Mechanism of the Reaction of Iron(III) Dithiocarbamates with Iodine

Guido Crisponi, Paola Deplano, and Emanuele F. Trogu *
Istituto di Chimica Generale, Inorganica ed Analitica, Università degli Studi di Cagliari, I09100 Cagliari, Italy

The reaction between $[Fe(S_2CNR_2)_3]$ (R = CH_2Ph or Et, NR_2 = morpholino) and iodine in methylene chloride has been studied by means of spectrophotometric methods. Intermediate and product spectroscopic analyses have led to the following reaction scheme:

$$[Fe(S_2CNR_2)_3] + I_2 \overset{K_{eq}}{\rightleftharpoons} [Fe(S_2CNR_2)_3]\cdot I_2 \underset{k_2,\ -\frac{1}{2}I_2}{\overset{k_1,\ +\frac{1}{2}I_2}{\rightleftharpoons}} [Fe(S_2CNR_2)_3]^+ + I_3^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [Fe(S_2CNR_2)_2I] + \tfrac{1}{2}(S_2CNR_2)_2 + I_2$$

A fast equilibrium reaction to give a 1 : 1 adduct $[Fe(S_2CNR_2)_3]\cdot I_2$ precedes oxidation of iron(III) to iron(IV) to give $[Fe(S_2CNR_2)_3]I_3$, which is in equilibrium with the five-co-ordinated $[Fe(S_2CNR_2)_2I]$, tetra-alkylthiuram disulphide, and iodine.

Iodine has been extensively used as an oxidizing agent towards dithiocarbamato-derivatives. It is known that it can give rise to (*i*) metal oxidation as in the reaction with gold(I), copper(II), and nickel(II) derivatives,[1] (*ii*) ligand oxidation as in the case of zinc(II), cadmium(II), and mercury(II) dithiocarbamates,[2] and (*iii*) several types of products as with dithiocarbamatoiron(III).[3] However, the mechanisms of these reactions have not yet been studied.

We have recently shown that tris(dithio- and tris(diselenocarbamato)cobalt(III)[4] and tris(dithiocarbamato)chromium(III)[5] give 1:1 charge-transfer (c.t.) adducts with iodine. Moreover we have observed that a c.t. adduct between the reagents is a precursor in the oxidation of bis(morpholinoselenocarbonyl) triselenide[6] and bis(morpholinothiocarbonyl) disulphide[7] with iodine.

In order to clarify and hopefully to find a general mechanism for these reactions we are at present investigating the reactivity of dithiocarbamato-derivatives towards iodine. We report here the results obtained with some iron(III) dialkyldithiocarbamates. The reaction of iodine with iron(III) tris(dialkyldithiocarbamates) in aprotic solvents was initially reported by Pasek and Straub[3] and then by others.[8,9] It yielded a variety of products, and although a study of the effects of the solvent, temperature, and concentration of the absorbing species was not undertaken it was suggested that the nitrogen substituents R affect the course of the reaction and consequently the composition of the products, *e.g.* $[Fe(S_2CNR_2)_2I_2]$ (R = Me, Pr^i, *etc.*) and $[Fe(S_2CNR_2)_3]I_3$ (R = CH_2Ph or Pr^i).

Electrochemical studies on a series of $[Fe(S_2CNR_2)_3]$ derivatives in aprotic solvents[10] have defined their oxidation as a one-electron reversible process, $[Fe(S_2CNR_2)_3] \rightleftharpoons [Fe(S_2CNR_2)_3]^+ + e$, and moreover have described the effect of the nitrogen substituents R on the redox potential, showing, *inter alia*, that the dibenzyl derivative is the least easy to oxidize of the derivatives studied. Moreover chronopotentiometric studies with the current reversed[11] have shown that the activation energies of the process $[Fe(S_2CNR_2)_3] \longrightarrow [Fe(S_2CNR_2)_3]^+$ are low and in a rather narrow range. The discrepancy between the electrochemical results[10] and those obtained in the preparative study[3] adds further interest to the investigation of this reaction.

