Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

CARBON MONOXIDE EXCHANGE IN PENTACARBONYLIRON AND TETRACARBONYL(TRIPHENYLPHOSPHINE)IRON

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(Received February 2nd, 1969)

SUMMARY

The exchange of pentacarbonyliron and tetracarbonyl(triphenylphosphine)-iron with labelled carbon monxide (either ^{13}CO or $C^{18}O$) is initiated by ultraviolet light. Statistical exchange of all the carbonyl groups is revealed by the infrared spectra of the ^{13}CO and $C^{18}O$ enriched compounds. For $Fe(CO)_5$, the reaction is catalysed with palladium supported on alumina or charcoal. The decomposition of $Fe_2(CO)_9$ to $Fe(CO)_5$ in the presence of $C^{18}O$ leads to $C^{18}O$ incorporation in the $Fe(CO)_5$. In a mixture of $Fe(C^{16}O)_5$ and $Fe(C^{18}O)_5$ scrambling is observed in the presence of ultraviolet light or palladium.

The $C^{18}O$ exchange in $Fe(CO)_5$ and $Fe(CO)_4P(C_6H_5)_3$ can also be catalysed by trifluoroacetic acid. A non-statistical mixture of labelled species is obtained in this case. With both compounds the monosubstituted product is disfavored with respect to higher substituted products. This can be explained by a mechanism in which two carbonyls exchange at once.

INTRODUCTION

In 1959, Keeley and Johnson[1] reported that $Fe(CO)_5$ is inert towards exchange with radioactive ^{14}CO under uncatalysed conditions. Later, Basolo and coworkers[2] found that an exchange of ^{14}CO with $Fe(CO)_5$ or $Fe(CO)_4P(C_6H_5)_3$ is catalysed by trifluoroacetic acid in 1,2-dichloroethane as solvent. In the triphenylphosphine complex only three of the four carbonyl groups could be exchanged. From the rate data for $Fe(CO)_5$, it was concluded that two carbonyl groups exchange more readily than the other three. This would imply that the axial and the radial CO groups retained their identity for a rather long period (at least 30 minutes at $-20°$) without intramolecular exchange. This seemed rather surprising in view of the ^{13}C NMR measurements on $Fe(CO)_5$, which showed only one single resonance for the different CO groups[3,4]. While this is in itself not conclusive proof for a rapid intramolecular exchange[4], such an exchange is nevertheless very likely, since it would involve only a bending of the C–Fe–C angles[5]. Similar exchange was shown to take place in several other trigonal-bipyramidal molecules.

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In addition to the reported exchange in solution the exchange of CO with $Fe(CO)_5$ in the gas phase was reported[6]. It was found that the reaction is in this case catalysed by nickel or platinum metals. Composite rates were interpreted as due to different active sites on the catalyst surface rather than to different lability of the different CO groups.

We thought that following the exchange of the two molecules with ^{13}CO and $C^{18}O$ by infrared spectroscopy could result in more direct information concerning the exchange. This method has recently been employed to distinguish between axially and radially substituted species in pentacarbonyl methylmanganese and related compounds[7].

In order to apply the infrared method to the present problem the frequencies of all the different labelled species must be known. They can be calculated by using the method of Bor[8] and the comparison with the experimental values yields a check on the method of calculation.

EXPERIMENTAL

Enriched ^{13}CO (56%) was prepared from enriched barium carbonate[9]. Enriched $C^{18}O$ (92%) was purchased from Miles Laboratories, Inc. $Fe(CO)_5$ was distilled prior to use.

Labelled $Fe(CO)_5$ was synthesized from iron powder and labelled CO at atmospheric pressure[10]. Active iron powder was prepared, following the method of Reppe, by reduction of $Fe_2(CO)_9$ with hydrogen[11]. Iron powder (5 g) was suspended in 30 ml heptane and activated by shaking for 15 min in an atmosphere of H_2S. A slight gas evolution on the surface of the iron particles was observed. The suspension was then stored under nitrogen. A small part of it was used for each synthesis. After introduction of the suitably labelled ^{13}CO or $C^{18}O$ at atmospheric pressure, the mixture was magnetically stirred at room temperature. The stirring must be very vigorous in order to have reasonably fast reaction of the iron particles. The solution turned slowly red, because of $Fe_3(CO)_9S_2$ formed as a by-product[12]. After about 20 h, the solution was evaporated *in vacuo* and condensed at about −80°. The $Fe_3(CO)_9S_2$ is not volatile and stays in the residue from which it can be recovered by extraction. The heptane solution of the labelled $Fe(CO)_5$ was directly used as such (see Fig. 1).

Tetracarbonyl(triphenylphosphine)iron was prepared[13] by the reaction of pentacarbonyliron and triphenylphosphine. 1,2-Dichloroethane, trifluoroacetic acid and UV-grade heptane were commercial products. The palladium metal supported or not was from Fluka, Switzerland. The infrared spectra were taken on a Perkin–Elmer mod. 521 grating spectrophotometer in the range from 2200 to 1500 cm^{-1} with a 5 times expanded wavenumber scale ($10\ cm^{-1} = 1\ cm$).

