FORMATION AND OXIDATION–REDUCTION CHANGES
OF THE CYANATE COMPLEXES OF IRON IN METHANOL

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The formation and oxidation–reduction changes of the cyanate complexes of iron in methanol were investigated by spectrophotometric methods. It was found that the addition of cyanate to solutions of both ferric and ferrous salts always leads to the formation of a Fe(III) complex, which is, in the case of a ferrous salt, formed after the oxidation-reduction changes discussed in this paper. The oxidation of the initial ferrous salt is complete if $Fe(ClO_4)_2$ is used, but with $FeCl_2$ an equilibrium is formed, the equilibrium mixture containing about 75% Fe(III) The rate of the oxidation of Fe(II) to Fe(III) is considerably retarded if atmospheric oxygen is removed. For complete oxidation, an $[Fe(II)] : [NCO^-]$ ratio equal to at least 1 : 3 is required, which is stoichiometrically necessary for the formation of a binuclear complex with cyanate groups acting as bridges between the two iron atoms.

Only relatively few data are available[1-9] on the formation and stability of the cyanate complexes of the transition metals in solution. Quastlerová and Valtr[10-12] studied the formation and time changes of cyanate copper(II) complexes in methanol and acetone. They explained the changes observed in methanol solution[12] by oxidation–reduction processes conditioned by the mutual influences of ligands in complexes with a heterogeneous co-ordination sphere.

The present paper is linked with these results; spectrophotometric methods are employed fo. the study of the formation of the cyanate complexes of iron and their oxidation-reduction changes in methanol solutions.

EXPERIMENTAL

Sodium cyanate was prepared according to the ref.[13]; ferrous perchlorate was prepared by the reaction[14] of FeS with $HClO_4$ p.a. and was recrystallized several times. Ferric perchlorate was prepared by the reaction[14] of $Fe(OH)_3$ with $HClO_4$ p.a., and ferric chloride by direct synthesis from the elements, being purified by repeated sublimation in a stream of chlorine. Ferrous chloride was prepared by the reduction of $FeCl_3$ with hydrogen. Methanol p.a. was pre-dried with metallic sodium, distilled, dried with magnesium, re-distilled, and rectified. The absorption spectra of solutions in the UV region were measured with the SF 4 spectral photometer (USSR) and with the CF 4 recording spectral photometer (Optica, Milan). The absorption spectra

of solutions in the visible region were measured with the S F 10 recording spectral photometer (USSR).

RESULTS

The isomolar series $(5 . 10^{-4} M)$, $Fe(ClO_4)_2.6 H_2O$-NaNCO-CH_3OH, $FeCl_2$-NaNCO-CH_3OH, $Fe(ClO_4)_3.10 H_2O$-NaNCO-CH_3OH, $FeCl_3$-NaNCO-CH_3OH was measured. The yellow solutions, formed by the reactions of both a ferric and a ferrous salt with sodium cyanate show no absorption band in the visible region of the spectrum; in the UV region, a very intense band was found at 305 nm, as well as a less intense band at 240 nm. It was concluded, on the basis of a comparison of the absorption spectra of solutions containing ferric and ferrous salts, that addition of cyanate to a solution of either a ferric or a ferrous salt always leads to the formation of the same complex (Fig. 1).

The absorbances of the solutions were measured immediately after mixing the components. During a certain time, the absorbance of the, solution prepared from the Fe(II) salt approaches that of the solution prepared from the Fe(III) salt. This is evidently the result of the formation of Fe(III) complexes, which is, for a ferrous salt, a consequence of redox processes. The rate of the Fe(II) → → Fe(III) oxidation, in dependence on the amount of cyanate ions added at a constant ferrous ion concentration, was determined by measuring the time changes of the absorbance at 305 nm for various [Fe(II)] : [NCO⁻] ratios. It was found that the absorbance at 305 nm reached higher values with perchlorate than with chloride (Figs 2, 3). Further, the absorbance value corresponding to the ferric complex is reached after only c. 10 min for a [Fe(II)] : [NCO⁻] ratio of 1 : 14, within c. 60 min for 1 : 8, while even 280 min is insufficient at the ratio 1 : 3.