Experimental

Materials.—The compounds $[Fe(S_2CNR_2)_3]$,[12] $[Fe(S_2CNR_2)_2I]$,[13] $[Fe(S_2CNR_2)_3]I_3$,[8] $[Fe(S_2CNR_2)_3]BF_4$,[14] and $(S_2CNR_2)_2$[15] (R = CH_2Ph or Et, NR_2 = morpholino) were synthesized by literature methods. Doubly sublimed iodine was purchased from Carlo Erba. Methylene chloride was Merck Reagent Grade and stored over 4-Å molecular sieves.

Instrumentation.—U.v.-visible spectra were obtained by means of a Cary model 219 spectrophotometer equipped with a Lauda K2RD thermostat (±0.1 °C), using 1.00- and 0.10-cm matched quartz cells. All the calculations were performed on a HP-85 Hewlett-Packard computer programmed in BASIC.

Reactions.—The progress of the reaction between $[Fe(S_2CNR_2)_3]$ and iodine was followed at 20 °C, by monitoring the absorbances *versus* time at 295 nm using 1- and 0.1-cm quartz cells. For each derivative, 6—16 kinetic runs were performed at a constant complex concentration (about 2×10^{-5} and 2×10^{-4} mol dm^{-3}) and increasing the amount of iodine from $[I_2]:[Fe(S_2CNR_2)_3]$ ratios of 1:1 up to 50:1. The complete u.v.-visible spectra of the reaction mixtures were also recorded after 300 s and after 24 h ('infinite' time).

An experiment under the same conditions but with argon-degassed solutions gave similar results, showing no evidence of O_2 activity in this reaction.

Calculations.—The absorbance data *vs.* time were analyzed with the program KINET written in BASIC which performs a numerical integration of the differential equations (1) and (2) taking into account the equilibrium (3) and the mass relations (4) and (5) where $[I_2]_T$ and $[Fe]_T$ are the starting concentrations of I_2 and $[Fe(S_2CNR_2)_3]$ respectively.

$$d[Fe(S_2CNR_2)_3{}^+]/dt = k_1[Fe(S_2CNR_2)_3\cdot I_2] - k_2[Fe(S_2CNR_2)_3{}^+] - k_3[Fe(S_2CNR_2)_3{}^+] + k_4[I_2][Fe(S_2CNR_2)_2I] \quad (1)$$

$$d[Fe(S_2CNR_2)_2I]/dt = k_3[Fe(S_2CNR_2)_3{}^+] - k_4[I_2][Fe(S_2CNR_2)_2I] \quad (2)$$

$$[Fe(S_2CNR_2)_3] + I_2 \overset{K_{eq}}{\rightleftharpoons} [Fe(S_2CNR_2)_3]\cdot I_2 \quad (3)$$

$$[I_2]_T = [I_2] + [Fe(S_2CNR_2)_3\cdot I_2] + \tfrac{3}{2}[Fe(S_2CNR_2)_3{}^+] + \tfrac{1}{2}[Fe(S_2CNR_2)_2I] \quad (4)$$

$$[Fe]_T = [Fe(S_2CNR_2)_3] + [Fe(S_2CNR_2)_3{}^+] + [Fe(S_2CNR_2)_3\cdot I_2] + [Fe(S_2CNR_2)_2I] \quad (5)$$

Table. Formation constants, ε values, and kinetic constants for the reaction of iron(III) dithiocarbamates with iodine

	$10^{-3}\ K_{eq}$	$10^{-3}\ \varepsilon_{295}$	k_1	k_2	$10^4\ k_3$	k_4
	$dm^3\ mol^{-1}$	$dm^3\ mol^{-1}\ cm^{-1}$	s^{-1}			$dm^3\ mol^{-1}\ s^{-1}$
$[Fe(S_2CNC_4H_8O)_3]$	2.7 ± 0.2	28.5 ± 0.7	$(6.0 \pm 0.5) \times 10^{-2}$	$(7 \pm 1) \times 10^{-3}$	1.3 ± 0.2	0.5 ± 0.1
$[Fe(S_2CNEt_2)_3]$	5.0 ± 0.3	30.1 ± 0.7	$(9 \pm 1) \times 10^{-3}$	$(2 \pm 1) \times 10^{-4}$	2.2 ± 0.5	4.9 ± 0.5
$[Fe\{S_2CN(CH_2Ph)_2\}_3]$	2.3 ± 0.2	53.0 ± 0.9	$(9.5 \pm 0.5) \times 10^{-2}$	$(7.5 \pm 0.8) \times 10^{-3}$	2.0 ± 0.2	0.6 ± 0.1

