Molecular Nitrogen Activation by Vanadium Hydroxides and the Environmental Symmetry

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The electronic structure of $[V(OH)_5(N_2)]^q$ complexes ($q = -3, -4, -5$) is investigated using a semiempirical quasi-relativistic CNDO method. The environmental electron density of various symmetries is approximated by point charges localized in various axial and equatorial positions. The degree of nitrogen activation is evaluated using the π-acceptor and Wiberg indices, the charge distributions and the bicentric portion of the total energy.

The most simple system for molecular nitrogen fixation is formed by aqueous or aqueous—alcoholic suspension of fresh V(II) and Mg(II) hydroxides [1—5]. This system reacts very effectively with dinitrogen at normal conditions. Depending on the reaction conditions, the hydrazine or ammonia is produced. Any details on the structure of active centre are not yet known. It is supposed that the reduction takes place in vanadium clusters at the Mg(OH)$_2$ surface.

Pelikán and *Boča* studied some model systems of molecular nitrogen activation by quantum-chemical treatment [6, 7]. The electronic structure of $^k[V(OH)_4Cl(N_2)]^q$ complexes in various formal oxidation (modelled by total cluster charges $q = -3, -4, -5$) and spin states ($k = 1, 2, 3, 4, 5, 6$) was investigated by CNDO—UHF method of MO—LCAO—SCF calculations. Among their results the most important are the conclusions that low oxidation states of the central vanadium atom support the dinitrogen activation (metal-to-dinitrogen charge transfer) and only low ($k = 1, 2$) and medium ($k = 3, 4$) spin states of the system allow the two-electron activation.

The molecular nitrogen activation depends on the environment of the active centre, too. The present communication is focused on the comparative study of the active centre properties where particular environmental effects are taken into account. $[V(OH)_5(N_2)]^q$ centre is surrounded by several point charges modelling the environmental electron density of various symmetries.

METHOD

The quasi-relativistic CNDO—UHF version [8, 9] of molecular orbital calculations is used in order to investigate the electronic structure of the systems under study. The point-charge model of the environmental influence is simulated by an additional term to the Hamiltonian

$$\mathscr{H} = -\sum_{i=1}^{m} \sum_{C=1}^{M} \frac{Q_C}{r_{iC}} + \sum_{A=1}^{N} \sum_{C=1}^{M} \frac{Z_A Q_C}{r_{AC}} \qquad (1)$$

where m is the number of valence electrons in the complex, N number of nuclei, Z_A their charges, M number of point charges Q_C.

The problem reduces to the evaluation of two-centre Coulomb integrals

$$V_{nn} = \left\langle \Phi_n(1) \left| \frac{1}{r_{1C}} \right| \Phi_n(1) \right\rangle \qquad (2)$$

over Slater type atomic orbitals Φ_n [10]. They are used in the modification of the diagonal matrix elements of the effective Hamiltonian (Fock operator).

The quantitative criteria descriptive of the degree of dinitrogen activation are considered as follows [6, 7]:

The Wiberg index W_{N-N} which represents the N—N bond order. Its value is equal to 3.0, 2.5, 2.0, and 1.5 for free N_2, N_2^-, N_2^{2-} ($^1\Delta_g$ state) and N_2^{2-} ($^3\Sigma_g^-$ or $^1\Sigma_g^+$ states), respectively.

The bicentric portion of the total molecular energy E_{N-N} which reflects the N—N bond strength. E_{N-N} adopts a negative value, its increase corresponds to an N—N bond softening.

The π-acceptor index $X(\pi)$ which represents an electron density on the dinitrogen π^* orbitals, so that it can be accepted as a criterion of dinitrogen π-acceptor ability. Moreover, the σ donation (ni-

trogen-to-metal) transfer does not reach significant values and is approximately equal for all characteristics of the central atom considered. Thus the π-acceptor index may be regarded as the most suitable criterion of the degree of dinitrogen activation. $X(\pi)$ equal to 0, 1, and 2 corresponds to no activation, one-electron activation, and two-electron activation, respectively. It may be useful to distinguish orthogonal projections of $X(\pi)$ in x and y axes.

