10})$_2Fe(CO)_3$ occurs with the same quantum yield (i.e., $\Phi_{eff} \simeq \Phi_{cat}$), one can estimate the quantum yield for the photocatalytic 1-pentene isomerization: $\Phi_{isom} = \Phi_{cat} \times$ turnover number. The active catalyst was reported[13] to bring about up to 2000 turnovers. Taking this value and $\Phi_{cat} = 0.2$, one obtains $\Phi_{isom} = 400$, which is in excellent agreement with the quantum yield determined under continuous irradiation of $Fe(CO)_5$ in the presence of 1-pentene (in neat 1-pentene: $\Phi_{isom} \simeq 400$;[10,11] with pulsed-laser irradiation[11] Φ_{isom} approaches 1000, depending on the repetition rate).

Appendix

Kinetics and Quantum Yields of Two Consecutive Photoreactions. In the following, two procedures will be developed for the evaluation of the quantum yields Φ_1 and Φ_2 of the two photochemical steps involved in the reaction sequence displayed in eq 4. Both procedures, a numerical and a graphical one, take into account the internal light filter effects caused by all three compounds A–C (with extinction coefficients ϵ_A, ϵ_B, and ϵ_C) being present in such a system. For the sake of simplicity, the derivations will be restricted to the case of the initial concentrations of B and C being zero, $c_B{}^0 = c_C{}^0 = 0$.

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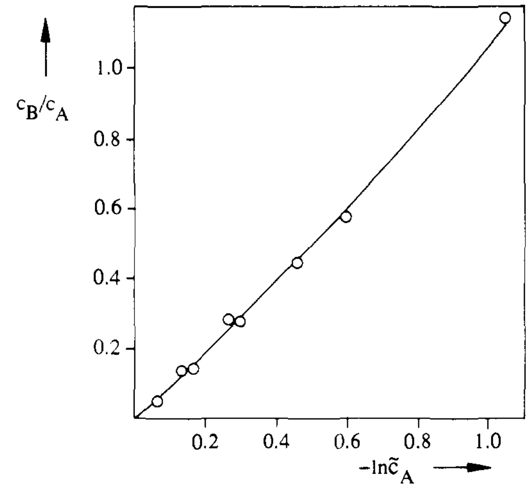

Figure 5. Plot of c_B/c_A vs $-\ln \tilde{c}_A$ [c_B = concentration of complex **1**; c_A = concentration of $Fe(CO)_5$; $\tilde{c}_A = c_A/c_A{}^0$] based on the data in Table I (λ = 302 nm); cf. eq A-7.

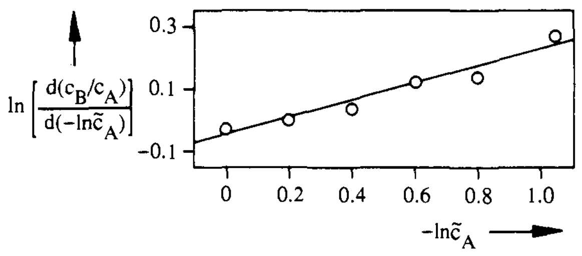

Figure 6. Plot of ln [d(c_B/c_A)/d($-\ln \tilde{c}_A$)] (logarithm of the slope of the curve in Figure 5) vs $-\ln \tilde{c}_A$. The slope of the plot is $1 - \gamma = 0.27$, which yields $\Phi_2 = 0.57$ [cf. text and eq A-7], a result close to the value obtained from the irradiation of complex **1** and excess (*E*)-cyclooctene (Table II).

The rate expressions for A–C, with consideration of the internal light filter effect, are given by eq A-1a–c. Q_i represents the rate

$$-dc_A/dt = \Phi_1 Q_A \qquad \text{(A-1a)}$$

$$-dc_B/dt = \Phi_2 Q_B - \Phi_1 Q_A \qquad \text{(A-1b)}$$

$$-dc_C/dt = -\Phi_2 Q_B = dc_A/dt + dc_B/dt \qquad \text{(A-1c)}$$

of light absorption (einstein L^{-1} s^{-1}) by a particular compound *i*, as defined in eq A-2a, where x_i is the so-called "photochemical mole fraction" (eq A-2b)[25] and Q_{abs} is the rate of total light

$$Q_i = x_i Q_{abs} \qquad \text{(A-2a)}$$

$$x_i = \epsilon_i c_i / \sum(\epsilon_j c_j) \qquad \text{(A-2b)}$$

$$Q_{abs} = Q_{inct} - Q_{transd} \qquad \text{(A-2c)}$$

absorption (eq A-2c). Equations A-1a and A-1b can be integrated to give c_B as a function of c_A.[25] Depending on the value of the quantity $\gamma = \epsilon_B\Phi_2/(\epsilon_A\Phi_1)$, the function c_B takes different analytical forms, namely eq A-3a in the case $\gamma \neq 1$ and eq A-3b in the case