The values of K_{eq} and ε_{295}, and the relative errors, were estimated by our least-squares program KEPS 1 : 1[5] using zero time values obtained by a sixth-degree polynomial regression as experimental absorbances. The reported k values and the relative errors are respectively the mean values and the standard deviations of their individual determinations from 16 kinetic runs for the dibenzyl derivative and 6 for the morpholino and diethyl cases, at different $[I_2]:[Fe(S_2CNR_2)_3]$ ratios. Optimization of the kinetic constants was performed for each run by use of the least-squares program KINET.

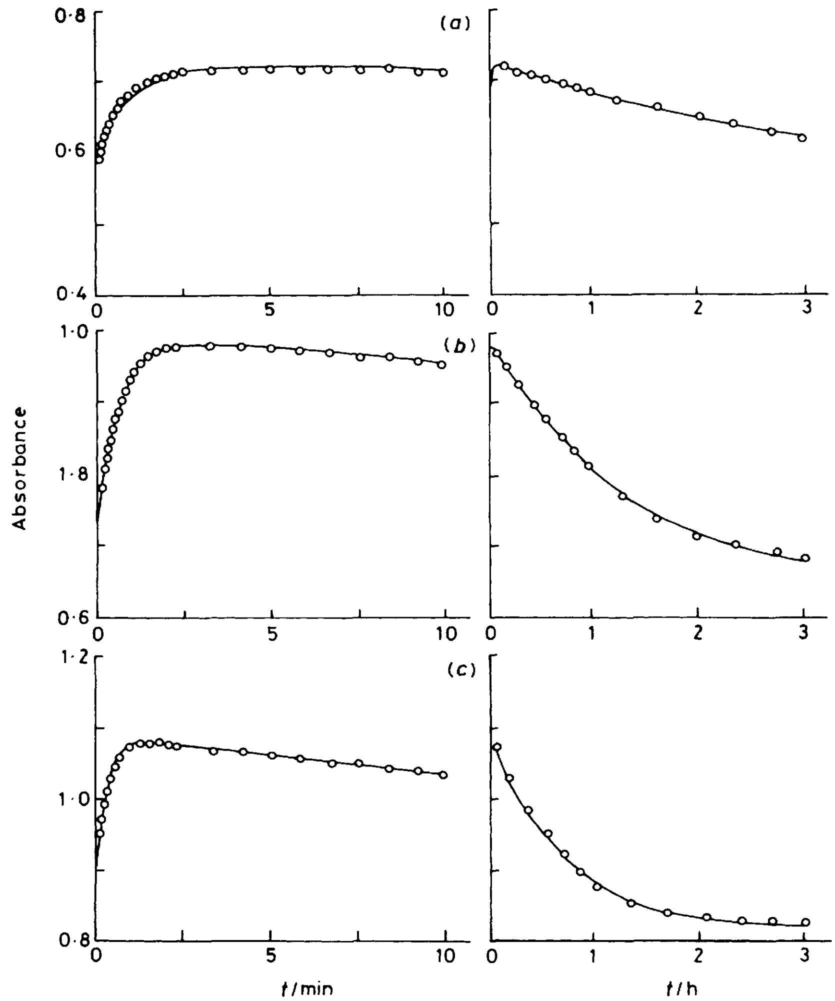

Figure 1. Trends in absorbance at 295 nm, calculated from the parameters in the Table (full lines) and experimental points (○) for three kinetic runs at 20 °C in CH_2Cl_2. Initial concentration of $[Fe\{S_2CN(CH_2Ph)_2\}_3]$ = 2.41×10^{-5} mol dm^{-3}. Concentration of iodine = 2.41×10^{-5} (*a*), 1.2×10^{-4} (*b*), and 3.6×10^{-4} mol dm^{-3} (*c*)

Knowing the molar absorption coefficients of the various species, we can calculate the absorbance of the reaction mixture at any time. The values of the parameters were obtained by a Gauss–Newton non-linear least-squares procedure, minimizing the sum of the squares of the deviations between the experimental and calculated absorbances. The derivatives of the absorbance with respect to the kinetic parameters were evaluated numerically. The program gave a good convergence to the final estimates of the parameters which are obtained as output together with their standard deviations and correlation coefficients.