The exchange reactions were performed under many different conditions: most room temperature runs were made in very small (2 ml) glass tubes with a three-way stopcock for evacuation and as gas inlet. $Fe(CO)_5$ or $Fe(CO)_4P(C_6H_5)_3$ solutions (1 ml) of appropriate concentration plus catalyst and 1 ml of enriched carbon monoxide were normally used in each run.

Low temperature and also some room temperature runs were done in the recently described infrared high pressure equipment[14]. The autoclave was filled with 8 ml of the appropriate solution and evacuated, 8 ml of enriched carbon monoxide were admitted under atmospheric pressure and the solution mixed and pumped through the attached infrared cell. The autoclave and the infrared cell were cooled to −20° with cold methanol from a circulating low temperature thermostat. To avoid condensation of water vapor on the cell windows the whole apparatus was put in a plexiglass box mounted over the sample compartment of the spectrophotometer and flushed with dry air. The reference cell was also held at the same temperature. Path lengths of 0.25 and 1 mm were generally employed.

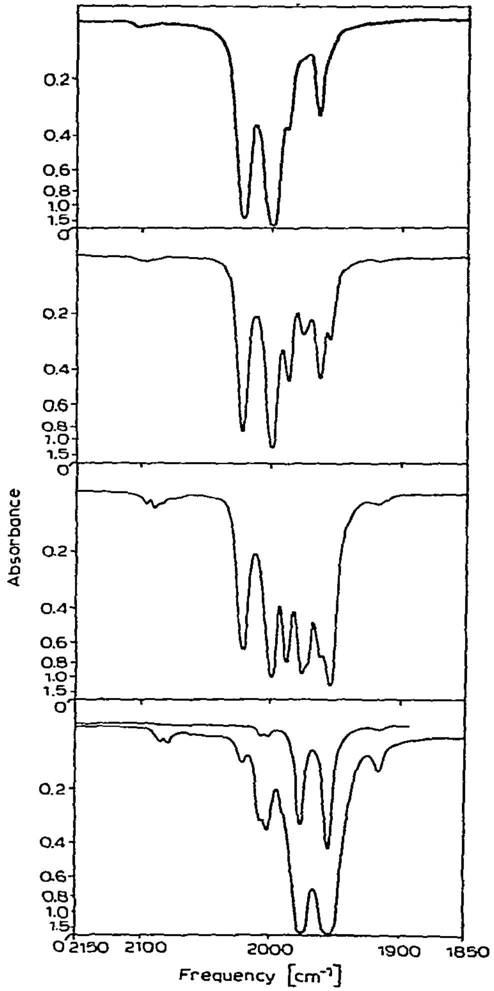


Fig. 1. Spectra of enriched $Fe(CO)_5$, from Fe+enriched CO. Upper spectrum: 6.5%, second: 25%, third: 56% ^{13}CO; lower: 92% $C^{18}O$.

The 1,2-dichloroethane solutions from the exchange reactions catalysed with trifluoroacetic acid were in most cases diluted 5 or 10 times with heptane before measuring the spectra. This sharpens the carbonyl stretching bands which are very broad in pure dichloroethane.

TABLE I

CALCULATED INFRARED ACTIVE CO-STRETCHING FREQUENCIES OF THE $Fe(CO)_{5-n}(C^{18}O)_n$ MOLECULES[a]

1[b]	2	3	4	5	6	7	8	9	10	11	12
$n=0$	$n=1$	$n=1$	$n=2$	$n=2$	$n=2$	$n=3$	$n=3$	$n=3$	$n=4$	$n=4$	$n=5$
											
D_{3h}	C_{3v}	C_{2v}	D_{3h}	C_{2v}	C_s	D_{3h}	C_{2v}	C_s	C_{3v}	C_{2v}	D_{3h}
a'_1	a_1	a_1		a_1	a'		a_1	a'	a_1	a_1	
2114	2105.4	2108.0		2101.8	2097.5		2086.8	2090.1	2082.6	2075.0	
	(2105.8)	(2108.3)		(2102.8)	(2098.3)		(2088.3)	(2091.4)	(2084.7)	(2078.6)	
2031	2029.6	2028.3		2021.9	2028.8		2000.6	2022.5	2008.1	2001.6	a''_2
	(2029.3)	(2028.4)		(2021.7)	(2029.1)		(2002.9)	(2022.4)	(2008.6)	(2002.4)	
a''_2	1985.5	1962.2		1974.1	1985.5		1961.2	1991.0	1980.0	1971.6	1975.0
2023.6	(1988.6)	(1965.2)		(1976.7)	(1988.3)		(1964.4)	(1994.3)	(1984.5)	(1974.0)	(1978.5)
					1961.0			1968.6			
					(1964.2)			(1971.2)			
e'	e	b_1	e'	b_1	a''	e'	b_1	a''	e	b_1	e'
2000.9	2000.9	2000.9	2000.9	1952.8	2000.9	1952.8	2000.9	1952.8	1952.8	1952.8	1952.8
	(2000.9)	(2000.9)	(2000.9)	(1956.3)	(2000.9)	(1956.3)	(2000.9)	(1956.3)	(1956.3)	(1956.3)	(1956.3)
		b_2	a''_2	b_2		a''_2	b_2				
		2023.6	1975.0	2023.6		2023.6	1975.0			1975.0	
		(2023.6)	(1978.4)	(2023.6)		(2023.6)	(1978.5)			(1978.5)	

[a] Values for ^{13}CO substituted species in brackets. [b] Observed values; a'_1 infrared inactive but Raman active, taken from ref. 20.