For a quantitative estimation of the Fe(II) → Fe(III) oxidation in the systems studied, the photocolorimetric method[15] for Fe(III) determination with sulphosalicylic acid in a strongly acid medium was used. The amount of iron in the systems measured was kept constant and only the amount of cyanate ions was varied. It was found that the rate of the Fe(II) → Fe(III) oxidation depends on the amount of cyanate added; a [Fe(II)] : [NCO⁻] ratio of at least 1 : 3 is required for complete oxidation (Table I). Only partial oxidation takes place with lower [NCO⁻] : [Fe(II)] ratios. It was observed that complete oxidation takes place with ferrous perchlorate, while a certain equilibrium is arrived if ferrous chloride is used. During the oxidation, the conversion of about 80% of the Fe(II) to Fe(III) was noted; the reduction of Fe(III) to Fe(II) follows, and equilibrium amounts of Fe(III) are established at about 75% (Table I).
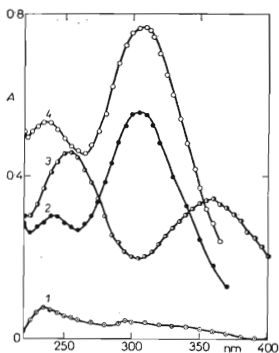

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The Absorptions of Solutions of Ferrous and Ferric Salts and of the Cyanate Complexes Formed [Fe(II)] = [Fe(III)] = const. = $2 . 10^{-4} M$,

1 $Fe(ClO_4)_2$; *2* $Fe.(ClO_4)_2$ after adding NaNCO in a ratio of 1 : 3, *3* $Fe(ClO_4)_3$; *4* $Fe(ClO_4)_3$ after adding NaNCO in a ratio of 1 : 3, 1 cm cell.

An attempt was made to find out which component of the system is reduced during the oxidation of Fe(II) to Fe(III). The cyanate group is not reduced in the system studied since the presence of cyanide was not detected[16]. Further, the possibility of Fe(II) oxidation to Fe(III) in the system, at the expense of atmospheric oxygen was examined. The initial solutions were deaerated for 10 minutes with purified and dried nitrogen before the reaction. Nitrogen was also passed through the solutions after their mixing, and ferric ions were determined after certain time intervals. The
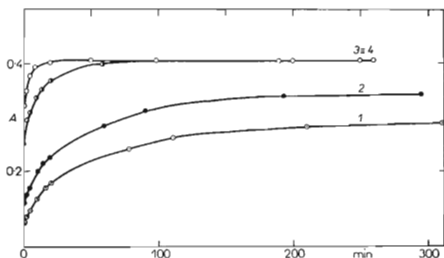

Fig. 2

The Absorbance Change with Time in the System $Fe(ClO_4)_2 . 6 H_2O$–$NaNCO$–CH_3OH in Dependence on the $[Fe(II)] : [NCO^-]$ Ratio

$[Fe(ClO_4)_2] = const. = 6 \cdot 6 . 10^{-5} M$, 1 $[Fe(II)] : [NCO^-] = 1 : 1$; 2 $[Fe(II)] : [NCO^-] = 1 : 3$; 3 $[Fe(II)] : [NCO^-] = 1 : 8$; 4 $[Fe(II)] : [NCO^-] = 1 : 14$; 305 nm, 1 cm cell.
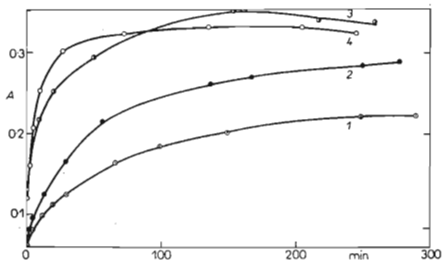
Fig. 3

The Absorbance Change with Time in the System $FeCl_2$–$NaNCO$–CH_3OH in Dependence on the $[Fe(II)] : [NCO^-]$ Ratio

