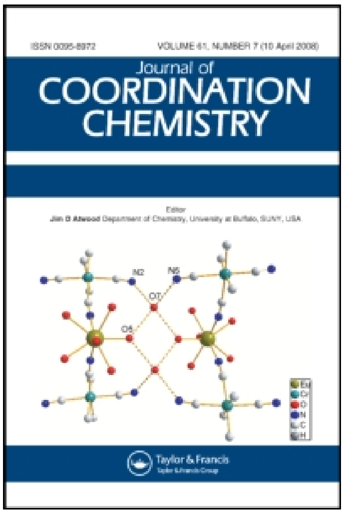

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NITROGEN DERIVATIVES OF IRON CARBONYLS
II. - Kinetics of Carbon Monoxide Exchange with $Fe_3(CO)_9NR\text{-}NR'$ Complexes

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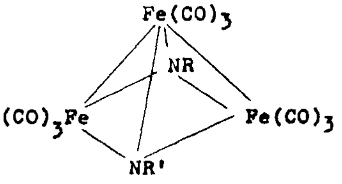
Investigations on the kinetics of ^{14}CO exchange with $Fe_3(CO)_9NR{\cdot}NR'$ ($R,R' = H, CH_3, C_2H_5, C_6H_5$) complexes are reported. The reaction rates are independent of the CO concentration and indicate that all the carbonyl groups in the substrate are equivalent. The results show a correlation between the kinetic and thermodynamic parameters and CO stretching frequencies, which results from the nature of the R and R′ groups. Two mechanisms are suggested, both implying the "labilization" by the N-ligands of the Fe–CO or Fe–Fe bonds.

INTRODUCTION

The reaction between monodentate ligands and $Fe_3(CO)_9XY$ complexes (in which X and Y are chalcogen atoms) is thought to proceed by two simultaneous mechanisms of dissociative- and associative-type, respectively[1]. Either one or both may prevail depending on the nature of the chalcogen atoms and the nucleophilicity of the ligand. Since both the decreasing electronegativity of the chalcogen atoms and the increasing nucleophilic power of the ligand favour the occurrence of the associative mechanism, we have concluded that the attack of the entering ligand probably takes place on the chalcogen rather than on the metal atoms. Thus the chalcogen atoms in these complexes should be regarded as Lewis acids on account of their energetically available empty d orbitals.

A further examination of this hypothesis from another point of view has induced us to study the kinetics and reaction mechanism of complexes such, as $Fe_3(CO)_9NR{\cdot}NR'$ (R and R′ are H, CH_3, C_2H_5 and C_6H_5 groups) which are strictly analogous to the chalcogen-iron carbonyls. A structure (I) has been reported for the $Fe_3(CO)_9NR{\cdot}NR'$ ($R=R'=NC(C_6H_5)_2^2$; $R=R'=CH_3^3$) and it is very similar to the configuration (II) ($X=Y=Se^4$; $X=Y=S^5$), in which the NR groups are replaced by the chalcogen atoms. In the complexes (I) the possibility of attack by the ligand on the tetracoordinated nitrogen atom can be eliminated so it could be expected, if the previous mechanism is operative, that the first-order process is more probable than in the analogous reactions with the complexes (II). Such a study also can give information about the effect of the tetracoordinated nitrogen on the reactivity of the substrate and about the influence of the group bonded on it.



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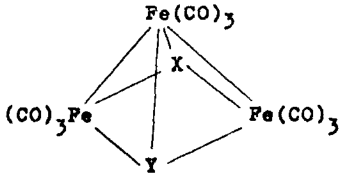


II

EXPERIMENTAL PART

Compounds and Solvents

$Fe_3(CO)_9(NCH_3)_2$ was provided initially by Professor G. R. Knox and subsequently prepared by the known method[6].

$Fe_3(CO)_9(NC_6H_5)_2$ was obtained by the reaction of $Fe_3(CO)_{12}$ with nitrobenzene in benzene solution. More detailed data on this preparation are previously reported[7].

$Fe_3(CO)_9(NC_2H_5)_2$ and $Fe_3(CO)_9NH{\cdot}NC_2H_5$ have not been previously described. Both were isolated from the reaction of an equimolar mixture of triiron dodecacarbonyl and nitroethane in boiling benzene. Data on this reaction will be given elsewhere[8].