CALCULATION OF THE FREQUENCIES

The carbonyl stretching frequencies of the ^{13}CO- and $C^{18}O$-substituted species of $Fe(CO)_5$ and $Fe(CO)_4P(C_6H_5)_3$ were calculated using Cotton–Kraihanzel's force field[15] and the force constants reported by Bor[16]. No attempts were made to optimise these force constants by using the rather large number of experimentally available frequencies, since our work was mainly concerned with the mechanistic aspects of the carbon monoxide exchange. The frequencies calculated from Bor's force constants fit satisfactorily the observed frequencies. The greatest deviations are about 4 wave-

TABLE 2

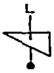
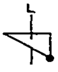
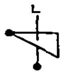
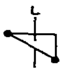
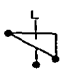
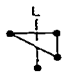
OBSERVED CO-STRETCHING FREQUENCIES OF THE ISOTOPICALLY ENRICHED $Fe(CO)_5$ MOLECULES[a]

$C^{18}O$	^{13}CO
2106^b (2, 3)	2105^b (2, 3)
2100^b (5, 6)	2097^b (5, 6)
2092^b (8, 9)	2090^b (8, 9)
2085^b (10)	2084^b (10)
2078^b (11)	2076^b (11)
2023 (1, 3, 5, 7)	2023 (1, 3, 5, 7)
2008 (10)	
2001 (1, 2, 3, 4, 6, 8, 11)	2001 (1, 2, 3, 4, 6, 8, 11)
1988 (2, 6, 9)	1988 (2, 6, 9)
1976 (4, 5, 11, 12)	1976 (4, 5, 11, 12)
	1972 (9, 11)
1964 (3, 6, 8)	1964 (3, 4, 8)
1955 (5, 7, 9, 10, 11, 12)	1955 (5, 7, 9, 10, 11, 12)

[a] In brackets: species from Table 1. [b] Weak, ±1 cm^{-1}, all others ±0.5 cm^{-1}.

TABLE 3

CALCULATED CO-STRETCHING FREQUENCIES OF THE $Fe(CO)_{4-n}(C^{18}O)_nP(C_6H_5)_3$ MOLECULES[a]

1	2	3	4	5	6	7	8
$n=0$	$n=1$	$n=1$	$n=2$	$n=2$	$n=3$	$n=3$	$n=4$
							
C_{3v}	C_{3v}	C_s	C_s	C_s	C_{3v}	C_s	C_{3v}
a_1	a_1	a'	a'	a'	a_1	a'	a_1
2051.7	2040.5	2042.2	2030.1	2033.6	2024.5	2017.8	2002.4
	(2040.9)	(2042.6)	(2031.3)	(2034.4)	(2025.8)	(2019.7)	(2005.9)
1979.1	1940.6	1976.5	1941.3	1971.6	1956.0	1942.1	1931.6
	(1943.6)	(1976.3)	(1943.9)	(1971.9)	(1958.2)	(1944.7)	(1935.0)
		1909.8	1908.9	1922.5		1919.7	
		(1912.7)	(1912.0)	(1924.7)		(1921.7)	
e	e	a''	a''	a''	e	a''	e
1946.4	1946.4	1946.4	1946.4	1899.6	1899.6	1899.6	1899.6
	(1946.4)	(1946.4)	(1946.4)	(1903.0)	(1903.0)	(1903.0)	(1903.0)

[a] ^{13}CO-substituted species in brackets.

numbers, all the observed wavenumbers being rather higher than those calculated. The rather good fit is a test for these force constants, which were obtained from the all-$^{12}C^{16}O$ molecules alone. The calculated frequencies are given in Table 1 for $Fe(CO)_5$, in Table 3 for $Fe(CO)_4P(C_6H_5)_3$ and the observed values are shown in table 2 and 4 respectively. From Table 1 it can be seen that in $Fe(CO)_5$ many of the theoretically expected frequencies lie rather close together, especially between 1990 and 1970 cm^{-1}. Many species have also some identical frequencies. Thus one cannot expect to observe all the calculated bands. Table 2 gives the probable assignments for each of the different species, taking the statistical distribution qualitatively into account.

TABLE 4

OBSERVED CO-STRETCHING FREQUENCIES OF THE ISOTOPICALLY ENRICHED $Fe(CO)_4P(C_6H_5)_3$ MOLECULES[a]

$C^{18}O$	^{13}CO
2052 (1)	2052 (1)
2045 (2, 3)	2045 (2, 3)
2038 (5)	2038 (5)
2031 (4, 6?)	2028 (4, 6?)
2019 (7)	2015[b] (7)
2006 (8)	Not observed
1979 (1)	1979 (1)
1975 (3)	1975 (3)
1970 sh (5)	1969 sh (5)
1946 (1, 2, 3, 4, 7)	1946 (1, 2, 3, 4, 7)
1934 (8)	Not observed
1921.5 (5)	1922 (5)
1920.5 (7)	Not observed
1910 (3, 4)	1910 (3, 4)
1901 (5, 6, 7, 8)	1901 (5, 6, 7)

[a] In brackets: species from Table 3. [b] Weak, ±1 cm^{-1}, all others ±0.5 cm^{-1}.