The total dinitrogen charge $Q(N_2)$ which represents both the metal-to-ligand and the ligand-to-metal charge transfer *via* the donor-acceptor interaction. Consequently it adopts a fractional negative value only. Owing to weak σ donor properties (dinitrogen-to-central atom charge transfer) it belongs to the set of criteria for dinitrogen activation. Subsequent protonation of the coordinated dinitrogen seems to be more efficient if the negative charge is mostly localized on the terminal nitrogen atom. Thus the individual charges on inner N_a and terminal N_b nitrogens are presented in our study.

RESULTS AND DISCUSSION

Fig. 1 shows the sterical arrangement of the square-bipyramidal $[V(OH)_5(N_2)]^q$ complex and describes the considered positions of point charges Q. The geometries of studied systems are presented in Fig. 2 and Table 1; the actual interatomic dis-
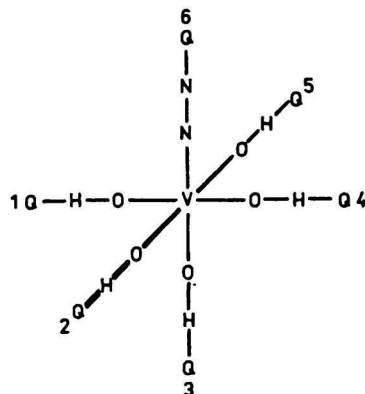

Fig. 1. Description of the point charges positions Q around the $[V(OH)_5(N_2)]^q$ complex.

tances [6, 7] are listed in Table 2. The molecular charges q of -3, -4, and -5 correspond to V(II), V(I), and V(0) oxidation states, respectively [6, 7]. $^k[V(OH)_5(N_2)]^q + nQ$ systems ($n = 0$, 1 or 2) are considered to be in the electronic states of the lowest spin multiplicities ($k = 1$ or 2). The calculated values of the Wiberg indices of the N_a—N_b bond W_{N-N}, x and y projections of the π-acceptor indices $X(\pi)$, the nitrogen charges $Q(N_a)$ and $Q(N_b)$, and the bicentric portion of the total energy E_{N-N} are listed in Tables 3—6. From the obtained results the following conclusions may be drawn:

The molecular nitrogen activation increases with the decreasing oxidation state of vanadium. V(II) systems cannot cause any two-electron activation.
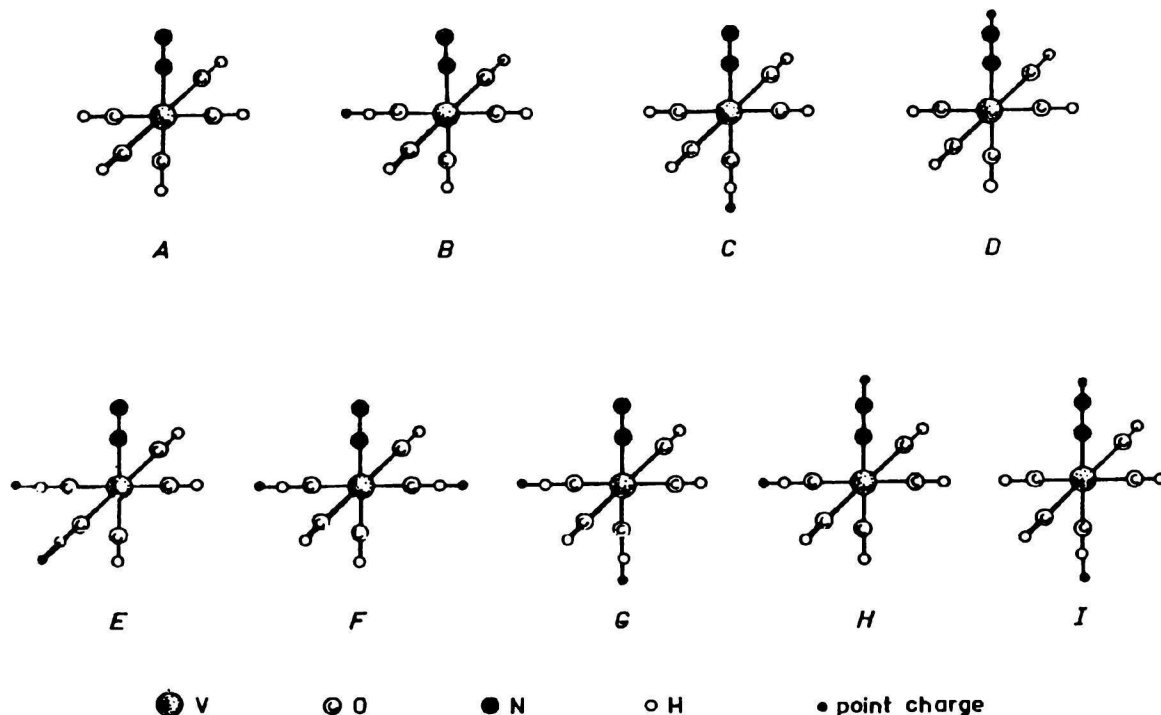