The solvents used were purified by distillation, carefully dried and stored under an inert atmosphere. Nitrogen, carbon monoxide or CO/Ar mixtures were high-purity commercial gases: they were dried through $CaCl_2$-silica gel columns before use. Radioactive carbon-14 monoxide was purchased from Amersham Centre; it was diluted with inactive CO to obtain a suitable specific activity.

Kinetic studies

The method used to investigate the rate of ^{14}CO exchange with nitrogen-iron complexes was similar to that described earlier[9]. Owing the slow reaction rates we prefer to exchange inactive CO with previously labelled complexes. To do this, an inactive complex solution was sealed in a glass vial under a radioactive CO atmosphere and kept in a thermostated bath at appropriate temperature for a suitable long time. All the kinetic runs were performed in *n*-heptane solution in the dark. Complexes are stable during the time of the kinetic experiments: samples of the reaction mixtures did not show changes on their IR spectra after two or three half-lives.

All the exchange reactions investigated were found to follow the McKay equation[10] and give satisfactory linear plots of $\log(A_t - A_\infty/A_0 - A_\infty)$vs. time, where A_t, A_0 and A_∞ are the complex activities at time t, initial time and equilibrium time, respectively. From these plots the half-exchange time $t½$ was determined and used to estimate the value of the observed rate constant k_{obs} by:

$$k_{obs} = \frac{0.693}{t_{\frac{1}{2}}} = \frac{n[CO]}{n[Fe_3(CO)_9NR\cdot NR'] + [CO]}$$

where n is the number of exchangeable CO's in the metal carbonyl and [CO] is the total number of moles of CO in the vials (moles of CO in gas phase plus moles of CO dissolved in the solvent) divided by the number of liters of solvent used. The solubility of CO in *n*-heptane at room temperature is known[11]. Duplicate runs carried out under the same conditions showed that the values of rate constant were generally reproducible to better that 5%.

Apparatus

Measurements of the specific activity in solution were performed a PackardTriCarb Liquid Scintillation Spectrometer Model 2002. Liquid scintillator was a toluene solution of PPO (5 g/l) and of 2,2'dimethyl POPOP (0.2 g/l).

A Beckman IR 12 grating Spectrophotometer was used to record the infrared spectra.

RESULTS

All the CO's in each complex are kinetically equivalent, that is, the experimental values of the activity at equilibrium time are in good agreement with the value calculated on the basis of the exchange of nine CO molecules.

The kinetic data for the CO exchange reaction are collected in Table I. It can be easily seen that in all cases the observed rate constants at various carbon monoxide concentration remain constant, so the exchange reaction follows a first order rate law, independent of the CO concentration. Table II reports the values of the first-order rate constants calculated as averages of the observed values from Table I. The activation parameters for the same reaction are given in Table III. The error is in all cases one standard deviation.

DISCUSSION

In order to evaluate the result of our kinetic experiments it appears useful to compare them with those which we have obtained from the reaction of the chalcogen-iron complexes[1]. The two series of compounds, owing to their analogous structures, have quite similar IR spectra in the carbonyl stretching region, showing three strong bands between 2000 and 2070 cm^{-1}. The frequencies of these bands clearly depend on the nature of the ligands: a linear relationship between ν_{CO} and the electronegativities of the chalcogen atoms has been noted[13]. An analogous trend is observed with the nitrogen derivatives, when the values of the Taft σ^* constant for the R and R' groups are used as a measure of the inductive effect of these groups[14]. As shown in Fig. 1, the larger σ^* values, which indicate a greater electron attracting power, correspond, as expected, to the higher ν_{CO}.

Tentative correlations between the metal-carbon bond strengths and the rates of CO dissociation have often been made on the basis of carbonyl stretching data. In some cases, even if the M CO bond strength is not known, the higher carbonyl stretching frequencies are indicative of less metal-to-carbon π-bonding and consequently of a weaker M CO

TABLE I
Observed rate constants of the ^{14}CO exchange with $Fe_3(CO)_9NR{\cdot}NR'$ complexes in *n*-heptane.

