Contribution from the Institute of Chemistry,
University of Turin, Italy.

Chalcogen Derivatives of Iron Carbonyls. III. Effect of the Solvents in CO Isotopic Exchange Reaction on $Fe_3(CO)_9Te_2$

P. L. Stanghellini, G. Cetini, O. Gambino and R. Rossetti

Received August 1, 1969

Different solvents exercise two effects, electrostatic and nucleophilic, in CO exchange reaction rates on the $Fe_3(CO)_9Te_2$ complex. These effects are discussed and a kinetic mechanism is proposed. A comparison is also made between the electron attracting power of Te atoms and the diphenylacetylenic group in the similar complexes, $Fe_3(CO)_9Te_2$ and $Fe_3(CO)_9C_2(C_6H_5)_2$.

Introduction

Determination of reaction rates in CO isotopic exchange and in the substitution of CO with ligands has been applied to carbonyl complexes of the type $Fe_3(CO)_9X_2$ (where X = S, Se, Te) to assess the effect of the chalcogen X on the electronic structure of the complex and, in the second place, to evaluate the nucleophilic character of the ligand on the reaction kinetics.[1,2] The present work was undertaken as a continuation of this research and reports the effect of the solvents on this type of reaction: the CO isotopic exchange reaction on $Fe_3(CO)_9Te_2$ was chosen because the reaction rate also depends on the CO (poor nucleophile) and a more pronounced effect of the solvents was therefore foreseeable. We also considered it of interest, bearing in mind the structural similarity between the compounds under study and complexes of the type $Fe_3(CO)_9C_2RR'$, where C_2RR' is an acetylene derivative,[3,4] to extend our investigation to one of these complexes, $Fe_3(CO)_9C_2(C_6H_5)_2$, so as to compare the effect of the acetylene group and that of the chalcogen atoms on the $Fe_3(CO)_9$ cluster, particularly on the Fe–CO bond.

Experimental Section

Compounds and solvents. Methods reported in the literature[3,5] were used to prepare and purify $Fe_3(CO)_9C_2(C_6H_5)_2$ and $Fe_3(CO)_9Te_2$. The solvents were dried and distilled, usually at reduced pressure, in accordance with known methods.[6]

High specific activity ^{14}CO was supplied by the Amersham Radiochemical Centre and appropriately diluted with inactive CO which had previously been dried on $CaCl_2$ and silica gel columns.

Isotopic exchange. Our technique for CO isotopic exchange reactions has already been described.[7] Thin-layer chromatography did not reveal any decomposition during the course of the reaction. Our experimental data were in close agreement with the well-known Mc Kay's relation.[8] This meant that the half-exchange time $t_{1/2}$ could be calculated from the best straight line obtained by plotting the values of $\ln A_t - A_\infty / A_0 - A_\infty$ as a function of time (A_0, A_t and A_∞ = specific activity of the solution at t = 0, t = t and t = ∞). Equations (1) and (2) were used to determine the specific reaction rate k and the reaction orders a and b for the complex and CO respectively:

$$R = \frac{0{,}693}{t_{1/2}} \times \frac{n[Fe_3(CO)_9X_2][CO_{tot}]}{n[Fe_3(CO)_9X_2]+[CO_{tot}]} \qquad (1)$$

$$R = k[Fe_3(CO)_9X_2]^a[CO_d]^b \qquad (2)$$

where $[Fe_3(CO)_9X_2]$ and $[CO_d]$ are the molar concentration of the complex and of CO dissolved, $[CO_{tot}]$ that of the CO, assuming total dissolution, and n is the number of exchangeable carbonyls per complex molecule: in all the reactions we studied, n = 9.

Specific activity of the solutions was measured with a Tricarb Liquid Scintillation Spectrometer (model 314 EX) (Packard Instrument Co).

The solubility of CO in the solvents used has been reported in the literature.[9,10] In the case of xylene and diethoxydiethylether, values at 50°C were extrapolated from the values there given; in that of chlorobenzene, interpolation was employed. This process is felt to have been justified on the ground

---

(1) G. Cetini, P. L. Stanghellini, R. Rossetti and O. Gambino, *J. Organometal. Chem.*, *15*, 373 (1968).

(2) G. Cetini, P. L. Stanghellini, R. Rossetti and O. Gambino, *Inorg. Chim. Acta*, *4*, 433 (1968).

(3) W. Hübel, E. H. Braye, A. Clauss, E. Weiss, U. Kruerke, D. A. Brown, G. S. D. King and C. Hoogzand, *J. Inorg. Nucl. Chem.*, *9*, 204 (1959).