$[FeCl_2] = const. = 6 \cdot 6 . 10^{-5} M$. 1 $[Fe(II)] : [NCO^-] = 1 : 1$; s $[Fe(II)] : [NCO^-] = 1 : 3$; 3 $[Fe(II)] : [NCO^-] = 1 : 8$; 4 $[Fe(II)] : [NCO^-] = 1 : 14$; 305 nm, 1 cm cell.

reagents for the Fe(III) determination were also deaerated with nitrogen. Solutions with [Fe(II)] :
: [NCO⁻] ratios of 1 : 1, 1 : 3, 1 : 8, and 1 : 14 were studied in this way. A parallel solution,
through which no nitrogen was passed, was prepared with each deaerated solution (Table II).
It was found that the Fe(II) → Fe(III) oxidation proceeds substantially slower in the solutions
deaerated with nitrogen than in those from which oxygen was not removed. The Fe(III) determina-
tion was not carried out in a nitrogen atmosphere. In the evaluation of the Fe(III) content, the
fact that ferrous perchlorate and chloride solutions themselves contain certain amounts of ferric
ions must be taken into account (2 to 5% in a fresh solution, which does not increase by more
than 1% during six hours). It was found that the methanol solution of a ferrous salt is relatively
stable since, 24 h after its preparation, it does not contain more than about 10% Fe^{3+} ions. Solu-
tions of $Fe(ClO_4)_2$ always contain somewhat more Fe^{3+} ions than $FeCl_2$ solutions. The graph
of the dependence of the absorbance on the isomolar series composition in both the systems
containing a ferric salt shows that the complex is formed at an [Fe(III)] : [NCO⁻] ratio of 1 : 3.
This ratio was verified by the method of monovariant changes. At higher excesses of cyanate ions

TABLE I

The Fe(III) Content (%) in the Systems Studied, in Dependence on the Time Elapsed from the
Mixing of the Components

Time, min	$Fe(ClO_4)_2 . 6 H_2O^a$	$FeCl_2{}^a$	Time, min	$Fe(ClO_4)_2.6 H_2O^a$	$FeCl_2{}^a$
[Fe(II)] : [NCO⁻] = 1 : 1				1 : 8	
0	5	9	0	46	33·5
45	14	21	10	89	67
60	16·5	24	30	99	74·5
120	22	28·5	60	100	78
260	26	32	120	100	79·5
300	27	34	260	100	75
360	28·5	37	300	100	75
570	36	43	450	100	75
22^b	45	56	21^b	100	74
27^b	46·5	57			
				1 : 14	
1 : 3			0	56·5	49·5
0	20	22	5	91·5	67·5
30	60	61	10	100	74
45	73	67	15	100	76
120	92	70	20	100	79
180	96·5	72	60	100	79·5
320	100	75	120	100	77·5
460	100	75	300	100	75
21^b	100	75	450	100	75
			21^b	100	75

^{a} The initial Fe(II) salt; ^{b} time in h.

(starting at a [Fe(III)] : [NCO⁻] ratio of about 1 : 20), a new increase in the absorbance occurs during these monovariant changes. Within the time interval followed (about 4 h), the absorbance value of the peak at 305 nm was constant, showing that the complexes present are stable in time.

DISCUSSION

It follows from the results given that during the cyanate group reaction with a ferrous salt in a methanol medium, a spontaneous oxidation-reduction processes takes place in which Fe(II) is oxidized to Fe(III) and cyanate-ferric complexes are formed. Analogous oxidation–reduction changes have also been observed[17-19] in the reactions of ferrous salts with other ligands having the ability to form dative π-bonds, *e.g.* with thiourea and some of its derivatives. This phenomenon is formally opposite to findings[20-23] on the consequences of the mutual interactions of ligands with different π-acceptor abilities in Cu(II) complexes, in which reduction of the central atom and oxidation of one of the ligands takes place. These differences in the behaviour of Fe(II) and Cu(II) complexes can be explained by the fact that Fe(II) complexes are much harder to reduce than Cu(II) complexes and that the dative π-bond between ligands and the Fe(II) central atom may, to a certain extent, enhance its oxidation. This can be understood in view of the fact that the Fe(II) → NCO π-interaction facilitates the change of the $t_{2g}^4 e_g^2$ asymmetrical configuration into the substantially more stable $t_{2g}^3 e_g^2$ configuration, which exhibits[24] a higher exchange energy. The formation of this configuration may, therefore, be a driving force for the Fe(II) → → Fe(III) oxidation if the oxidation were initiated in a suitable way.