Complex	Complex conc. mM	CO conc.[a] mM	t°C	$k_{obs}\cdot 10^5$ sec^{-1}
$Fe_3(CO)_9(NC_6H_5)_2$	0.473	8.0	50.0	0.267
	0.806	5.9		0.262
	1.013	4.4		0.256
	1.296	2.0		0.243
	0.475	6.2	60.0	1.29
	0.795	4.6		1.20
	1.002	3.5		1.21
	1.293	1.6		1.13
	0.475	4.4	70.0	4.99
	0.795	3.3		4.95
	1.002	2.5		4.81
	1.293	1.3		4.91
$Fe_3(CO)_9NH{\cdot}NC_2H_5$	0.57	6.1	60.0	1.01
	0.78	4.7		1.01
	1.14	3.1		1.16
	1.71	1.9		1.02
	0.46	4.5	70.0	3.75
	0.91	2.1		4.16
$Fe_3(CO)_9(NCH_3)_2$	0.425	7.7	50.0	0.481
	0.703	5.8		0.411
	0.994	3.7		0.437
	1.400	2.1		0.478
	0.412	6.2	60.0	1.84
	0.726	4.6		1.78
	1.005	2.8		1.77
	1.421	1.6		1.72
	0.442	4.4	70.0	6.32
	0.775	3.1		6.19
	1.024	2.1		6.53
	1.320	1.2		6.15
$Fe_3(CO)_9(NC_2H_5)_2$	0.440	7.9	50.0	0.182
	0.724	6.0		0.195
	1.117	4.6		0.197
	1.503	2.1		0.201
	0.440	6.3	60.0	0.736
	0.724	4.8		0.813
	1.117	3.7		0.792
	1.503	1.7		0.830
	0.440	4.5	70.0	3.20
	0.724	3.4		3.27
	1.117	2.6		3.24
	1.503	1.2		3.48

[a] The values of the CO solubility in *n*-heptane at the reaction temperature have been extrapolated from the data already reported.[12]

bond[15]. Moreover, an appropriate linear relationship between kinetic and/or thermodynamic parameters and CO stretching frequencies strongly supports a CO dissociation mechanism[16]. It must be pointed out, however, that this is not always true. Dobson and coworkers report, for example, that in some octahedral Cr and Mo derivatives the M–C and C–O stretching frequencies are both strengthened or weakened, depending on the nature of the ligands[17] and that the expected reciprocal relationship between ν_{CO} and ν_{MC} is observed only within series of complexes containing the same donor atom[18].

We have reported in Fig. 2 a free energy plot of log k_1 for CO exchange at 60.0° vs. the highest ν_{CO} frequency for all the chalcogen and nitrogen-iron complexes and in Fig. 3 the analogous relationship

TABLE II
First-order rate constant of the ^{14}CO exchange with $Fe_3(CO)_9NR{\cdot}NR'$ complexes in *n*-heptane.

Complex	t°C	$k_1 \cdot 10^4$ sec^{-1}
$Fe_3(CO)_9(NC_6H_5)_2$	50.0	0.26 ± 0.01
	60.0	1.21 ± 0.07
	70.0	4.92 ± 0.08
$Fe_3(CO)_9NHNC_2H_5$	60.0	1.05 ± 0.07
	70.0	4.0 ± 0.3
$Fe_3(CO)_9(NCH_3)_2$	50.0	0.45 ± 0.03
	60.0	1.78 ± 0.05
	70.0	6.3 ± 0.2
$Fe_3(CO)_9(NC_2H_5)_2$	50.0	0.194 ± 0.008
	60.0	0.79 ± 0.04
	70.0	3.3 ± 0.1

TABLE III
Activation parameters of the ^{14}CO exchange with $Fe_3(CO)_9NR{\cdot}NR'$ complexes in *n*-heptane.

Complex	ΔH^* Kcal/mole	ΔS^* e.u.
$Fe_3(CO)_9(NC_6H_5)_2$	31.8 ± 1.4	18.8 ± 2.5
$Fe_3(CO)_9NH\,NC_2H_5$	29.4 ± 2.6	11.5 ± 5.6
$Fe_3(CO)_9(NCH_3)_2$	28.2 ± 1.5	8.7 ± 2.7
$Fe_3(CO)_9(NC_2H_5)_2$	30.5 ± 1.4	14.0 ± 2.6