(4) J. F. Blount, L. F. Dahl, C. Hoogzand and W. Hübel, *J. Am. Chem. Soc.*, *88*, 292 (1966).

(5) W. Hieber and J. Gruber, *Z. Anorg. Allg. Chem.*, *296*, 91 (1958).

(6) Technique of organic chemistry Vol. VII A. Weissemberg ed. Interscience N. Y. 1955.

(7) G. Cetini, R. Ercoli, O. Gambino and G. A. Vaglio, *Atti Accad. Sci. Torino, Classe Sci. Fis. Mat. Nat.*, *99*, 1123 (1964).

(8) H. A. C. McKay, *Nature*, *142*, 997 (1938).

(9) W. F. Linke and A. Seidell « Solubilities of inorganic and metal-organic compounds » Vol. I ed. D. Van Nonstrand Co. Priceton 1958 pag. 453-458.

(10) F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, *1*, 30 (1962).

Table I. ^{14}CO isotopic exchange rates on $Fe_3(CO)_9C_2(C_6H_5)_2$ and $Fe_3(CO)_9Te_2$ in various solvents

Complex	Solvent	Compl. conc. mM	CO_d mM	CO_{tot} m. moles	t °C	$R\times10^8$ M sec^{-1}	$k_1\times10^5$ sec^{-1}	$k_2\times10^3$ M^{-1} sec^{-}
$Fe_3(CO)_9C_2(C_6H_5)_2$	n-heptane	0.676	8.0	0.253	40.0	3.25	4.81	6.0
		1.348	4.3	0.120		3.57	2.65	6.2
		0.676	6.8	0.266	50.0	6.73	9.96	15
		1.025	5.3	0.212		7.13	6.96	13
		1.348	3.6	0.125		8.22	6.10	17
		0.663	4.0	0.185	60.0	7.37	11.1	28
		1.34	6.1	0.255		24.3	18.1	30
$Fe_3(CO)_9Te_2$	chlorobenzene	0.400	1.6	0.228	50.0	0.529	1.32	8.2
		0.741	3.1	0.425		1.79	2.42	7.8
		1.063	4.3	0.573		3.27	3.08	7.2
		1.478	5.8	0.907		5.87	3.97	6.9
	xylene	0.716	4.0	0.491		1.30	1.82	4.6
		1.061	5.3	0.693		2.39	2.25	4.2
		1.469	6.8	0.823		4.77	3.25	4.8
	β-β′-diethoxy-diethylether	0.794	3.4	0.414		1.59	2.00	5.9
		1.107	4.9	0.592		2.95	2.67	5.4
		1.478	6.6	0.914		5.40	3.65	5.5
	n-butyl alcohol	0.751	4.8	0.656		3.69	4.91	10.2
		1.104	6.5	0.798		7.53	6.44	10.5
	n-propyl alcohol	0.460	5.1	0.723		3.50	7.62	14.9
		0.750	7.2	0.937		7.68	10.2	14.3
	ethyl alcohol	0.447	4.1	0.429		3.17	7.10	17.2
		0.617	5.0	0.547		5.46	8.84	17.9
		0.700	5.7	0.653		6.48	9.26	16.4
	methyl alcohol	0.313	4.6	0.400		3.47	11.1	24.3
		0.446	5.9	0.564		5.77	12.9	22.0
		0.725	7.9	0.740		12.8	17.7	22.3

Table II. Specific rates and effect of the solvents on CO isotopic exchange on $Fe_3(CO)_9C_2(C_6H_5)_2$ and $Fe_3(CO)_9Te_2$

Complex	Solvent	t °C	$k_2\times10^3$ M^{-1} sec^{-1}	D [a]	$\frac{D-1}{2D+1}$
$Fe_3(CO)_9C_2(C_6H_5)_2$ [b]	n-heptane	40.0	6.0 ±0.1		
		50.0	14 ±1.5		
		60.0	29 ±1.4		
$Fe_3(CO)_9Te_2$	n-heptane	50.0	4.14±0.16 [c]	1.92	0.191
	xylene		4.6 ±0.2	2.40	0.241
	β-β′ diethoxydiethylether		5.5 ±0.2	5.68 [d]	0.379
	chlorobenzene		6.8 ±0.2	5.62	0.378
	n-butyl alcohol		10.0 ±0.2	17.1	0.457
	n-propyl alcohol		14.3 ±0.6	20.1	0.464
	ethyl alcohol		16.8 ±0.9	24.3	0.470
	methyl alcohol		22 ±1	32.6	0.477

[a] Values taken from A. A. Maryott and E. A. Smith «Table of dielectric constants of pure liquids» NBS Circular 514, Aug. 10, 1953. [b] $\Delta H^* = 15.6\pm0.4$ Kcal/mole; $\Delta S^* = -19.0\pm0.8$ e.u. [c] From ref. 2. [d] From ref. 10.

that CO solubility shows only a slight, and in any case linear, variation with temperature, at least in the range in question here.