The direct reaction (step k_1) is first order with respect to the adduct concentration, $[Fe(S_2CNR_2)_3{\cdot}I_2]$, which depends on I_2. Therefore the oxidant I_2 enters in the rate law indirectly. A first-order rate constant (step k_3) gave a better fit than a rate law dependent on the concentration of I_3^-. This does not imply a

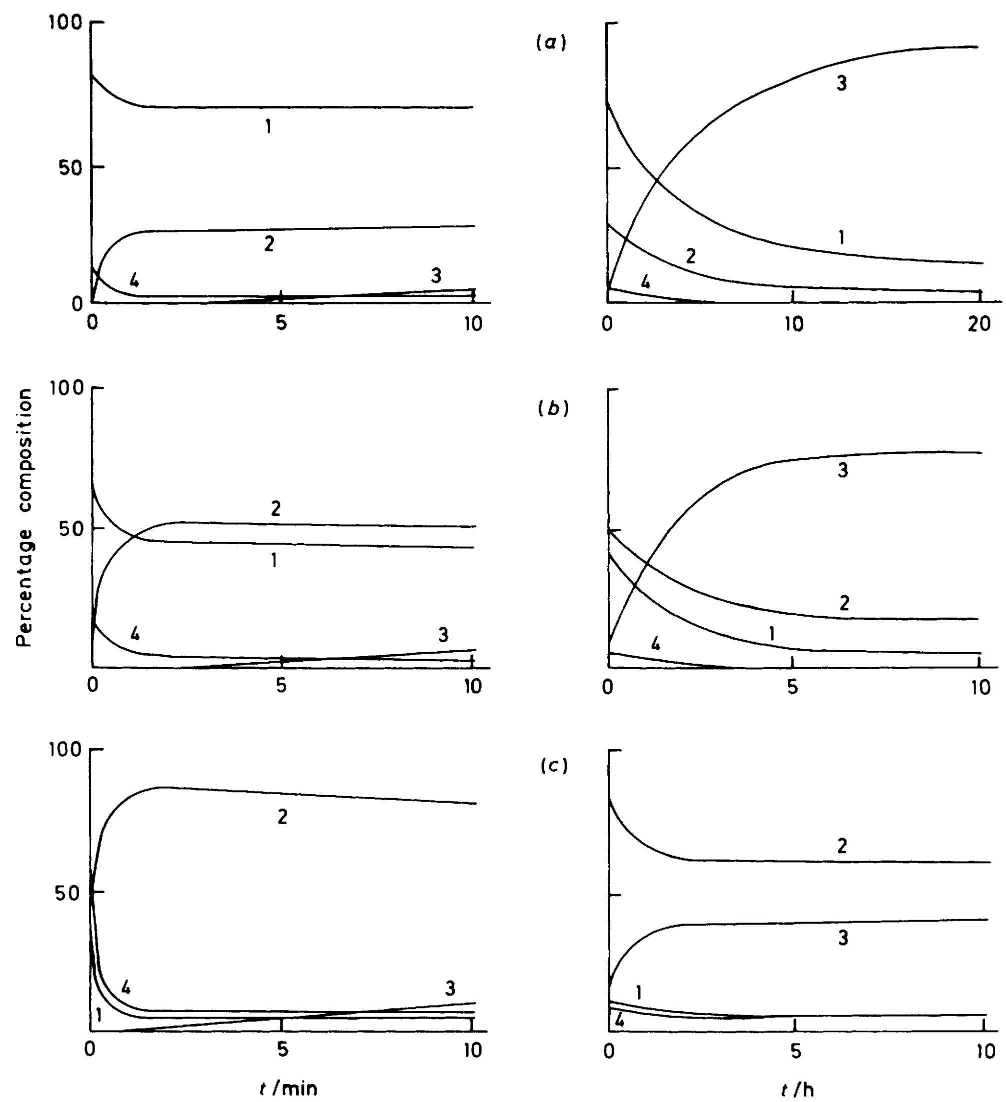

Figure 2. Time dependence of the concentrations of the various species: 1, $[Fe(S_2CNR_2)_3]$; 2, $[Fe(S_2CNR_2)_3]I_3$; 3, $[Fe(S_2CNR_2)_2I]$; 4, $[Fe(S_2CNR_2)_3]{\cdot}I_2$; calculated with the k values in the Table for $[Fe\{S_2CN(CH_2Ph)_2\}_3]$ (initial concentration = 1.96×10^{-4} mol dm^{-3}). Concentration of iodine = 0.98×10^{-4} (*a*), 1.96×10^{-4} (*b*), and 7.84×10^{-4} mol dm^{-3} (*c*)

redox step independent of I^-. In fact in the presence of I_2, I^- is associated according to the equlibrium $I^- + I_2 \overset{K'_{eq}}{\rightleftharpoons} I_3^-$, therefore its concentration is given by $[I^-] = [I_3^-]/K'_{eq}[I_2]$. Since K'_{eq} is very large and $[I_3^-]$ is also dependent on $[I_2]$, $[I^-]$ is regarded as very low and constant.

The formation constants for the adduct were calculated from absorbances extrapolated to zero time using a sixth-degree polynomial regression, using our least-squares program KEPS 1:1[5] (see Table).

Results and Discussion