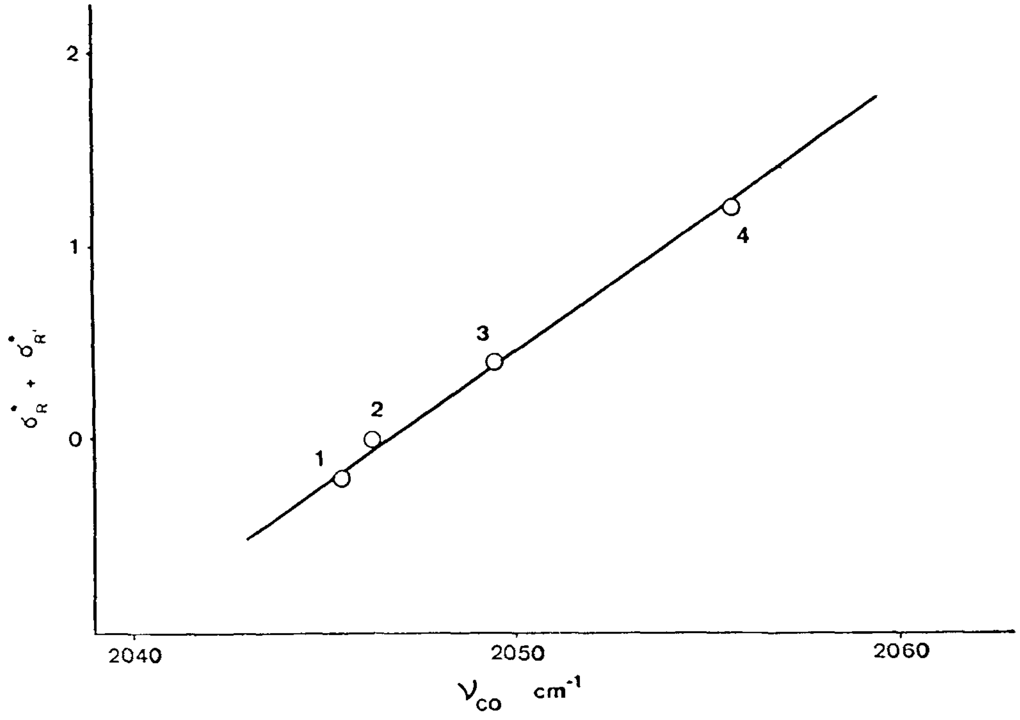


FIGURE 1 Plot of $\sigma^*_R + \sigma^*_{R'}$ vs. the highest ν_{CO} for $Fe_3(CO)_9NR{\cdot}NR'$ complexes. 1, $Fe_3(CO)_9(NC_2H_5)_2$; 2, $Fe_3(CO)_9(NCH_3)_2$; 3, $Fe_3(CO)_9NH{\cdot}NC_2H_5$; 4, $Fe_3(CO)_9(NC_6H_5)_2$.