A B C D

E F G H I

◑ V ◉ O ● N ○ H • point charge

Fig. 2. Model systems of $[V(OH)_5(N_2)]^q + nQ$ (Q is the point charge; $n = 0$ for A model, $n = 1$ for B—D models, $n = 2$ for E—I models).

Table 1. Environmental Symmetry Description

Model	Symmetry	Point charge position					
		1	2	3	4	5	6
A	C_{4v}	—	—	—	—	—	—
B	C_s	Q_1	—	—	—	—	—
C	C_{4v}	—	—	Q_1	—	—	—
D	C_{4v}	—	—	—	—	—	Q_1
E	C_s	Q_1	Q_2	—	—	—	—
F	C_{2v}, C_s	Q_1	—	—	Q_2	—	—
G	C_s	Q_1	—	Q_2	—	—	—
H	C_s	Q_1	—	—	—	—	Q_2
I	C_{4v}	—	—	Q_1	—	—	Q_2

Table 2. Geometrical Characteristics of the $[V(OH)_5(N_2)]^q$ $+ nQ$ Systems [6, 7]

A	B	q	$d_{A—B}/(10^{-10}\,m)$
V	N_a	−5	2.335
		−4	1.984
		−3	2.110
N_a	N_b	−5	1.252
		−4	1.220
		−3	1.146
V	O		2.0
O	H		0.984
N_b	Q		1.0
H	Q		1.0

Table 3. The Values of N_a—N_b Bond Wiberg Index in the Systems under Study

Model	Q_1	Q_2	$W_{N—N}$		
			V(0)	V(I)	V(II)
A	—	—	1.536	2.110	2.753
B	+1	—	1.978	2.045	2.788
	−1	—	1.526	1.990	2.708
C	+1	—	1.556	2.192	2.816
	−1	—	1.521	2.026	2.666
D	+1	—	1.880	1.720	2.144
	−1	—	1.749	2.450	2.881
E	+1	+1	1.564	2.077	2.817
	+1	−1	1.968	2.014	2.747
	−1	−1	1.971	1.971	2.658
F	+1	+1	1.980	2.082	2.819
	+1	−1	1.537	2.011	2.746
	−1	−1	1.972	1.974	2.660
G	+1	+1	1.575	2.110	2.841
	+1	−1	1.976	1.999	2.710
	−1	+1	1.977	2.032	2.781
	−1	−1	1.513	1.965	2.214
H	+1	+1	1.458	1.895	2.156
	+1	−1	2.191	2.411	2.881
	−1	+1	1.864	1.869	2.135
	−1	−1	2.115	2.277	2.879
I	+1	+1	1.460	1.799	2.158
	+1	−1	2.191	2.515	2.884
	−1	+1	1.847	1.867	2.133
	−1	−1	1.883	2.401	2.871

V(II) systems are maximally influenced by environmental charges, V(0) systems exhibit minimal environmental influence.

The maximal influence on the nitrogen activation is exhibited by the point charges at dinitrogen (position 6). Positive charges support the activation, the negative ones have the opposite consequences.

Negative point charges at equatorial hydroxyls (position 1) cause higher dinitrogen activation, the positive ones on the contrary lower. Further point charges at equatorial hydroxyls (positions 2 or 4) are less important.

The lowest influence on the nitrogen activation is exhibited by the point charges at the axial OH group (position 3). They may support the influence of the charges in other positions.

