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The Acid Attack on Octahedral Tris(dithio- or diseleno-carbamate)iron(III). A Kinetic Study in Benzene

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The kinetics of the reaction of Fe(modsc)$_3$ and Fe(et$_2$dtc)$_3$ (where modsc = morpholinediselenocarbamate and et$_2$dtc = diethyldithiocarbamate) with chloroacetic acids (labelled HX) to produce the pentacoordinated species Fe(modsc)$_2$X and Fe(et$_2$dtc)$_2$X have been investigated by a spectrophotometric method in benzene.

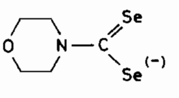
A reaction mechanism is proposed and the difference in kinetic behaviour between dsc and dtc derivatives is tentatively explained.

Introduction

In a previous paper [1] we reported that Fe(dsc)$_3$ reacted with HCl to yield the pentacoordinated Fe(dsc)$_2$Cl derivatives, according to eqn. (1), as found for Fe(dtc)$_3$ [2]

$$FeL_3 + HCl \longrightarrow FeL_2Cl + HL \qquad (1)$$

where L = dithio or diseleno carbamic ligand. In this paper we report the kinetic study of the substitution reaction (1) of mono-, di- and tri-chloroacetic acids**, labelled HMCA, HDCA and HTCA respectively, or HX collectively, on FeL$_3$ complexes where L is



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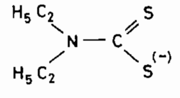

(modsc) (et$_2$dtc)

The reaction medium is benzene, in which the complexes are soluble and quite inert.

Results and Discussion

The progress of the reaction was followed spectrophotometrically by monitoring the changes in absorbance values at the wavelength at which $|\epsilon_{product} - \epsilon_{reagent}|$ = maximum, *i.e.* at 434 nm for Fe(modsc)$_3$ and at 442 nm for Fe(et$_2$dtc)$_3$.

An isosbestic point in the explored range (at 469 nm and 417 nm for Fe(modsc)$_3$ and Fe(et$_2$dtc)$_3$ respectively), present for *ca.* 65% of the reaction, demonstrates that the decomposition process of the pentacoordinated species is rather slow; hence the kinetic curves were analyzed until the isosbestic point persisted.

By plotting the absorbances of the dsc derivatives against time and by extrapolating them to zero time, we obtained an A_0' value which differs from the absorbance value A_0 read before the acid addition. This change in absorbance suggests an unmeasurably rapid process, but unfortunately the difference between A_0 and A_0' is too highly affected by the uncertainty in the A_0' value to provide any information about the kinetics of this process.

Working in high excess of chloroacetic acid, *i.e.* in pseudo-first order with respect to the entering ligand, the reaction is of the first order with respect to the substrate; in fact by plotting $\ln(A_\infty - A_t)$ against time, straight lines were obtained whose slopes are the k_{obs}.

The k_{obs} dependence on the HX concentration is shown in Fig. 1 where, as trend pattern, the plot k_{obs}/[HDCA] is reported.

Then the rate equation must be:

$$k_{obs} = k_1 + k_2[HX] \qquad (2)$$

The k_1 and k_2 specific rate constant values, obtained as intercept and slope of the plots k_{obs}/[HX], are listed in Table I.

On the basis of these results we suggest the following mechanism:

$$\begin{tikzcd}[FeL_2L{\cdot}HX] \arrow[r, "k_1"] \arrow[r, bend right=60, "k_2", "+HX"'] & FeL_2X\end{tikzcd} \qquad (3)$$

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**HCl makes the reaction too fast for our spectrophotometric determinations.

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TABLE I. $10^3 k_1$ (sec^{-1}) and $10^3 k_2$ ($l\,mol^{-1}\,sec^{-1}$) obtained from the Intercept and the Slope of the Plots $k_{obs}/[HX]$.