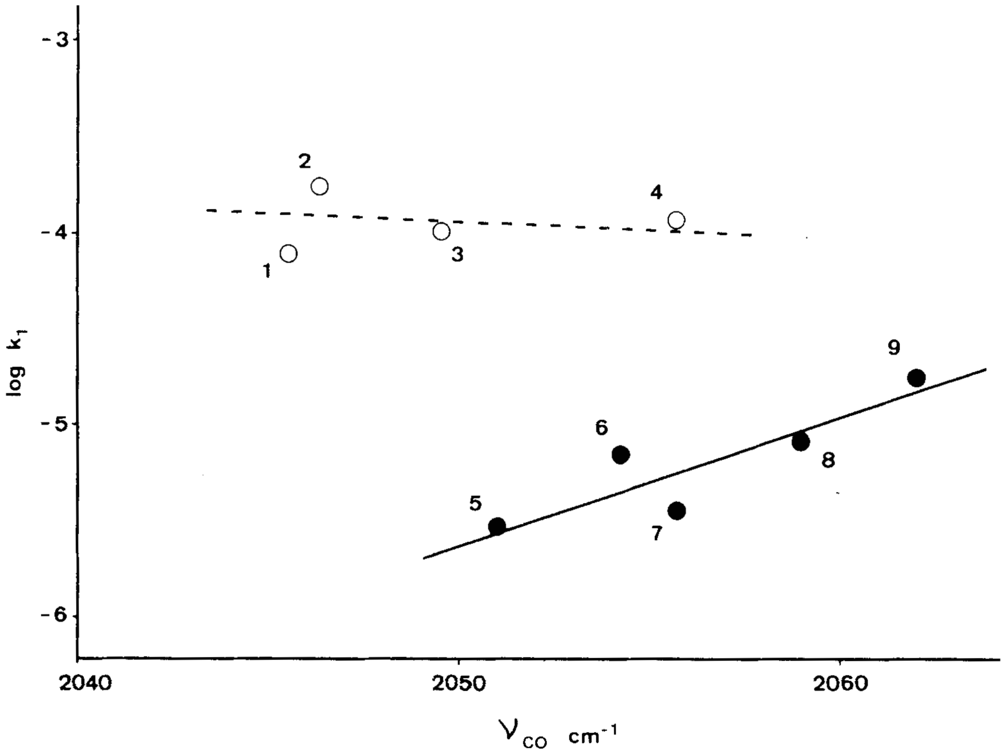


FIGURE 2 Free energy plot of log k_1 vs. ν_{CO} for $Fe_3(CO)_9NR{\cdot}NR'$ and $Fe_3(CO)_9XY$ complexes. 1–4, see Fig. 1; 5, $Fe_3(CO)_9SeTe$; 6, $Fe_3(CO)_9STe$; 7, $Fe_3(CO)_9Se_2$; 8, $Fe_3(CO)_9SSe$; 9, $Fe_3(CO)_9S_2$.

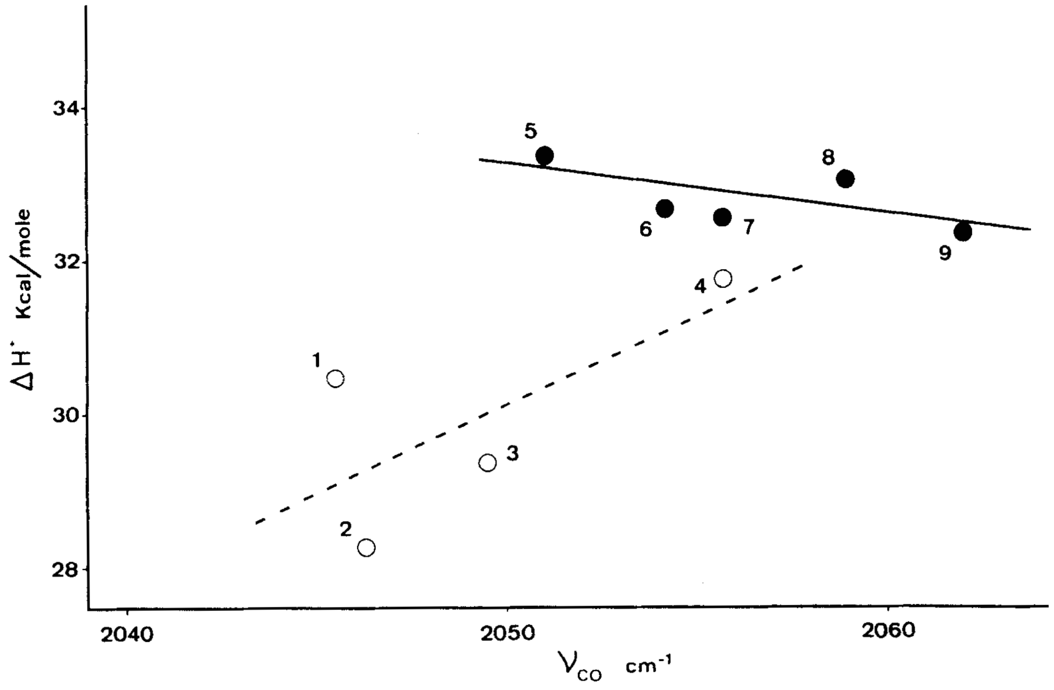


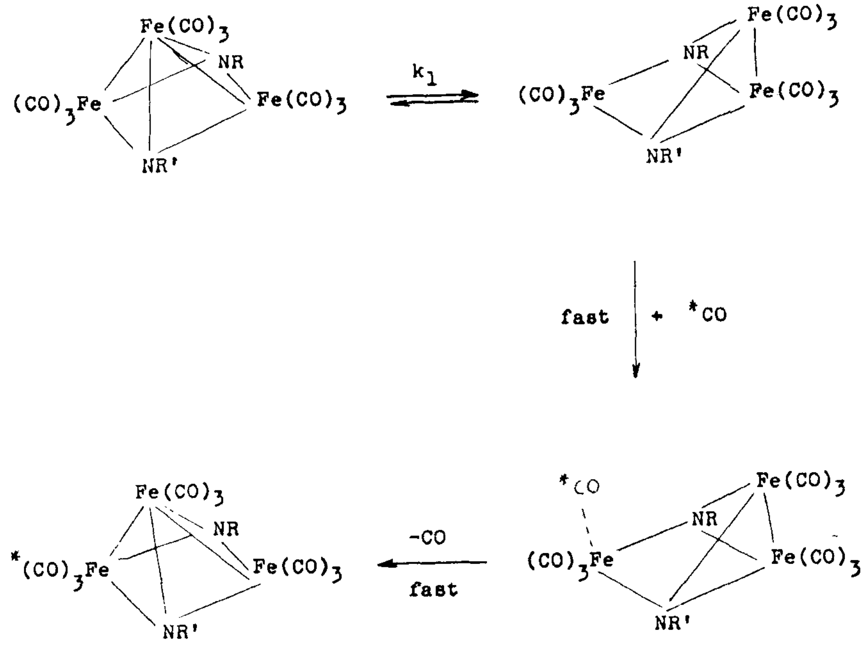
FIGURE 3 Plot of ΔH_1 vs. ν_{CO} for $Fe_3(CO)_9NR{\cdot}NR'$ and $Fe_3(CO)_9XY$ complexes. Numbers are those from Figs. 1 and 2.