The reaction of iodine with $[Fe(S_2CNR_2)_3]$ (R = CH_2Ph or Et, NR_2 = morpholino) in CH_2Cl_2 has been followed spectrophotometrically in the u.v.–visible range at 20 °C. In a typical experiment, the change of the absorbance with time was followed at 295 nm for a set of solutions containing constant concentrations of $[Fe(S_2CNR_2)_3]$ and various amounts of iodine in the ratio 1:1 to 1:50.

In Figure 1 some examples of plots of absorbance *versus* time are shown for $[Fe\{S_2CN(CH_2Ph)_2\}_3]$ ($c = 2.41 \times 10^{-5}$ mol dm^{-3}). The other derivatives exhibited similar behaviour. These plots show three distinct features. (*a*) The absorbance extrapolated to zero time (obtained by fitting the plots over the first 300 s with a sixth-degree polynomial)[16] is higher than the sum of the initial absorbances of the individual reagents, and increases with the iodine concentration. This can be explained by taking into account the existence of a fast equilibrium between the reagents. From the extrapolated absorbances and by applying a method previously described[5] for a 1:1 stoicheiometry, the equilibrium constants and the molar absorption coefficients reported in the Table were evaluated.

The existence of association equilibria between iodine and tris(dialkyldithiocarbamates) of Cr^{III} and Co^{III} has been recently demonstrated by us.[4,5] Spectroscopic evidence showed that stable 1:1 c.t. adducts are formed, and that this interaction mainly involves a sulphur atom of a ligand (which retains its basic properties even though co-ordinated). We suggest that