The inner nitrogen charges $Q(N_a)$ are positive in V(II) and negative in V(0) systems. $Q(N_a)$ depends on the environmental charges less than the terminal one $Q(N_b)$. In the activated systems, the $Q(N_b)$ values are more negative than the $Q(N_a)$ ones. This fact supports the hypothesis that the terminal nitrogen N_b is hydrogenated first.

The sign change of point charge at equatorial hydroxyls for the systems of the same symmetry causes the change of the activation direction (x and y projections of $X(\pi)$). This tendency is less observable for the point charges at dinitrogen (Table 4).

Table 4. The Values of x and y Projections of the Dinitrogen π-Acceptor Index $X(\pi)$ in the Systems under Study

Model	Q_1	Q_2	V(0)		V(I)		V(II)	
			x	y	x	y	x	y
A	—	—	0.94	0.94	0.47	0.47	0.11	0.11
B	+1	—	1.85	0.00	1.27	0.00	0.06	0.12
	−1	—	0.95	0.94	0.00	1.46	0.13	0.17
C	+1	—	0.92	0.92	0.42	0.42	0.05	0.09
	−1	—	0.95	0.95	0.52	0.52	0.11	0.20
D	+1	—	1.95	0.01	0.72	0.72	0.98	0.01
	−1	—	0.73	0.73	0.28	0.28	0.02	0.03
E	+1	+1	0.90	0.90	0.59	0.59	0.05	0.10
	+1	−1	1.84	0.02	1.37	0.00	0.14	0.08
	−1	−1	0.95	0.95	0.77	0.77	0.11	0.19
F	+1	+1	1.80	0.00	1.18	0.00	0.07	0.07
	+1	−1	0.93	0.94	1.39	0.00	0.15	0.07
	−1	−1	0.95	0.95	0.00	1.53	0.10	0.21
G	+1	+1	0.89	0.91	1.10	0.00	0.08	0.08
	+1	−1	1.88	0.00	1.44	0.00	0.09	0.17
	−1	+1	0.00	1.86	0.00	1.31	0.06	0.11
	−1	−1	0.96	0.96	0.00	1.58	0.95	0.00
H	+1	+1	0.98	0.98	1.72	0.03	0.96	0.01
	+1	−1	0.97	0.00	0.54	0.07	0.01	0.03
	−1	+1	1.95	0.01	1.82	0.03	0.03	0.99
	−1	−1	0.00	1.17	0.05	0.76	0.02	0.04
I	+1	+1	0.97	0.97	0.64	0.64	0.97	0.02
	+1	−1	0.33	0.64	0.24	0.24	0.01	0.02
	−1	+1	0.95	0.04	0.17	0.17	0.03	1.01
	−1	−1	0.49	0.85	0.31	0.31	0.02	0.04

Table 5. The Values of the Nitrogen Charges $Q(N_a)$ and $Q(N_b)$ in the Systems under Study

Model	Q_1	Q_2	V(0)		V(I)		V(II)	
			$Q(N_a)$	$Q(N_b)$	$Q(N_a)$	$Q(N_b)$	$Q(N_a)$	$Q(N_b)$
A	−	−	−0.40	−0.97	0.10	−0.64	0.28	−0.21
B	+1	−	−0.39	−0.93	−0.10	−0.69	0.28	−0.17
	−1	−	−0.40	−1.00	−0.15	−0.80	0.28	−0.26
C	+1	−	−0.37	−0.92	−0.20	0.14	0.30	−0.16
	−1	−	−0.42	−1.01	0.07	−0.72	0.26	−0.28
D	+1	−	−0.20	−1.36	0.18	−1.16	0.19	−0.85
	−1	−	−0.45	−0.45	−0.04	−0.08	0.01	0.27
E	+1	+1	−0.38	−0.89	−0.07	−0.63	0.27	−0.13
	+1	−1	−0.39	−0.96	−0.12	−0.74	0.28	−0.22
	−1	−1	−0.40	−1.03	−0.17	−0.85	0.28	−0.31
F	+1	+1	−0.38	−0.89	−0.07	−0.63	0.27	−0.13
	+1	−1	−0.39	−0.97	−0.13	−0.75	0.28	−0.22
	−1	−1	−0.40	−1.03	−0.17	−0.85	0.28	−0.31
G	+1	+1	−0.36	−0.88	−0.02	−0.60	0.29	−0.11
	+1	−1	−0.41	−0.97	−0.16	−0.77	0.26	−0.24
	−1	+1	−0.37	−0.96	−0.08	−0.72	0.30	−0.20
	−1	−1	−0.42	−1.04	−0.20	−0.86	−0.06	−0.52
H	+1	+1	−0.21	−1.33	−0.05	−1.18	0.18	−0.82
	+1	−1	−0.38	−0.18	−0.09	−0.05	−0.01	0.31
	−1	+1	−0.20	−1.39	−0.07	−1.25	0.20	−0.88
	−1	−1	−0.37	−0.36	−0.13	−0.19	0.02	0.24
I	+1	+1	−0.19	−1.33	0.23	−1.09	0.20	−0.82
	+1	−1	−0.39	−0.17	−0.02	−0.01	0.01	0.31
	−1	+1	−0.21	−1.39	−0.09	−1.26	0.19	−0.89
	−1	−1	−0.44	−0.43	−0.06	−0.12	0.02	0.23

