SINDO Studies on Reactivity of $[M(CN)_5NO]^{n-}$ Complex Ions for M = Fe, Mn, Cr

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It is well known that the physical and chemical properties of nitrosylpentacyanometallate complexes depend considerably on the central ion and the total charge [1–3]. Theoretical analysis of the electronic structure and its relation to the properties of the first series transition metal nitrosylpentacyanides was carried out by Manoharan and Gray [4], Fenske and DeKock [5] and Nikolskii [6]. The calculations were performed using the Wolfsberg–Helmholtz approach [4, 5] or simple version of CNDO [6]. The studies were mostly qualitative and were focused on the character of bonding [4–6], ESR and electronic spectra [4]. In addition, the electrophilic reactivity of some of the ML_5NO complexes was studied by Bottomley and Grein [7]. By means of the INDO method, they analyzed the character and the energy of LUMO orbitals as a function of ligand electronegativity, number of electrons and nature of the metal.

In order to give a wider interpretation of the physical and chemical properties of the first series transition metal nitrosylpentacyanides, calculations based on the more advanced SINDO method [8] were performed. In a previous paper [9] the influence of the central ion and its oxidation state on physical properties such as bond lengths and frequencies ν_{NO}, ν_{CN} in the series $[Fe(CN)_5NO]^{2-}$, $[Mn(CN)_5NO]^{2-,3-}$, $[Cr(CN)_5NO]^{3-,4-}$, $[V(CN)_5NO]^{3-}$ was explained. The discussion was restricted to the analysis of the trends resulting from the indices characterizing the bond strength: E_{AB} (the diatomic contributions to the total energy of the complex ion) and p_{AB}^{σ}, p_{AB}^{π} (σ- and π-electronic contributions to the total bond order between atoms A and B).

Correlation diagrams were obtained. The SINDO method also gave a reasonable interpretation of electronic spectra and photochemical reactivity of the $[Fe(CN)_5NO]^{2-}$ ion [10]. The aim of the present work is the interpretation of the differences in reactivity of the first series transition metal nitrosylpentacyanides for which experimental data are available. The explanation is based on the characteristics of the frontier orbitals and the charge distribution within the NO ligand.

According to present and previous calculations [4, 5, 7], the two highest occupied orbitals in $[M(CN)_5NO]^{n-}$ complexes are the 8e and $2b_2$ orbitals (Table I), and the LUMO is the 9e orbital (Table II). The characteristic feature of the SINDO results is the significant contribution of π^*CN orbitals in the 8e and 9e molecular orbitals. As concerns the $2b_2$ orbital in the SCCC MO approach, it has mainly d character; the INDO method localises it on CN^- ligands, whereas according to SINDO, the $2b_2$ orbital is of mixed character. The net charge on the nitrosyl ligand in the complexes under consideration has been a subject of much discussion. The best information comes from XPS studies made by Folkesson [11]. The net charge on nitrogen and oxygen atoms of nitrosyl group calculated by SINDO [9] correlate well with those obtained by Folkesson. Although the net charges estimated by the SINDO method are usually overestimated, the relative values are generally consistent with other calculations and with experimental data [8].

Among the first series transition metal nitrosylpentacyanides, only $[Fe(CN)_5NO]^{2-}$ and $[Mn(CN)_5NO]^{2-}$ are susceptible to nucleophilic attack, whereas

TABLE I. Characteristics of the Highest Occupied Orbitals (8e, $2b_2$) in $[M(CN)_5NO]^{n-}$ Complexes According to SINDO Method

Quantity	$[Fe(CN)_5NO]^{2-}$		$[Mn(CN)_5NO]^{3-}$		$[Cr(CN)_5NO]^{3-}$		$[Cr(CN)_5NO]^{4-}$	
	8e	$2b_2$	8e	$2b_2$	8e	$2b_2$	8e	$2b_2$
Energy [eV]	−10.86	−11.70	−5.68	−5.60	−5.64	−0.13	−0.73	+0.62
%d	24	40	22	57	22	58	21	55
%NO	39		55		55		59	
%CN$_{trans}$	8		4		5		4	
%CN$_{cis}$	29	60	19	43	18	42	16	45

TABLE II. Characteristics of the LUMO (9e) Orbital in $[M(CN)_5NO]^{n-}$ Complexes According to SINDO Method

Quantity	$[Fe(CN)_5NO]^{2-}$	$[Mn(CN)_5NO]^{3-}$	$[Cr(CN)_5NO]^{3-}$
Energy (eV)	−0.224	+5.02	+5.38
%d	26	16	15
%NO	44	26	17
%CN_{trans}	14	36	40
%CN_{cis}	16	22	28
$\Delta p^\pi_{M-CN_{trans}}$	+0.252	+0.358	+0.368
$\Delta p^\pi_{M-CN_{cis}}$	+0.234	+0.258	+0.272
Δp^π_{M-NO}	−0.636	−0.365	−0.315