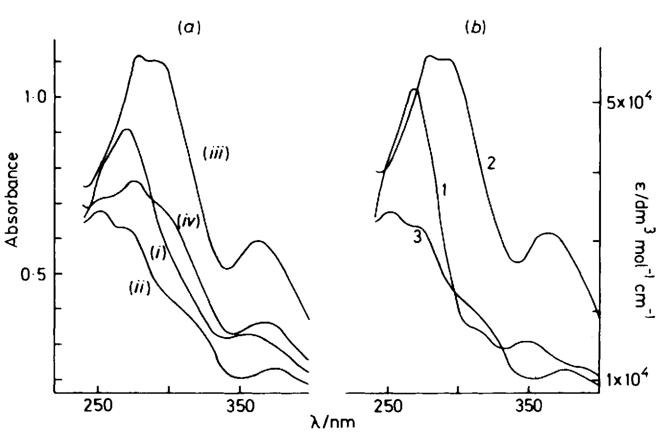

Figure 3. (*a*) The experimental spectra of a reaction mixture in CH_2Cl_2 at 20 °C and initial concentration of $[Fe\{S_2CN(CH_2Ph)_2\}_3]$ = 1.96×10^{-4} mol dm^{-3} at different reaction times and initial iodine concentrations: 1.96×10^{-4} mol dm^{-3}, t = 4 min (*i*) and 24 h (*ii*); 7.84×10^{-4} mol dm^{-3}, t = 4 min (*iii*), and 24 h (*iv*). (*b*) The experimental spectra of $[Fe\{S_2CN(CH_2Ph)_2\}_3]$ (1), $[Fe\{S_2CN(CH_2Ph)_2\}_3]I_3$ (2), and the sum of $[Fe\{S_2CN(CH_2Ph)_2\}_2I]$ and $[S_2CN(CH_2Ph)_2]_2$ (3)

also in the $[Fe(S_2CNR_2)_3] + I_2$ case the species in equilibrium with the reagents is a c.t. adduct.

(*b*) The absorbance increases according to a first-order law and reaches a plateau whose value depends on the initial iodine concentration. This behaviour suggests a kinetic process going to an equilibrium position. The spectrum of the solution at equilibrium indicates the presence of $[Fe(S_2CNR_2)_3]I_3$.

(*c*) The absorbance then decreases according to a first-order law (much slower than in the above step), reaching a value still dependent on the iodine concentration. As above, this step is indicative of a kinetic process going to equlibrium. The final spectrum shows the presence of $[Fe(S_2CNR_2)_2I]$, $(S_2CNR_2)_2$, and I_2 when the reagent ratio is 1:1, and in addition increasing amounts of $[Fe(S_2CNR_2)_3]I_3$ as the iodine concentration rises.

We therefore propose the following reaction Scheme, which seems to be that which best fits the experimental data. The values of k_1, k_2, k_3, and k_4 have been calculated by numerical integration of the absorbance data as described in the Experimental section, and are reported in the Table.

$$[Fe(S_2CNR_2)_3] + I_2 \xrightleftharpoons{K_{eq}} [Fe(S_2CNR_2)_3]{\cdot}I_2 \xrightleftharpoons[k_{2},\ -\frac{1}{2}I_2]{k_{1},\ +\frac{1}{2}I_2}$$
$$[Fe(S_2CNR_2)_3]^+ + I_3^- \xrightleftharpoons[k_4]{k_3}$$
$$[Fe(S_2CNR_2)_2I] + \tfrac{1}{2}(S_2CNR_2)_2 + I_2$$

Scheme.

The time dependences of the concentrations of the various species calculated by using the reported constants (see Table) are plotted in Figure 2 for the case of R = CH_2Ph, and by means of these the calculated absorbances can be compared with the experimental ones (Figure 1). The absorbances calculated at 4 min and at infinite time for the 1:1 ratio case show a good correspondence with the experimental spectra (Figure 3).

The proposed mechanism is followed by all the iron(III) tris-(dithiocarbamates) studied, and is expected to be of general applicability. The following points support this conclusion. (*a*) The effect of the substituents R on the redox potential of $[Fe(S_2CNR_2)_3]$ has been extensively studied by Martin and co-workers,[10] and the experimentally observed sequence of the ease of oxidation (dibenzyl and aryl substituents < saturated chains < α-branched, saturated chains) has been rationalized in terms of electronic and steric effects related to the R_2N group. Since iodine easily oxidizes $[Fe\{S_2CN(CH_2Ph)_2\}_3]$ to the iron(IV) derivative, this process is even more facile with the other derivatives. (*b*) In non-acidic media, $[Fe(S_2CNR_2)_3]$ complexes are inert towards nucleophiles X such as Cl^- or I^-, while the reaction of X with $[Fe(S_2CNR_2)_3]^+$ results in the immediate formation of $[Fe(S_2CNR_2)_2X]$ and $(S_2CNR_2)_2$ in stoicheiometric amounts.

We therefore think that the previously invoked hypothesis that the nature of the substituents R is the main factor influencing the composition of the products [five-co-ordinated iron(III) or octahedral iron(IV)] should be rejected. The possibility of isolating the iron(IV) or iron(III) species seems to depend on the concentrations of the reagents, as revealed by the equilibrium constants involved.

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