Results

Second order reaction kinetics for CO isotopic exchange in $Fe_3(CO)_9Te_2$ was observed with all the experimented solvents:

$$\text{rate} = k_2[Fe_3(CO)_9Te_2][CO] \tag{3}$$

The data set out in Table I show that constant values were obtained for k_2, not for k_1 (determined from (2) by taking a = 1 and b = 1 or b = 0, respectively). Table II shows the specific rate values k_2 calculated as the best inclination of the straight line k_1 *vs.* [CO] (the error is the standard deviation).

A second-order reaction of type (3) was also observed in the case of the complex $Fe_3(CO)_9C_2(C_6H_5)_2$. The relevant data are also set out in Tables I and II.

Discussion

Effect of solvents. Close study of the effect of solvents on CO exchange reactions and on the substitution of CO with ligands in the metal carbonyls and their derivatives has only been carried out in a few instances. This is probably due to the fact that the reactions in question take place between neutral molecules and also give rise to non-ionisable neutral molecules, whose polarity is not usually very different from that of the reagents: solvents may thus be presumed to have a small and, in most cases, insignificant effect on reaction rates. Previous studies include those of Angelici and Basolo[11] on CO substitution reactions on $Mn(CO)_5Br$ with ligands, Calderazzo and Cotton[10] and Basolo *et. al.*[12] on CO insertion reactions in $CH_3Mn(CO)_5$, Werner and Prinz[13] and Angelici and Leach[14] on CO substitution with ligands in $Mo(CO)_6$ and in $Ni(CO)_4$, respectively. These workers reported two effects of the solvent: a) as a polar molecule, exercising a purely electrostatic action on the reagent compound and on the activated complex;[10,11] b) as a nucleophile, which will coordinate on the substrate in the place of the dissociated CO molecule:[12,13,14] the resulting kinetics has been described as a « solvent assisted S_N1 mechanism ».

To obtain a better evaluation of these two possible effects, we chosen solvents with different polarity and nucleophilic characters. The polarity of a solvent is determined on the basis of its dielectric constant D: our values (Table II) for D show that the solvents employed covered a wide range (approx. 2÷33). The nucleophilic character of a solvent, however, is not so easily evaluated since there is no parameter expressing this property in quantitative terms: resort must therefore be had to a merely qualitative assessment.

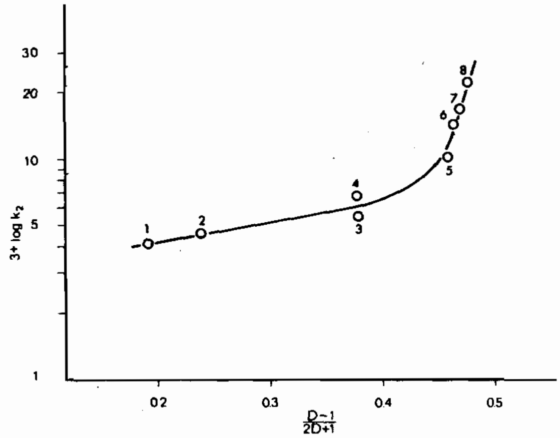

Figure 1. Plot showing the dependence of the specific reaction rates k_2 on the dielectric constants of the solvents. 1: n-heptane; 2: xilene; 3: β-β′-diethoxydiethylether; 4: chlorobenzene; 5: n-buthyl alcohol; 6: n-propyl alcohol; 7: ethyl alcohol; 8: methyl alcohol.