The most advantageous arrangements of charges (dinitrogen activation according to at least one

Table 6. The Values of Bicentric Portion of the Total Energy of Dinitrogen in the Systems under Study

Model	Q_1	Q_2	E_{N-N}/eV		
			V(0)	V(I)	V(II)
A	−	−	−61.02	−74.79	−87.30
B	+1	−	−61.56	−69.58	−87.75
	−1	−	−60.66	−66.95	−86.68
C	+1	−	−61.90	−76.37	−88.20
	−1	−	−60.32	−73.08	−85.94
D	+1	−	−59.90	−68.84	−77.23
	−1	−	−66.21	−79.75	−88.72
E	+1	+1	−61.97	−70.85	−88.10
	+1	−1	−61.18	−68.22	−87.21
	−1	−1	−60.33	−65.72	−85.98
F	+1	+1	−62.14	−71.01	−88.12
	+1	−1	−61.06	−68.09	−87.19
	−1	−1	−60.42	−65.92	−86.01
G	+1	+1	−62.47	−72.11	−88.48
	+1	−1	−60.74	−67.26	−86.58
	−1	+1	−61.51	−69.23	−87.79
	−1	−1	−60.01	−65.05	−76.53
H	+1	+1	−60.19	−63.97	−77.32
	+1	−1	−74.21	−78.83	−88.76
	−1	+1	−59.58	−62.74	−77.11
	−1	−1	−71.30	−76.02	−88.65
I	+1	+1	−60.52	−70.92	−77.50
	+1	−1	−74.23	−80.84	−88.79
	−1	+1	−59.31	−62.34	−76.92
	−1	−1	−68.40	−78.91	−88.53

Table 7. The Most Advantageous Model System of Molecular Nitrogen Activation

Model	Q_1	Q_2
D	+1	−
G	−1	−1
H	+1	+1
H	−1	+1
I	+1	+1
I	−1	+1

criterion for all the oxidation states) are collected in Table 7.

In this context, it must be pointed out that the d electron population of vanadium d^x depends more on the environmental charges than on the total complex charges (*i.e.* formal oxidation states). The d^x values (from 2.9 to 3.5) indicate that the real oxidation state is most probably V(II).

If restricting to monomeric vanadium hydroxides, the negatively charged particles of environment cannot contact the negatively charged active centre. Thus the positive particles contacting the dinitrogen and simultaneously the equatorial (position 1) and/or axial (position 3) hydroxyls are the most profitable for the dinitrogen activation. This process is supported by negative hydroxyl and dinitrogen charges, too (see Table 5).

The situation in the case of polymeric vanadium hydroxides is not so simple. Here the point charges may represent the charged particles and/or real atoms. Negative point charges may represent oxygen atoms, V and Mg may correspond to the positive ones. Thus, all the models in Table 7 could be considered. However, the problem must be treated carefully and our study represents only the most simple and rough approximation. For understanding the molecular nitrogen activation in real polymeric systems the more complex models are to be considered.

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