°C	HTCA			HDCA			HMCA		
	k_1	k_2	r^a	k_1	k_2	r^a	k_1	k_2	r^a
10	0.41 ± 0.01	3.9 ± 0.2	0.998	0.25 ± 0.01	1.73 ± 0.06	0.999	0.10 ± 0.02	3.3 ± 0.1	0.998
15	0.55 ± 0.02	5.5 ± 0.2	0.997	0.41 ± 0.01	2.89 ± 0.05	0.999	0.16 ± 0.02	4.7 ± 0.1	0.999
20	0.74 ± 0.02	7.8 ± 0.2	0.999	0.56 ± 0.01	3.9 ± 0.2	0.999	0.22 ± 0.02	7.2 ± 0.3	0.998
25	0.98 ± 0.02	11.0 ± 0.2	0.999	0.86 ± 0.01	6.0 ± 0.2	0.998	0.34 ± 0.02	9.8 ± 0.2	0.999
30	1.38 ± 0.03	14.5 ± 0.4	0.998	1.29 ± 0.02	8.4 ± 0.3	0.999	0.46 ± 0.05	13.5 ± 0.5	0.998
E_a	10.2 ± 0.3	11.3 ± 0.3		13.7 ± 0.3	13.3 ± 0.4		13.0 ± 0.9	12.1 ± 0.3	
$\Delta H^{\neq}$	9.6 ± 0.3	10.7 ± 0.3		13.1 ± 0.3	12.7 ± 0.4		12.4 ± 0.9	11.5 ± 0.3	
$\Delta S^{\neq}$	−40 ± 3	−31 ± 1		−28 ± 3	−26 ± 1		−33 ± 1	−29 ± 1	
r^b	0.999	1.000		0.998	0.999		0.998	0.999	

E_a, $\Delta H^{\neq}$ = Kcal mol^{-1}; $\Delta S^{\neq}$ = cal $mol^{-1}\,K^{-1}$. [a] r = correlation coefficient for the plot $k_{obs}/[HX]$. [b] r = correlation coefficient for the Arrhenius plot.

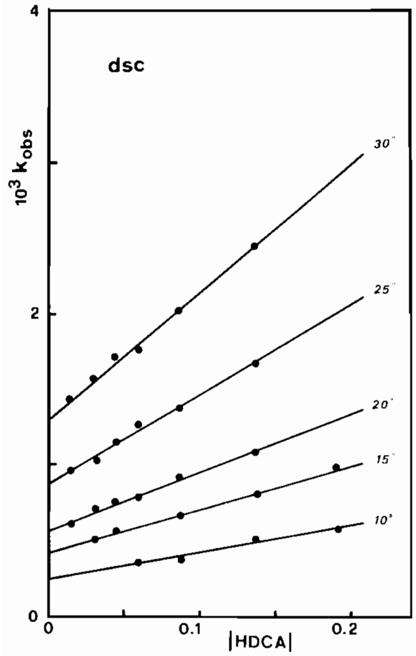

Fig. 1. Dependence of k_{obs} values on the HDCA concentration at various temperatures in $Fe(modsc)_3$ reactions.

in which the observed reactant is not the FeL_3 species, but its protonated derivative $[FeL_2L{\cdot}HX]$.

In fact : i) the initial change in absorbance values indicates that the reaction proceeds via a very rapid production of an intermediate species which then undergoes the observed transformation; ii) although the specific rate of the k_1 process is not dependent on the entering nucleophile concentration, [HX], we observe the k_1 dependence on the acid strength, showing that the reactant is not $Fe(modsc)_3$, but its HTCA-, HDCA-, HMCA- adducts which are able to react differently.

Very probably the intermediate species is an adduct due to the interaction between the proton of HX molecule and the $\geq NCSe_2$ group of the complexed ligand. In fact, in our several attempts using non-protonic acids, the reaction did not occur while it was very fast with HCl or other strong mineral acids.