with the activation enthalpy values. The plots show that in the chalcogen series the higher the CO frequencies, the faster the reactions: that clearly illustrates the previously suggested CO dissociation mechanism[1]. The behaviour of the nitrogen complexes seems to differ from the previous one. In spite of the large experimental errors in the ΔH^* determination and of the little difference in reactivity of the complexes, nevertheless it could be possible to observe that a decreasing ν_{CO}, i.e. an increasing ligand basicity, parallels a greater reactivity. Furthermore, it can be noted that the nitrogen complexes react more readily than the other ones: complexes with nearly equal frequency values show both faster rate and smaller activation enthalpy. This behaviour can be explained in two ways: first, by a CO dissociation, as it occurs with the chalcogen series; second, by invoking a rupture of another bond in the molecule, as the rate determining step.

In the first case, the "anomalous" reactivity can be interpreted both in terms of stabilization of the transition state and of destabilization of the ground state. Angelici and coworkers[19] have found that in Cr(O), Mo(O) and Mn(I) octahedral complexes the CO groups have been substantially labilized by ligands which have as donor atoms either first row elements or halogens. I.e., in terms of "hardness" and "softness" of the ligands[20], "hard" bases are labilizing and "soft" bases are non-labilizing. This labilization can be explained as a stabilization of the transition state of the dissociative reaction, which results from a greater capacity of the ligand to provide electron density on the metal atom during the CO dissociation. Furthermore, it has been suggested[17] that "hard" bases can "neutralize" a large part of the metallic Lewis acidity, inhibiting the carbon-to-metal bonding and so labilizing the CO groups: in this case the "anamalous" kinetic behaviour may be interpreted as destabilization of the ground state. Both stabilization and destabilization phenomena predict an increasing reactivity with the increasing basicity of the ligands, so both can explain the kinetic behaviour of the N-complexes referring to the properties of R and R′ groups and their greater reactivity with respect to that of the chalcogen compounds.

The alternative mechanism (III) would involve a Fe Fe bond breaking as the rate-determining step, followed by a rapid coordination of the entering CO to the vacant site on the substrate and subsequent rearrangement.

An intermediate formed by the rupture of the Fe Fe bond would not seem unreasonable in view of the



III

values of the kinetic parameters. ΔH^* is very close to the value of 32 Kcal/mole calculated for the energy of the Fe–Fe bond in $(\pi\text{–}C_5H_5)_2Fe_2(CO)_4$[21] and ΔS^* values are, presumably, generally less than those of the $Fe_3(CO)_9XY$ reactions[1], which occur via a dissociative mechanism. The different basicity of the N-ligands could explain the different reactivity of the compounds in terms of different strength of Fe–Fe bonds. Really, the increasing σ-donor character of the ligand enhances the electron density on the metal atoms thus weakening the Fe–Fe bonds by increasing the repulsion between the non-bonding electrons. A similar trend has been observed for the reaction of the Co–Co bonded-systems with stannous halides. The increasing reactivity of $[CO(CO)_3L]_2$ complexes as the L donor capacity increases has suggested that the strength of the Co–Co bond is the important factor in determining the rates[22].

It is not possible at this time to prefer one mechanism to the other one. Indeed, it is possible that both mechanisms are operating simultaneously, as proposed for the reaction of $Fe_2(CO)_9$ with (p-tolyl)phosphine[23]. Data on the Fe–CO and Fe–Fe IR stretching modes and studies on the possible inhibition by CO of the substitution reactions with ligands could probably offer the opportunity to make a choice between them.