In $Fe(CO)_4P(C_6H_5)_3$ overlapping of bands was also observed, but to a lower extent than in $Fe(CO)_5$. Unfortunately, the characteristic bands of the radially and axially monosubstituted species No. 2 and 3 are so close together that they cannot be resolved and the second band of the species No. 2 is shifted to 1941 cm^{-1} and concealed under the strong band of the unsubstituted compound at 1946 cm^{-1}. There is therefore little hope of detecting axially substituted molecules in a mixture of the unsubstituted and weakly enriched species. Fortunately, the highly enriched compounds can be easily distinguished by their regularly shifted bands between 2050 and 2000 cm^{-1}.

Since the reduced masses of $^{13}C^{16}O$ and $^{12}C^{18}O$ are very similar, the spectra of the corresponding $C^{18}O$ and the ^{13}CO-substituted species are almost identical, the shifts due to $C^{18}O$ being very slightly higher.

In the spectra of the highly $C^{18}O$ enriched compounds additional weak bands appear at frequencies lower than those of the fully substituted products. These bands come from $^{13}C^{18}O$-substituted species formed from the natural amount of $^{13}C^{18}O$ in $^{12}C^{18}O$.

RESULTS

CO exchange in $Fe(CO)_5$, catalysed by Pd

We observed that a heptane solution of a 1/1 mixture of natural $Fe(CO)_5$ and $Fe(C^{18}O)_5$ in the absence of a catalyst did not show any scrambling of the $C^{16}O$ and the $C^{18}O$ between the $Fe(CO)_5$ molecules during several hours at room temperature. Irradiation by the Nernst glower of the infrared spectrophotometer did not induce an exchange. Rapid exchange and complete scrambling occurred, however, upon addition of a small amount of supported palladium. With Pd on Al_2O_3 (10% Pd) the statistical distribution was reached in about 15 minutes. With Pd on charcoal (10% Pd) the reaction was even faster and equilibrium was reached in less than two minutes.

This observation suggested that palladium metal might also catalyse the exchange with dissolved carbon monoxide at room or even lower temperature, and this was found to be the case. A statistical distribution was reached rapidly by shaking a heptane solution of natural $Fe(CO)_5$ with suspended Pd on alumina or charcoal in an atmosphere of ^{13}CO or $C^{18}O$ at room temperature. The spectra obtained from such a solution were identical with those of $Fe(CO)_5$ prepared from enriched carbon monoxide of the same concentration (see Fig. 1).

Pentacarbonyliron was also treated with $C^{18}O$ in the presence of supported palladium at −20° as the solution was circulated through the infrared cell at that temperature. In this way one could ascertain whether some CO groups exchanged preferentially at low temperature.

The characteristic band of the axially substituted $Fe(CO)_4C^{18}O$ at 1989 cm^{-1} appears as a shoulder on the side of the 2001 cm^{-1} band of the natural and both monosubstituted products. In order to eliminate the sloping background from this band, the rather concentrated solution of the natural $Fe(CO)_5$ in the reaction cell was carefully balanced by use of the same solution in the reference cell. In this way, even a small concentration of axially substituted $Fe(CO)_4C^{18}O$ could be detected. The band of the radially substituted species at 1964 cm^{-1} is much less overlapped. The experiment showed that no preferential increase of one of the two bands took place; they both increased at the same rate from the beginning of the exchange. This shows that in the palladium-catalysed exchange the equilibrium distribution is obtained immediately, and that either radial and axial CO groups exchange at the same rate, or the rate of the intramolecular conversion is faster than the exchange of any one CO group with $C^{18}O$.

No exchange with CO nor scrambling in the $Fe(CO)_5 + Fe(C^{18}O)_5$ mixture was observed with Al_2O_3 or charcoal alone.

Light-induced CO exchange in $Fe(CO)_5$

As stated above, the visible part of the infrared source did not induce the CO exchange in $Fe(CO)_5$. If however, the infrared cell containing an isooctane solution of the 1/1 ($Fe(CO)_5 + Fe(C^{18}O)_5$) mixture was exposed for only two to five minutes to the light from a high pressure mercury lamp complete scrambling of the CO groups was observed (see Fig. 2).

When an isooctane solution of natural $Fe(CO)_5$ in a Pyrex vessel was shaken with $C^{18}O$ under simultaneous illumination from a high pressure mercury lamp, CO exchange occurred within a few minutes. A statistical distribution was always obtained as in the palladium-catalysed exchange.

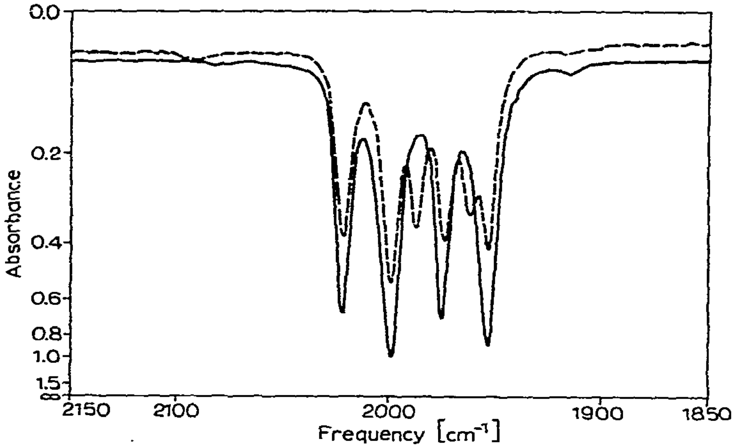


Fig. 2. 1/1 mixture of Fe($C^{16}O$)$_5$ and Fe($C^{18}O$)$_5$ (full trace) and after 5 min ultraviolet irradiation (dashed line).