This interaction produces a decrease of the electron density between the metal and the selenium atoms with a consequent lengthening of the linkage. Thus a nucleophilic attack on Fe may proceed both by the X ion of the hydrogen-bonded HX molecule (step related to k_1, independent of HX concentration), and by another HX molecule acting as nucleophile (step related to k_2, dependent on HX concentration).

The very negative activation entropy values suggest that the k_1 process is not a simple dissociative step.

The unexpected reactivity sequence in the k_2 process (HDCA $\ll$ HMCA $\simeq$ HTCA) may be explained by taking into account the fact that the acid strength and the donor ability of chloroacetic acids increase in opposite sequence.

As far as the $Fe(et_2dtc)_3$ reaction is concerned, we observe some divergence from the dsc behaviour: i) the absorbance value extrapolated at zero time, A'_o, coincides with the experimental value A_o; ii) by plotting k_{obs} values (obtained as slope of $\ln(A_\infty - A_t)/t$) against HX concentration, straight lines are obtained, but these cross the origin of the axis (see Fig. 2), iii) the sequence of the specific rates (HDCA > HMCA) follows the acid strength; iv) the enthalpy values are reduced by one half and the entropy values increased. Therefore we think that the observed steps in the dsc and dtc kinetics cannot be attributable to the same process.

We suggest that the observed step in the $Fe(dtc)_3$ reaction is due to the addition of an HX molecule to

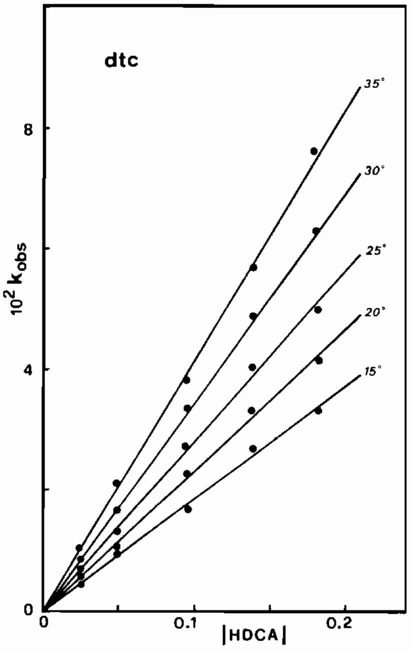

Fig. 2. Dependence of k_{obs} values on HDCA concentration at various temperatures in $Fe(et_2dtc)_3$ reactions.

TABLE II. 10^3 k (l mol^{-1} sec^{-1}) obtained from the Slope of the Plots k_{obs}/[HX].

°C	HDCA		HMCA	
	k	r^a	k	r^a
15	18.6 ± 0.5	0.999	5.6 ± 0.1	0.999
20	23.4 ± 0.6	0.999	7.2 ± 0.1	1.000
25	28.1 ± 0.8	0.999	9.6 ± 0.2	0.999
30	34.6 ± 0.4	1.000	10.4 ± 0.2	0.999
35	41.5 ± 0.8	0.999	13.9 ± 0.4	0.999
E_a	7.2 ± 0.2		7.7 ± 0.4	
$\Delta H^{\neq}$	6.6 ± 0.2		7.1 ± 0.4	
$\Delta S^{\neq}$	−43 ± 2		−44 ± 2	
r^b	0.999		0.990	

E_a, $\Delta H^{\neq}$ = Kcal mol^{-1}; $\Delta S^{\neq}$ = cal mol^{-1} $°K^{-1}$. [a]r = correlation coefficient for the plot k_{obs}/[HX]. [b]r = correlation coefficient for the Arrhenius plot.

the $=NCS_2$ group.* Then the unstabilized $Fe(et_2dtc)_2(et_2dtc \cdot HX)$ rapidly evolves into the pentacoordinated species. The reaction may therefore be synthesized in the form:

$$Fe(et_2dtc)_3 + HX \xrightarrow{k} Fe(et_2dtc)_2X + Het_2dtc \quad (4)$$

in which $k_{obs} = k\,[HX]$.