TABLE II

The Study of the Effect of Removing Atmospheric Oxygen on the Fe(III) Content (%) in the Systems Investigated

Time,[a] min	b	c	Time,[a] min	b	c
	[Fe(II)] : [NCO⁻] = 1 : 1				
	1 : 1			1 : 8	
75	11·5	8·5	45	99	24·5
210	22·5	11·5	180	100	38·5
			300	100	40
	1 : 3				
				1 : 14	
60	70·5	10	40	100	57·5
200	91·5	15	180	100	62
320	100	17·5	240	100	61·5

[a] After mixing; solution [b] without nitrogen passage, [c] with nitrogen passage.

The solutions studied contain Fe(III) complexes, and for this reason they exhibit no absorption bands in the visible and the near UV regions of the spectrum, which could be ascribed to transitions of the d–d type. The ^6S ground state of the Fe^{3+} ion produces only the high-spin state $^6A_{1g}$ in the weak ligand field O_h so that spin-allowed d–d transitions cannot take place. The band found in the near UV region at 305 nm can be assigned[25] to the n–π^* transition in the cyanate ion; this assignment is also supported by the molar absorption coefficient value, c. 900. The other, less intense band at 240 nm is probably of the charge transfer type.

The fact that the Fe(II)—Fe(III) oxidation proceeds completely with ferrous perchlorate as a starting substance, while, with ferrous chloride, an equilibrium between Fe(III) and Fe(II) is attained, is probably connected with a possible internal oxidation–reduction process, causing the reduction of Fe(III) to Fe(II). We suppose that these processes are conditioned by the chloride ion entering the inner sphere of the complex, and that they proceed as a consequence of the mutual interaction between the ligands, analogous to those considered[20–23] in the case of some Cu(II) complexes.

Since the Fe(II)—Fe(III) oxidation was strongly hindered in solutions deaerated with nitrogen, the conclusion can be made that primarily oxygen takes part in the oxidation process of the Fe^{2+} ions, although the influence of another component of the system (a ligand) on the process studied cannot be altogether excluded. The minimum $[Fe(II)] : [NCO^-]$ ratio, 1 : 3, required for complete Fe(II) → Fe(III) oxidation, is evidently the stoichiometric ratio for the formation of the ferric cyanate complex. From the shape of the continuous variation curves, showing a pronounced break, it follows that the cyanate group enters the inner sphere of the complex at this ratio and that the complex formed is stable. The $[Fe(II)] : [NCO^-]$ ratio mentioned, 1 : 3, indicates the formation of a binuclear complex, the cyanate groups functioning as bridges between two Fe(III) atoms. This may be due to the planar species, $Fe_2(NCO)_6$, in which the fifth and sixth co-ordination sites of each iron atom are occupied by methanol molecules, because of the tendency of the Fe^{3+} ion to form octahedral structures[26]. The manner in which the cyanate group functions as a bridge must be especially considered. Theoretically, the cyanate group could appear as a bridge in the following ways:

I   *II*   *III*

Case *I* seems most probable, taking into consideration the analogy with bridge-bonding in some solid cyanate complexes of the transition metals[27–29]. Case *II* may be regarded as having slight probability due to the small tendency of the NCO group

to form bonds through the oxygen atom[1,2]. For the same reason, case *III* does not seem probable either. It would, in addition, require a strong deformation of the bridge bond, or possibly the bending of the NCO group, which would lead to destabilization of the system. From the increase in the absorbance of the solutions with a higher excess of cyanate ions, it can be assumed[30] that higher, more intensely coloured cyanate complexes of ferric iron are formed in the system.

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