CO exchange in Fe(CO)$_5$, catalysed by CF$_3$COOH

Basolo and coworkers[2] have studied this reaction at −21° and reported half-lifes of the order of 30 minutes or less for the two more rapidly exchanging carbonyls and about one hour or less for the other three. They measured the decrease of radioactivity from ^{14}CO in the gas phase over the Fe(CO)$_5$ solution.

We have tried to follow the course of this exchange by infrared spectroscopy, using ^{13}CO and C^{18}O. At −20° we could observe no exchange during an extended period (~20 h) at comparable concentrations (100 mmole/l Fe(CO)$_5$, 300 mmole/l total CO, 300 mmole/l CF$_3$COOH). It should be borne in mind, however, that the bands are very broad in $C_2Cl_2H_4$, and the sensitivity is therefore not nearly as good as with hydrocarbon solutions. No exchange could, however, be observed even at room temperature with solutions of CF$_3$COOH in mixtures of dichloroethane/heptane (1/5) or in heptane, in which the carbonyl bands are narrow and the sensitivity is therefore much better.

There was, however, a slow exchange in undiluted 1,2-dichloroethane at room temperature. The infrared spectrum of the exchanged species (after dilution with heptane) showed that the two monosubstituted products (bands at 1889 and 1964 cm^{-1}) were formed to a much smaller extent and higher substituted species to a greater extent than would result from a statistical distribution of the CO groups. The statistical distribution was afterwards obtained by addition of a small amount of palladium on alumina (See Fig. 3).

We observed the CF$_3$COOH catalysed exchange to be much slower than reported by Basolo *et al.*[2]. Half-lifes at room temperature were greater than 2 hours whereas Basolo reports 16 and 50 minutes for the different CO groups resp. at −21°, under otherwise similar conditions. We are unable to offer an explanation for this difference in rates which of course can be thought to be due to some unknown

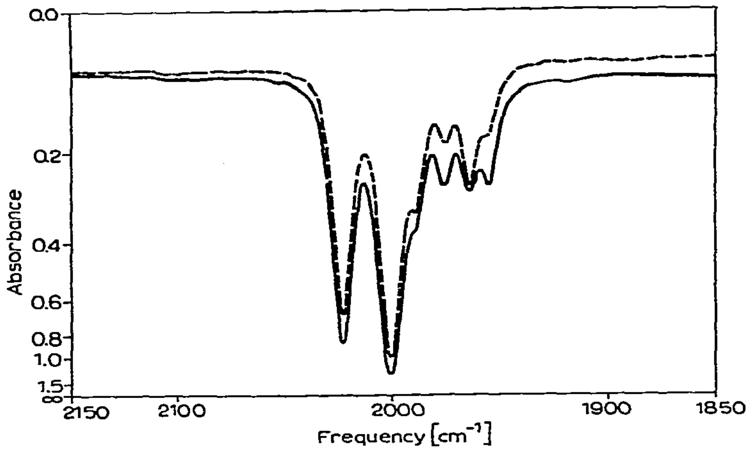


Fig. 3. Trifluoroacetic acid catalysed $C^{18}O$ exchange in $Fe(CO)_5$ (full trace) and after equilibration by addition of palladium metal (dashed line).

impurity, retarding the reaction in our case or accelerating in the earlier work. We feel however that impurities would accelerate rather than retard the exchange in $Fe(CO)_5$.

Reaction of $Fe_2(CO)_9$ with labelled CO

It is known[17] that $Fe_2(CO)_9$ in suspension in an inert solvent decomposes slowly to give almost exclusively $Fe(CO)_5$. It seemed worthwhile to carry out this decomposition in an atmosphere of labelled CO to see whether the $Fe(CO)_5$ formed has incorporated CO from the solution, and if so whether this incorporation leads to a statistical or a non-statistical distribution of the labelled CO groups.

$Fe_2(CO)_9$ was suspended in a hydrocarbon solution of $Fe(C^{18}O)_5$. The mixture obtained was not just natural $Fe(CO)_5$ [from $Fe_2(CO)_9$] and unchanged $Fe(C^{18}O)_5$; some scrambling of the CO groups having taken place during decomposition of the nonacarbonyldiiron. However, the obtained mixture was not a statistical distribution, since its spectrum changed further upon addition of some Pd on Al_2O_3. The bands at 2023 and 2001 cm^{-1} grow faster than the bands of intermediate products at 1988 and 1964 cm^{-1}.

$Fe_2(CO)_9$ was suspended in isooctane under one atmosphere of $C^{18}O$ and vigorously shaken. The resulting pentacarbonyliron again consisted of a mixture of labelled $Fe(CO)_5$ species.