TABLE III. Net Charges on Nitrogen and Oxygen Atoms of the Nitrosyl Group Calculated by SINDO Method

| Complex ion	q_N (e)	q_O (e)	q_{NO} (e)
$[Fe(CN)_5NO]^{2-}$	+0.503	−0.757	−0.254
$[Mn(CN)_5NO]^{2-}$	+0.334	−0.806	−0.472
$[Mn(CN)_5NO]^{3-}$	+0.192	−0.883	−0.691
$[Cr(CN)_5NO]^{3-}$	+0.179	−0.887	−0.708
$[Cr(CN)_5NO]^{4-}$	+0.122	−0.941	−0.819

the remaining complexes undergo electrophilic attack. The net charge on both the nitrogen and the oxygen atoms decreases significantly going from iron to chromium complexes (see Table III), which is in agreement with these experimental data. The most positive charge on nitrogen atom as well as the lowest energy of LUMO orbital in the $[Fe(CN)_5NO]^{2-}$ and $[Mn(CN)_5NO]^{2-}$ complexes explain their electrophilic behaviour. Reactions in which the NO group is substituted by a nucleophilic ligand are very typical for the $[Fe(CN)_5NO]^{2-}$ ion, although the Fe—NO bond length is the shortest one among the studied series. The characteristics of the frontier orbital seem to give a reasonable explanation of this fact. Let us consider the LUMO orbital on which, at the initial step, the free electron pair of the nucleophilic ligand is localized. The high contribution of the NO ligand in this orbital and the positive net charge on nitrogen atom in the case of $[Fe(CN)_5NO]^{2-}$ ion should enable a nucleophilic attack on the NO ligand. As a result of this attack, the bond order between the iron and the nitrosyl ligand decreases $\Delta p^\pi_{Fe-NO} = -0.643$, whereas bond orders between the iron and the other ligands increase (see Table II), thus facilitating the substitution of the NO ligand.

The calculations also allow for the interpretation of the redox properties of the studied complexes. The reducing behaviour decreases in the isoelectronic series: $[Cr(CN)_5NO]^{4-}$, $[Mn(CN)_5NO]^{3-}$, $[Fe(CN)_5NO]^{2-}$. Such differences may be easily explained

by the energy of the last occupied orbitals, which decreases on going from chromium to iron complex (see Table I), thus making oxidation more difficult. The positive energy of the HOMO orbital in the case of $[Cr(CN)_5NO]^{4-}$ ion explains why it can exist only in an anaerobic atmosphere. A more direct comparison between experimental and theoretical data is possible for the reaction with the OH radical. Kinetic studies of the oxidation of $[Cr(CN)_5NO]^{3-}$, $[Mn(CN)_5NO]^{3-}$ and $[Fe(CN)_5NO]^{2-}$ ions by OH radical were made by Jeżowska-Trzebiatowska et al. [12]. The reaction rate constant significantly decreases from the chromium to the iron complex. The authors have found that the logarithm of this rate constant correlates well with the frequency of the valence stretching vibration ν_{NO}. This relation was explained assuming that the OH radical accepts an electron from the NO ligand. The higher the ν_{NO} frequency, the less the π back bonding to the π NO orbital, and the smaller the electron density on the NO group; the result is a more difficult oxidation. The results obtained by the SINDO method are consistent with the assumption that the NO group plays an important role in the oxidation of the studied complexes by the OH radical. In order to interpret the differences in the rate constant of the reaction with the OH radical, the following quantities were considered: net charges on nitrogen and oxygen atoms within the NO group, and the energy and character of the last occupied orbitals. Good correlations between log K and the net charge on both nitrogen and oxygen atoms were found. The latter relation, however, seems to be physically more significant because of the negative value of the net charge on the oxygen atom (see Fig. 1a). The oxidation should be also easier when the energy of the HOMO orbital is higher. The HOMO orbital is 8e in $[Fe(CN)_5NO]^{2-}$ ion, whereas it is the $2b_2$ orbital in $[Mn(CN)_5NO]^{3-}$ and $[Cr(CN)_5NO]^{3-}$ ions. The energy of the HOMO orbitals increases in the positive direction; however, a more quantitative correlation can be obtained when the energies of the 8e level
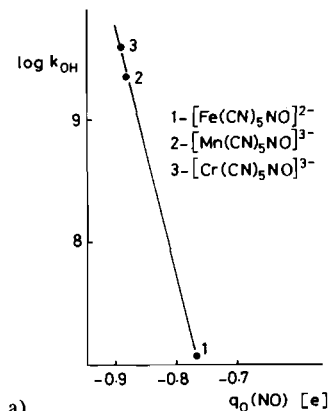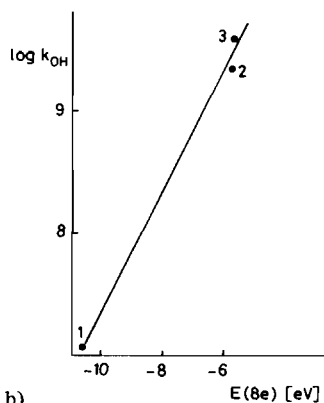
Fig. 1. Correlation between logarithm of rate constant of reaction with OH radical and results of SINDO calculations: (a) net charge on oxygen atom of NO ligand; (b) energy of 8e level.

orbital there is no such contribution. The NO character of the 8e orbital increases on going from iron to chromium complexes; metal and other ligand contributions decrease in this sequence.

One can conclude that SINDO calculations can give reasonable interpretation of both chemical and physical properties of the first series transition metal nitrosylpentacyanides.

Acknowledgments

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are considered in all cases (see Fig. 1b). The responsibility of the NO ligand for the differences in the oxidation rate constant is supported indeed by its contribution to the 8e level, whereas in the $2b_2$