Finally, the lack of the second-order mechanism in the CO exchange with nitrogen-iron complexes must be noted. Indeed, it is reasonable to expect that, for example, $Fe_3(CO)_9(NCH_3)_2$, which shows IR ν_{CO} values nearly equal to those of $Fe_3(CO)_9Te_2$, has practically the same k_2 value, if the second-order process is operative also in this case. So this effect should be clearly noted, because it should give a not negligible contribution to the total rate (e.g. at 60.0°, when CO is 6 mM, $k_2[CO]$ is about 40% k_1). The failure of this observation indicates that CO doesn't directly coordinate to the substrate in the nitrogen-iron complexes reaction and can give an indirect proof of the correctness of the kinetic mechanism suggested for the reactions with the chalcogen-iron complexes.

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REFERENCES

1. G. Cetini, P. L. Stanghellini, R. Rossetti and O. Gambino Inorg. *Chim. Acta* **2**, 433 (1968)
   R. Rossetti, P. L. Stanghellini, O. Gambino and G. Cetini *ibid.* **6**, 205 (1972)
2. P. E. Baikie and O. S. Mills *Chem. Comnun.* 1228 (1967)
3. R. J. Doedens *Inorg. Chem.* **9**, 570 (1969)
4. L. F. Dahl and P. W. Sutton *ibid.* **2**, 1067 (1963)
5. C. H. Wei and L. F. Dahl *ibid.* **4**, 493 (1965)
6. M. Dekker and G. R. Knox *Chem. Commun.* 1243 (1967)
7. P. L. Stanghellini and R. Rossetti *Atti Accad. Sci. Torino* **105**, 391 (1970–71)
8. R. Rossetti and P. L. Stanghellini manuscript in preparation
9. G. Cetini, O. Gambino, P. L. Stanghellini and G. A. Vaglio *Inorg. Chem.* **6**, 1225 (1967).
10. H. A. C. McKay *Nature* **142**, 997 (1938)
11. J. C. Gjaldbeck *Acta Chem. Scand.* **7**, 623 (1952)
12. P. L. Stanghellini, R. Rossetti, O. Gambino and G. Cetini *Inorg. Chem.* **10**, 2672 (1971)
13. R. Rossetti; G. Cetini, O. Gambino and P. L. Stanghellini *Atti Accad. Sci. Torino* **104**, 127 (1969–70)
14. R. W. Taft Jr In *Steric Effects in Organic Chemistry* Ed. M. S. Newman J. Wiley and Sons New York N.Y. 1956, p. 596
15. H. G. Schuster-Woldan and F. Basolo *J. Amer. Chem. Soc.* **88**, 1657 (1966); E. M. Thorsteinson and F. Basolo *ibid.* **88**, 3929 (1966); H. Wawersik and F. Basolo *ibid.* **89**, 4626 (1967); C. White and R. J. Mawby *Inorg. Chim. Acta* **4**, 261 (1970); R. J. Angelici and G. C. Faber *Inorg. Chem.* **10**, 514 (1971)
16. A. T. Brault, E. M. Thorsteinson and F. Basolo *Inorg. Chem.* **3**, 770 (1964)
17. G. R. Dobson and L. W. Houk *Inorg. Chim. Acta* **1**, 287 (1967); G. C. Faber and G. R. Dobson *Inorg. Chem.* **7**, 584 (1968)
18. R. A. Brown and G. R. Dobson *Inorg. Chim. Acta* **6**, 65 (1972)
19. R. J. Angelici and J. R. Graham *J. Amer. Chem. Soc.* **87**, 5586 (1965); R. J. Angelici and J. R. Graham *Inorg. Chem.* **6**, 988 (1967); R. J. Angelici, S. E. Jacobson and C. M. Ingemanson *ibid.* **7**, 2466 (1968)
20. R. G. Pearson *J. Amer. Chem. Soc.* **85**, 3533 (1963)
21. P. F. Barrett and K. K. W. Sun *Canad. J. Chem.* **48**, 3300 (1970)
22. F. Bonati, S. Cenini, D. Morelli and R. Ugo *J. Chem. Soc.* 1052 (1966); P. F. Barrett and A. J. Poe *ibid.* 429 (1968)
23. P. S. Braterman and W. J. Wallace *J. Organometall. Chem.* **30**, C17 (1971)