Exchange reactions in $Fe(CO)_4P(C_6H_5)_3$

We found that with this compound also CO exchange was readily induced by the light from a high pressure mercury arc. The spectrum of the product is shown in Fig. 4. It exhibits a number of bands in the range from 2050 to 2000 cm^{-1} which are well separated. They can be used to recognise the different species formed, their assignment and discussion will be referred to the following section.

The exchange reaction with $C^{18}O$ is also catalysed by trifluoroacetic acid in dichloroethane. Following very closely the procedure of Basolo *et al.*[2], we obtained, by evaporation of the solvent and dissolution of the residue in heptane, a solution the

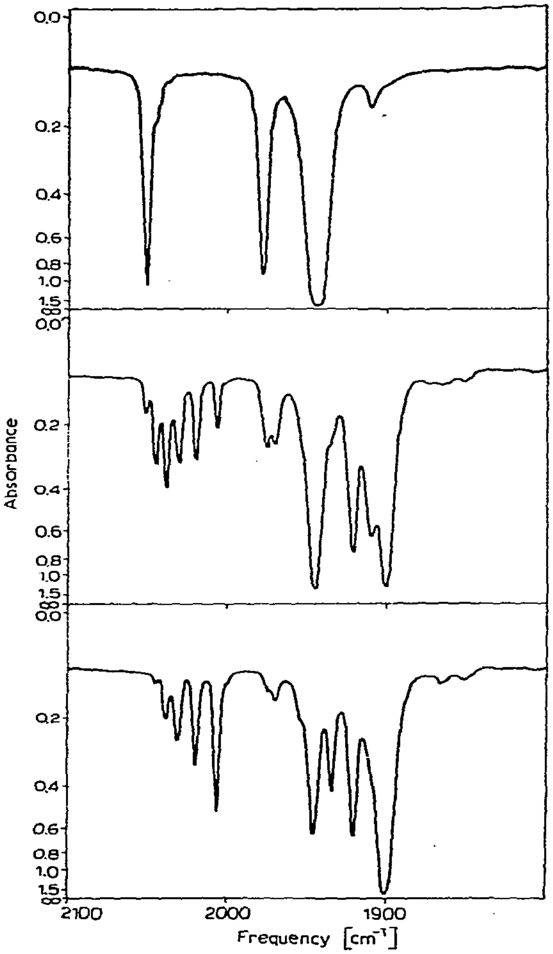


Fig. 4. Light induced $C^{18}O$ exchange in $Fe(CO)_4P(C_6H_5)_3$. Upper spectrum: natural product; medium spectrum: moderately enriched; lower spectrum: strongly enriched.

spectrum of which is shown in Fig. 5. When the solution was then exposed for about 10 minutes to ultraviolet light very significant changes in the relative intensities of the bands were produced especially in the region between 2060 and 2000 cm^{-1}. This suggests that, as with $Fe(CO)_5$, the trifluoroacetic acid catalysis leads to a non-statistical distribution of the labelled CO groups.

DISCUSSION

In the preceding section it was shown that CO exchange in the normally inert $Fe(CO)_5$ and $Fe(CO)_4P(COH_5)_3$ can easily be induced by irradiation with ultraviolet light. It is well known that substitution of $Fe(CO)_5$ with other ligands, *i.e.* maleic anhydride to give

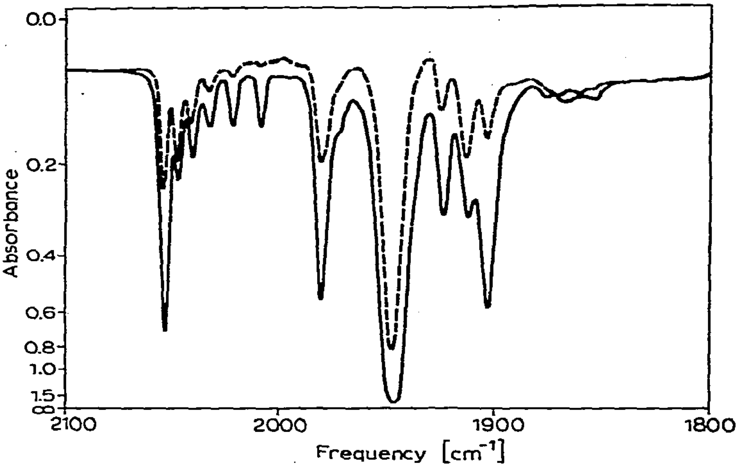
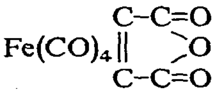


Fig. 5. Trifluoroacetic acid catalysed $C^{18}O$ exchange in $Fe(CO)_4P(C_6H_5)_3$ (full trace) and after equilibration by ultraviolet irradiation (dashed line).