Figure 1 shows log k_2 values as a function of a suitable combination of the solvent dielectric constant, $D-1/2D+1$. A linear behaviour of this function is known to indicate that the solvent has only electrostatic effect, measured in terms of its dielectric constant, whereas deviation from linearity is a sign to the presence of non-electrostatic interactions between solvent, reagents and activated complex.[15] The graph shows that some solvents maintained linearity, whereas the alcohols presented k_2 values that were distinctly higher than those that were deducible on the basis of their D values. In this second group, therefore, we may assume that the solvent molecule acts directly on the reagent complex by coordination in the place of CO, as follows:

$$\begin{gathered} Fe_3(CO)_9Te_2 + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Fe_3(CO)_9Te_2S^* \\ Fe_3(CO)_9Te_2S^* + {}^{14}CO \xrightarrow{k'} Fe_3(CO)_9Te_2 + CO + S \end{gathered} \tag{4}$$

where S the solvent and ^{14}CO the labelled carbon monoxide. On applying to eq. 4 the steady-state condition relating to the activated complex $Fe_3(CO)_9$-Te_2S^* we obtain:

$$\text{rate} = \frac{k_1k'[Fe_3(CO)_9Te_2][S][CO]}{k_{-1}+k'[CO]} = k_{obs}[Fe_3(CO)_9Te_2] \tag{5}$$

from which:

$$k_{obs} = \frac{k_1k'[S][CO]}{k_{-1}+k'[CO]} \tag{6}$$

We may reasonably assume $k'[CO] \langle\langle k_{-1}$ in our experimental conditions, since the concentration value of CO is very small; we can therefore write eq. (6) as:

$$k_{obs} = \frac{k_1k'}{k_{-1}}[S][CO] \tag{7}$$

Eq. (7) expresses a linear relationship between k_{obs} and CO concentration. This agrees with the experimental evidence: [S] can be taken as constant throughout the course of the reaction. On combining (3), (5) and (7) we obtain the following value for the specific second-order rate k_2:

$$k_2 = \frac{k_1k'}{k_{-1}}[S] \tag{8}$$

showing that the ratio $k_2/[S]$ is constant. The values obtained by dividing $k_2 \times 10^3$ by the « molar concentration of the solvent » are: n-butyl alcohol, 0.92; n-propyl alcohol, 1.07; ethyl alcohol, 0.98 and methyl alcohol, 0.89. These values are virtually constant and offer satisfactory proof of the probability that the mechanism suggested is correct.[16]

---

(11) R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, *84*, 2495 (1962).

(12) R. J. Mawby, F. Basolo and R. G. Pearson, *J. Am. Chem. Soc.*, *86*, 3994 (1964).

(13) H. Werner and R. Prinz, *Chem. Ber.*, *99*, 3582 (1966).

(14) R. J. Angelici and B. E. Leach - *J. Organometal. Chem.*, *11*, 203 (1966).

(15) S. Glasstone, K. J. Laidler and H. Eyring. « The Theory of Rate Processes », Mc Graw. Hill New York, N.Y. 1941 pagg. 419-423.

(16) This mechanism may be treated as a simplified example of a more complex mechanism of the type:

$$Fe_3(CO)_9Te_2 + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Fe_3(CO)_9Te_2S^*$$

$$Fe_3(CO)_9Te_2S^* \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Fe_3(CO)_9Te_2S$$

$$Fe_3(CO)_9Te_2S + {}^{14}CO \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} Fe_3(CO)_9Te_2SCO^*$$

$$Fe_3(CO)_9Te_2SCO^* \xrightarrow{k_4} Fe_3(CO)_9Te_2 + S + CO$$

It is, therefore, logical that the solvents involved in this type of reaction should be those with a strongly nucleophilic nature, such as alcohols. The literature does in fact contain reports of complexes derived from the metal-carbonyls in which an alcohol molecule acts as a coordinant;[17] in particular, isolation is reported of the cation complex $[Co(CO)_4\text{-}ROH]^+$, in which the ROH ligand may be substituted by other ligands of the same type, in relation to their differences in nucleophilic power.[18] According to what is reported by these workers, so too in our experimental data CH_3OH was found to be the solvent with the strongest nucleophilic properties.

It may be supposed that the other solvents influence the reaction by means of simple electrostatic interaction with the reagents and the activated complex, as is shown by the linear behaviour of the curve in Figure 1: such solvents are actually poor nucleophiles. The mechanism of exchange here is most probably that which has already been fully demonstrated in the case of n-heptane.

The behaviour of the function log k_2 *vs.* D–1/2D+1 indicates that the polarity of the activated complex is greater than that of the start compound; this agrees with the view that coordination of the entering ligand is on the Te rather than on the Fe.

It may, lastly, be found surprising that a solvent such as diethoxydiethylether, which has outstanding basic character due to the presence of unbonded electron pairs on the oxygen atoms, does not make this property clearly evident during the reaction. This is probably the result of a steric indrance, attributable to the size of the diethoxydiethylether molecule. A phenomenon of this kind is not by any means impossible in the case of the alcohols, too, in addition to their nucleophilic effect: this would tend to favour the coordination of small molecules, such as that of CH_3OH.