$$c_B = [c_A/(1-\gamma)][(c_A/c_A{}^0)^{\gamma-1} - 1] \qquad \text{(A-3a)}$$

$$c_B = -c_A \ln(c_A/c_A{}^0) \qquad \text{(A-3b)}$$

$\gamma = 1$. When eq A-3a and A-3b, respectively, are introduced into eq A-1a and the stoichiometric condition $c_A + c_B + c_C = c_A{}^0$ is used, integration gives eq A-4a and A-4b, which describe the time dependence of c_A (note that reduced quantities $\tilde{c}_A = c_A/c_A{}^0$ and $\tau = Q_{abs}t/c_A{}^0$ have been introduced).

$$\rho_1(\tilde{c}_A - 1) + \rho_2(\tilde{c}_A{}^\gamma - 1) + \epsilon_C \ln \tilde{c}_A = -\Phi_1\epsilon_A\tau \qquad \text{(A-4a)}$$

$$\rho_1 = (\epsilon_A - \epsilon_C) - (\epsilon_B - \epsilon_C)/(1-\gamma)$$

$$\rho_2 = (\epsilon_B - \epsilon_C)/[(1-\gamma)\gamma]$$

$$(\epsilon_A + \epsilon_B - 2\epsilon_C)(\tilde{c}_A - 1) + (\epsilon_C - \epsilon_B)\tilde{c}_A \ln \tilde{c}_A + \epsilon_C \ln \tilde{c}_A = -\Phi_1\epsilon_A\tau \qquad \text{(A-4b)}$$

Unfortunately, these equations give c_A only as an implicite, not as an explicite, function of time, and, therefore, they have to be solved numerically by means of a standard root-solving method.

Thus, with the knowledge of Φ_1 and Φ_2, the concentration of A at time *t* can be evaluated. Therefrom, c_B can be obtained by means of eq A-3a and A-3b, respectively, and c_C is fixed by the above stoichiometric condition.

Likewise, Φ_1 and Φ_2 can be evaluated from a set of measured $Q_{abs}t$ values and corresponding concentrations c_A, c_B, and c_C by, e.g., a least-squares procedure. In the case that Φ_2 is available from separate experiments starting with B, eq A-4a and A-4b can be used to determine Φ_1 from a single measurement of c_A and $Q_{abs}t$. For this purpose eq A-4a has been cast in a form convenient for the evaluation of $1 - \gamma$.[26]

As an alternative to the numerical procedure, Φ_1 and Φ_2 can be obtained from a graphical one as follows. Since Φ_1 is the coefficient of the linear term in the power series expansion of $\tilde{c}_A$ for small values of τ (eq A-5), it can be determined from the initial

$$\tilde{c}_A = 1 - \Phi_1\tau + k\tau^2 \qquad k = \Phi_1{}^2\epsilon_B/(2\epsilon_A) \qquad \text{(A-5)}$$

$$c_B/c_A = \Phi_1\tau + \{[(2-\gamma)/2]\Phi_1{}^2 - k\}\tau^2 \qquad \text{(A-6)}$$

slope of a plot of $\tilde{c}_A$ vs τ. Alternatively, Φ_1 is accessible from the initial slope of a plot of c_B/c_A vs τ on the basis of eq A-6, which is obtained by inserting eq A-5 into eq A-3a, followed by a binomial expansion. As long as $\gamma < 2$ and $\epsilon_A/\epsilon_B < [1 + \Phi_2/(2\Phi_1)]$, the quadratic term in eq A-6 is numerically smaller than that in eq A-5; i.e., the function c_B/c_A remains linear over a larger range of τ than does the function $\tilde{c}_A$. Therefore, with the above presumption, it is more advantageous to determine Φ_1 from a plot of c_B/c_A vs τ (Figure 4). In order to evaluate Φ_2, eq A-3a is rewritten to give eq A-7, whereby the identity $a^x = e^{x \ln a}$ is used.

$$c_B/c_A = \{\exp[-(1-\gamma)\ln \tilde{c}_A] - 1\}/(1-\gamma) \qquad \text{(A-7)}$$

The graphical procedure yielding Φ_2 involves two steps. At first, the values of c_B/c_A are plotted vs $-\ln \tilde{c}_A$ and a smooth curve is drawn, approximating the experimental points (Figure 5). Then the slope of this curve is determined at various values of $-\ln \tilde{c}_A$, and the logarithm of the slopes is plotted, again, vs $-\ln \tilde{c}_A$. The resulting graph (Figure 6) is a straight line, the slope of which is $1 - \gamma$; recalling the definition of γ, Φ_2 can now be calculated. It should be noted that eq A-3a, A-3b, and A-7 are valid regardless of the amount of light absorbed by the system. Therefore, the determination of γ does not require corrections for incomplete absorption; not even any actinometry is necessary.