can be promoted by ultraviolet irradiation at room temperature[18]. In the absence of a suitable ligand, $Fe(CO)_5$ reacts with the fragment arising from the decomposition ($[Fe(CO)_4]$) to give $Fe_2(CO)_9$. This is however an unusual reaction which occurs very reluctantly, or not at all, in inert solvents like heptane, but proceeds well in anhydrous acetic acid. On the other hand, $Fe_2(CO)_9$ is converted back into $Fe(CO)_5$ (although, of course, not quantitatively) when left in suspension in heptane even in the absence of CO. That this is not a simple reaction is shown by the fact that labelled CO is incorportated into the formed pentacarbonyliron when the reaction is carried out in the presence of $C^{18}O$. This uptake does not, however, lead to a mixture in equilibrium with the gas phase. About 10–15% $C^{18}O$ is incorporated in the presence of an excess of CO containing 92% $C^{18}O$. Also, the two monosubstituted species seem to be slightly favored with respect to the disubstituted. The latter are, however, present from the beginning of the reaction. If the reaction was simply $Fe_2(CO)_9 \rightarrow Fe(CO)_5 + [Fe(CO)_4]$ and $[Fe(CO)_4] + {}^*CO \rightarrow Fe(CO)_4{}^*CO$ mainly or only monosubstituted $Fe(CO)_5$ should be formed. It seems therefore that some active intermediate exchanges very rapidly with dissolved CO and with the carbonyl groups of dissolved $Fe(CO)_5$. The same conclusion can also be derived from the observation that $Fe_2(CO)_9 + Fe(C^{18}O)_5$ leads to a distribution of the $C^{18}O$ between the formed $Fe(CO)_5$ and the labelled $Fe(CO)_5$ in the solution, rather than simply to a mixture of unchanged $Fe(C^{18}O)_5$ and natural $Fe(CO)_5$. That the active intermediate is probably $[Fe(CO)_4]$ is suggested by the ready reaction of $Fe_2(CO)_9$ with olefins to give the corresponding $Fe(CO)_4$–olefin π-complexes[19]. In all the light-induced exchange reactions with labelled CO there was never any indication that mono-axially or di-axially substituted products were formed in preference to radially substituted ones, since the bands of all species appear simultaneously during the exchange reaction.

The complex $Fe(CO)_4P(C_6H_5)_3$ also readily exchanged its CO groups with labelled CO under ultraviolet irradiation. There was again no preference for a replacement of particular carbonyl groups, and axially and radially substituted species were both formed simultaneously. This can be seen very clearly from the sequence of bands between 2050 and 2000 cm^{-1}. Unfortunately, those due to the axially and radially monosubstituted species are so close together that they cannot be resolved. But there can be no doubt that the band at 2006 cm^{-1} is due to $Fe(C^{18}O)_4P(C_6H_5)_3$ and the other bands can be assigned to the species indicated in Tables 3 and 4. The band at 2031 cm^{-1} is much broader than the others and is certainly composed of the two of No. 4 and 6. The assignment of the 2006 cm^{-1} band to the tetra-substituted product is confirmed by the simultaneous appearance of a band at 1934 cm^{-1} which can only be due to this species. This appearance of the bands of $Fe(C^{18}O)_4P(C_6H_5)_3$ and of those of species 4 and 7 show clearly that also the *trans*, or axial CO group exchanged in the light-induced reaction.

In the case of $Fe(CO)_5$, the exchanges brought about by light were also promoted by supported palladium. Identical spectra were obtained from the light-induced and the palladium-catalysed reactions and no preference for axial or radial CO groups towards exchange could be detected even at $-20°$. In contrast to the behaviour of $Fe(CO)_5$, no CO exchange could be promoted in $Fe(CO)_4P(C_6H_5)_3$ by catalysis with palladium at room temperature.

The reactions with trifluoroacetic acid as catalyst show a very strange pattern which contrasts with the "normal" statistical pattern form the light-induced or palladium-catalysed reaction. In the case of $Fe(CO)_5$ and $Fe(CO)_4P(C_6H_5)_3$, products which have exchanged more than one CO group are found in preference to the monosubstituted products. The spectra in Fig. 3 and 5 show striking examples. In $Fe(CO)_5$, the two bands at 1976 cm^{-1} and 1955 cm^{-1} are enhanced more strongly than the bands of the monosubstituted products at 1989 cm^{-1} and 1964 cm^{-1}. If the mixture is then treated with palladium metal, the bands at 1976 cm^{-1} and at 1955 cm^{-1} decrease and those at 1989 and 1964 cm^{-1} increase. (Since there is also a slight overall decomposition only relative intensities should be compared). It thus seems that at least two CO groups are exchanged in one step. Unfortunately, it cannot be decided whether the two new bands at 1976 cm^{-1} and 1955 cm^{-1} are due to one single species or rather to a mixture of different higher substituted ones. If the bands were, however, due to one single species, it could only be the pentasubstituted product, which has its two bands just at these positions. But the observed spectrum could also be that of a mixture, since many other species absorb at the one or the other of the two positions. The only safe conclusion is that the monosubstituted product is disfavoured with respect to higher products in this exchange.