Behaviour of $Fe_3(CO)_9Te_2$ and $Fe_3(CO)_9C_2(C_6H_5)_2$. The structure of the complex $Fe_3(CO)_9C_2(C_6H_5)_2$ has been determined by Blount *et. al.*[4] and is very similar to that reported for the $Fe_3(CO)_9X_2$ complexes.[19] In both cases, there is a triangle of Fe atoms, each coordinated with three CO groups and with other ligands (the two chalcogen atoms or the acetylene group). The influence of these ligands is thus exercised on the iron atoms directly and the nine CO groups are thus all equivalent, as shown by the kinetic data.

The structure hypothesised by Blount *et. al.* shows that this complex is of the « electron deficient » type, since $C_2(C_6H_5)_2$ acts as donor of only 4 electrons; this may indicate a greater degree of positivity of the Fe atoms by comparison with the position in the case of chalcogen derivatives. Moreover it must be noted the high-energy-shift of the stretching frequencies in the various complexes: ν_{CO} values vary in the order $C_2(C_6H_5)_2 > S > Se > Te$ and this shows that the increase of positivity of the metal atoms varies in the same order.[2] In the case of the acetylene derivative, therefore, coordination of the incoming CO on Fe is to be expected whereas this was out of the question for the other complexes: the observed S_N2 kinetic may be explained by way of a mechanism which includes the coordination of CO on Fe as the reaction-determining step. Attachment of CO probably takes place on one of the two equivalent Fe atoms that are bonded to each other and to an acetylenic C by means of a tricentric bond, this bond being broken and the acetylenic C displaced on to the other Fe atom. A similar mechanism has been proposed for the reaction

$$Fe_3(CO)_9C_2(C_6H_5)_2 + C_2(C_6H_5)_2 \longrightarrow \underset{\text{(violet isomer)}}{Fe_3(CO)_8[C_2(C_6H_5)_2]_2 + CO}$$

and this shows that the tricentric bond is the probable coordination point of the incoming acetylenic group:[4] our results are fully in line with this hypothesis.

It may be noted, lastly, that the kinetic mechanism studied here indicates that the ligand (CO in our case) takes direct part as a rate determining factor in the attachment on the $Fe_3(CO)_9C_2(C_6H_5)_2$ complex; it also shows that differences in electron attracting power of the R and R′ groups in complexes having the general formula $Fe_3(CO)_9C_2RR'$ may be responsible for differences in electron distribution and hence in reactivity to nucleophile attachment. These two phenomena are probably the cause of the greater difficulty experienced in attaching $CH_3C_2C_6H_5$ to the complex $Fe_3(CO)_9C_2CH_3C_6H_5$ as opposed to the analogous complex $Fe_3(CO)_9C_2(C_6H_5)_2$.[4]

---

in which $Fe_3(CO)_9Te_2S$ represents a hypothetical intermediate corresponding to an energy minimum in the reaction coordinate and similar to the $Fe_3(CO)_9Te_2L$ intermediates identified in substitution reactions with ligands[2]. The mechanism is therefore closely analogous with that previously proposed. If the steady state condition is applied to the two activated complexes and to the intermediate, we obtain an expression of the type:

$$\text{rate} = k_4[Fe_3(CO)_9Te_2SCO^*] \qquad = k_{obs}[Fe_3(CO)_9Te_2]$$

$$k_{obs} = \frac{k_a[S][CO]}{k_b + k_c[CO]}$$

where k_a, k_b and k_c are function of the different specific reaction rates. If $k_b \gg k_c[CO]$, we obtain: $k_{obs} = \dfrac{k_a[S][CO]}{k_b}$ which is completely analogous to (7) in form.

(17) a) W. Hieber and G. Brendel, *Z. Anorg. allg. Chem.*, *289*, 338, (1957). b) W. Hieber and J. Sedlemeier, *Chem. Ber.*, *86*, 700 (1953). c) I. Wender, H. W. Sterberg and M. Orchin, *J. Am. Chem. Soc.*, *74*, 1216 (1952).

(18) E. R. Tucci and B. H. Gwynn, *J. Am. Chem. Soc.*, *86*, 4838 (1964).

(19) a) L. F. Dahl and P. W. Sutton, *Inorg. Chem.*, *2*, 1067 (1963). b) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, *4*, 493 (1965).