Also, in the substitution reaction on dithiocarbamate complexes of octahedrally coordinated Co(III) [9], the hydrogen bond precedes the nucleophilic attack on the metal centre.

The proposed mechanisms moreover agree with the previously reported studies of the acid attack on the inner salts of dithio and diseleno carbamic acids [3,4].

In conclusion we think that, both in free dsc or dtc ligand and in their iron(III) complexes, the first stage of the reaction is the protic attack of the acid molecule HX on the basic system of a ligand group, which produces an intermediate adduct species. This occurs very rapidly in dsc compounds, while in the case of dtc it is the rate determining step. Then the dsc adduct changes into the pentacoordinate species by means of two competitive rate determining steps, while the dtc intermediate evolves too quickly to be observed.

Experimental

Reagents

$Fe[O(C_2H_4)_2NCSe_2]_3$ and $Fe[(C_2H_5)_2NCS_2]_3$ were prepared as previously reported [1, 2].

Chloroacetic acids and solvents were of spectrophotometric grade and were used without further purification.

Instruments and Procedure

The spectrophotometric measurements were performed on a Perkin-Elmer mod. 402 recording instrument equipped with a thermostat-controlled cell compartment (±0.05 °C). The spectra were recorded in the range 390–590 nm.

The kinetics were studied at 434 nm for the dsc derivative ($\epsilon_{Fe(modsc)_3}$ = 9700 ± 20; $\epsilon_{Fe(modsc)_2X}$ = 3650–3400)* and at 442 nm for the dtc complex ($\epsilon_{Fe(et_2dtc)_3}$ = 8800 ± 30; $\epsilon_{Fe(et_2dtc)_2X}$ = 4500 ± 40). Each run was carried out in pseudo first order condition by adding a convenient amount of HX solution (about 1 *M*, in benzene) to 3 ml of FeL_3 in C_6H_6 solution (all solutions at constant temperature). The k_{obs} values are the average of 3–6 runs. The straight lines were calculated by the least squares method and the curves were averaged by our program of multiple regression.

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*Increases in the Fe–S bond length and in the magnetic moment are observed in the $Fe(modtc)_3$ molecule with H.B.D. acids, such as CH_2Cl_2, $CHCl_3$, H_2O, as a result of hydrogen bonding [5, 7]. Moreover recent studies have shown that a thiolato sulphur atom coordinated to a metal centre retains considerable Lewis basicity [8].

*$Fe(modsc)_2X$ is not stable in solid state. The $\epsilon_{Fe(modsc)_2X}$ values were calculated by using the A_∞ absorbance values obtained from a very fast stoichiometric transformation of a known amount of $Fe(modsc)_3$ into $Fe(modsc)_2X$ by means of a known high excess of chloroacetic acid.

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References

1 D. De Filippo, P. Deplano, A. Diaz and E. F. Trogu, *Inorg. Chim. Acta, 17,* 139 (1976).
2 R. L. Martin and A. H. White, *Inorg. Chem., 6,* 712 (1967).
3 F. Cristiani, F. Devillanova and G. Verani, *Tetrahedron, 33,* 1003 (1977).
4 F. Cristiani, F. Devillanova and G. Verani, *Rend. Sem. Fac. Sci., (A.K.) 47,* 33 (1977).
5 R. J. Butcher and E. Sinn, *J. Am. Chem. Soc., 98,* 2440 (1976); *Idem, 98,* 5159 (1976).
6 R. J. Butcher and E. Sinn, *J. Chem. Soc. Dalton,* 2518 (1975).
7 P. C. Healy and E. Sinn, *Inorg. Chem., 14,* 109 (1975).
8 I. K. Adzamli, D. L. Nosco and E. Deutsch, *J. Inorg. Nucl. Chem., 42,* 1364 (1980).
9 P. Deplano and E. F. Trogu, *IVX Congresso A.I.C.I.,* Turin (1981).