A similar situation prevails in the case of $Fe(CO)_4P(C_6H_5)_3$ as seen from Fig. 5. Here again higher substituted products are formed preferentially and the high proportion of tetrasubstituted product in presence of much residual unsubstituted and little monosubstituted product is very striking. The concentrations of the different species $Fe(CO)_{4-n}(C^{18}O)_nP(C_6H_5)_3$ can be calculated by the binominal distribution formula[8]

$$W_n = \binom{4}{n} p^n \cdot (1-p)^{4-n}$$

where W_n is the relative concentration of a species containing n $C^{18}O$ ligands and p is the $C^{18}O$ concentration of the gas mixture in equilibrium with the complex. Fig. 6

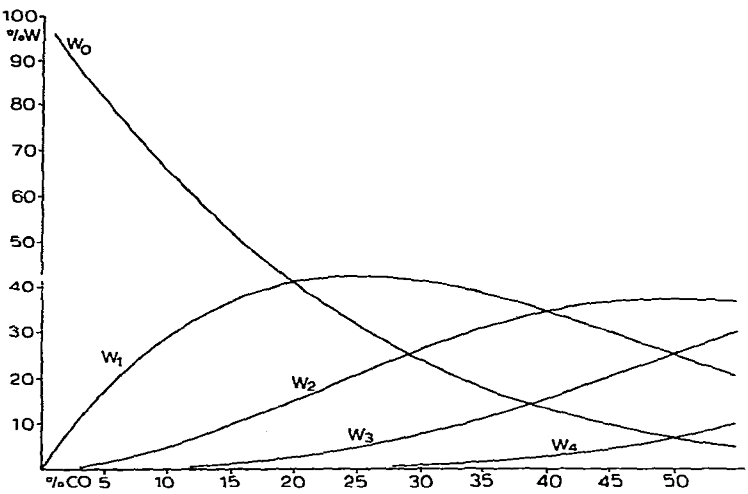


Fig. 6. Statistical distribution of the different $Fe(CO)_{4-n}(C^{18}O)_nP(C_6H_5)_3$ species.

shows the results of applying this formula. From this figure it is clear that when the tetrasubstituted species just begins to be detectable (~2%), there should be only about 20% of unsubstituted compound left and the concentrations of the mono and disubstituted ones should be almost equal, and both 35%. Thus, in the CF_3COOH-catalysed reaction, a state very far from equilibrium is obtained. Again in equilibration by ultraviolet illumination, the pattern changes completely, the bands of the mono and disubstituted species increase at the expense of the unsubstituted and the higher substituted ones. Thus a conclusion similar to that in the case of $Fe(CO)_5$ can be reached, *viz.*, that the mono-substituted product is disfavored with respect to higer substituted and unsubstituted compounds. In this case, however, it can be seen very clearly that not only the highest (tetra-) but also the di- and trisubstituted species are formed. There seems to be no preference for axial or radial CO groups with respect to exchange. Again, the first step consists of the exchange of at least two carbonyl groups at once. Supposing that two groups are exchanged at the time and this step repeated in the presence of highly enriched $C^{18}O$, tetra- or trisubstituted products are obtained, depending whether the two remaining $C^{16}O$ groups or one $C^{16}O$ and one $C^{18}O$ are exchanged. With this mechanism, the monosubstituted species can only be obtained either by simultaneous incorporation of one $C^{18}O$ and one $C^{16}O$, which would be the case if more weakly enriched $C^{18}O$ gas was employed, or by back exchange of a di-$C^{18}O$ species with $C^{16}O$.

$$Fe(CO)_4P(C_6H_5)_3 + 2\,C^{18}O \rightarrow Fe(CO)_2(C^{18}O)_2P(C_6H_5)_3 + 2\,C^{16}O$$

$$Fe(CO)_2(C^{18}O)_2P(C_6H_5)_3 + 2\,C^{18}O \begin{cases} \rightarrow Fe(C^{18}O)_4P(C_6H_5)_3 + 2\,C^{16}O \\ \rightarrow Fe(CO)(C^{18}O)_3P(C_6H_5)_3 + C^{16}O + (C^{18}O) \end{cases}$$

$$Fe(CO)_2(C^{18}O)_2P(C_6H_5)_3 + 2\,C^{16}O \begin{cases} \rightarrow Fe(CO)_4P(C_6H_5)_3 + 2\,C^{18}O \\ \rightarrow Fe(CO)_3(C^{18}O)P(C_6H_5)_3 + C^{18}O + (C^{16}O) \end{cases}$$

The statistical probability for the formation of trisubstituted species is twice as high as that of the tetrasubstituted one, since in the first case two sets of two carbonyls can be exchanged whereas in the second case only one set is exchanged. The monosubstituted product should be very much disfavoured if an excess of highly enriched $C^{18}O$ is used, even when a large amount of unsubstituted product is still present in the mixture. This is just what is shown by the spectrum in Fig. 5. We therefore conclude that a simultaneous exchange of two groups is the most likely explanation for this exchange pattern. We cannot at present offer any explanation of how trifluoroacetic acid acts to promote such exchange.

These observations show that the trifluoroacetic acid-catalysed exchange is much more complicated than Basolo and coworkers[2] supposed, and that their view of two faster and three slower exchanging groups in $Fe(CO)_5$ and of only three groups exchanging in $Fe(CO)_4P(C_6H_5)_3$ cannot be maintained. It is clear that direct observation of these exchanges is much more informative than a study of the overall rate.

The question of whether the different CO groups in $Fe(CO)_5$ retain their stereochemical identity cannot be answered unequivocally, but there is no evidence in favour of such retention. Certainly there is no *inter*molecular exchange under uncatalysed conditions.

ACKNOWLEDGEMENT

We thank Dr F. Calderazzo and Dr G. Bor for valuable discussions and Dr Bor for sending a detailed account of his lecture 1968 (ref. 16).

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