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Unrestricted CNDO–MO Calculations.
II. MnO_4^{2-} and CrO_4^{3-}

David A. Copeland

Department of Chemistry, University of Tennessee at Martin, Martin, Tennessee 38237

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The electronic structures of the tetrahedral molecule ions MnO_4^{2-} and CrO_4^{3-} have been investigated within an unrestricted CNDO–MO approximation [Theoret. Chim. Acta (Berl.) **20**, 317 (1971)]. Calculations assuming the unpaired electron occupies the $3a_1$, $2e$, and $4t_2$ molecular orbitals indicate that the $3a_1$ and $2e$ orbitals have similar orbital energies and that the $4t_2$ orbital is at a higher energy. The experimentally indicated $2e$ orbital for the unpaired electron is obtained with expanded O^{1-} type atomic orbitals for oxygen and valence metal orbitals of the expanded $3d$ and plus one ion $4p$ types. The metal $4s$ orbitals must be held to the neutral atom type. The "optimum" valence orbitals above with a slightly contracted $4s$ type metal orbitals yield the minimum total energy and places the unpaired electron in the $3a_1$ orbital. Since the contracted $4s$ metal orbital produces results that are not in agreement with experimental data, the method used apparently does not adequately take into account the increased electron-electron repulsions that contracted $4s$ orbitals produce.

Key words: Chromium (V) – Manganese (VI) – Tetrahedral complexes – Transition metal complexes.

1. Introduction

The unrestricted CNDO–MO scheme described in Paper I [1] and applied there to the tetrahedral VCl_4 molecule, has been used to investigate the electronic structures of the tetrahedral MnO_4^{2-} and CrO_4^{3-} molecule ions. All three of these molecules contain 33 valence electrons and are classified as d^1 systems in crystal field theory.

Semi-empirical calculations with tetrahedral transition metal complexes have been shown by Fenske and Sweeney [2] and by Oleari *et al.* [3] to be dependent on the initial assumptions involved in a calculation. In accord with crystal field theory and experimental ESR data [4, 5], most semi-empirical calculations [3, 6–9] indicate that the lone electron should occupy the $2e$ molecular orbital in MnO_4^{2-} (or that this orbital should be the lowest lying virtual orbital in MnO_4^-). Similar results [7, 8, 10] are assumed to hold for VCl_4, CrO_4^{3-} and other complexes although this may not be a valid assumption [1, 3, 11, 14].

In Paper I we indicated that the lone electron should occupy the $3a_1$ molecular orbital and that the $4t_2$ orbital energy is lower than the $2e$ orbital energy in VCl_4. Both of these results are not in accord with the "traditional" picture. Consequently we have attempted to determine what factors in the proposed unrestricted CNDO–MO scheme produce this unconventional result by considering MnO_4^{2-}

and then carry out a similar calculation on CrO_4^{3-}. We shall also interpret the previous VCl_4 result.

2. Radial Functions and Geometry

The radial functions for the central metal atom core electrons (1*s*, 2*s*, 2*p*, 3*s*, 3*p*) and all of the oxygen atom electrons were taken from Clementi's tables of extended Hartree-Fock (HF) functions [15]. All of the radial functions for the core electrons of the metals and oxygen (1*s*) are for the ground state atoms and are held constant for each molecule. Since inconsistent results were obtained with reduced basis set radial functions for the ligand valence electrons in our previous paper [1], extended HF functions were used for oxygen. Both the 2*s* and 2*p* were varied simultaneously with the three atomic (or ionic) configurations $O(s^2p^3)$, $O(s^2p^4)$, and $O(s^2p^5)$. Radial functions for the metal valence electrons (3*d*, 4*s*, 4*p*) were taken from the papers of Richardson *et al.* [16] and Copeland [17] with the notion from the latter paper being used.

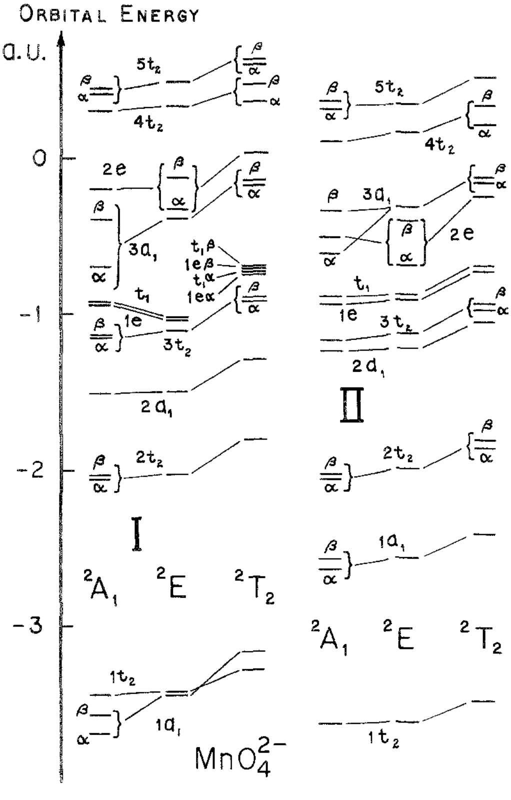

Fig. 1. Orbital energies for MnO_4^{2-}. (I) Those obtained for minimum total valence energy. The optimum atomic (or ionic) orbitals correspond to Mn $4s(s^2d^4)$ and $4p(d^5p^1)$ and $O(s^2p^5)$. The Mn *d* orbitals for the $^2A_1$ and ^2E states are of the $3d(d^{10})$ type and for the $^2T_2$ are of the $3d(d^9)$ type. (II) Orbital energies for Mn with $4s(s^2d^5)$. All other valence orbitals were optimized and correspond to $3d(d^9)$ and $4p(d^5p^1)$ for Mn and $O(s^2p^5)$

As in our investigation of VCl_4 [1], the valence electron orbitals of the atoms (metal 3*d*, 4*s*, 4*p*, and oxygen 2*s*, 2*p*) were varied with the possible radial functions cited above. During each variation the lone electron was assumed to occupy the $3a_1(^2A_1)$, $2e(^2E)$, and $4t_2(^2T_2)$ molecular orbitals.

The tetrahedral molecules are assumed to have bond distances of 1.63 Å and 1.66 Å for MnO_4^{2-} and CrO_4^{3-} [5], respectively.

3. Results and Discussion

The orbital energies obtained when the total valence energy, *E*, [1] is minimized are illustrated in Part I of Figs. 1 and 2 for MnO_4^{2-} and CrO_4^{3-} respectively. In these parts of the figures the $3a_1$ molecular orbital always has the lowest orbital energy. The *E*'s are −201.88 atomic units (a.u.), −201.60 a.u., and −197.90 a.u. for MnO_4^{2-} and −191.69 a.u., −191.42 a.u., and −187.74 a.u. for CrO_4^{3-} for the states $^2A_1$, ^2E, and $^2T_2$ states respectively. The minimum *E* for each molecule ion

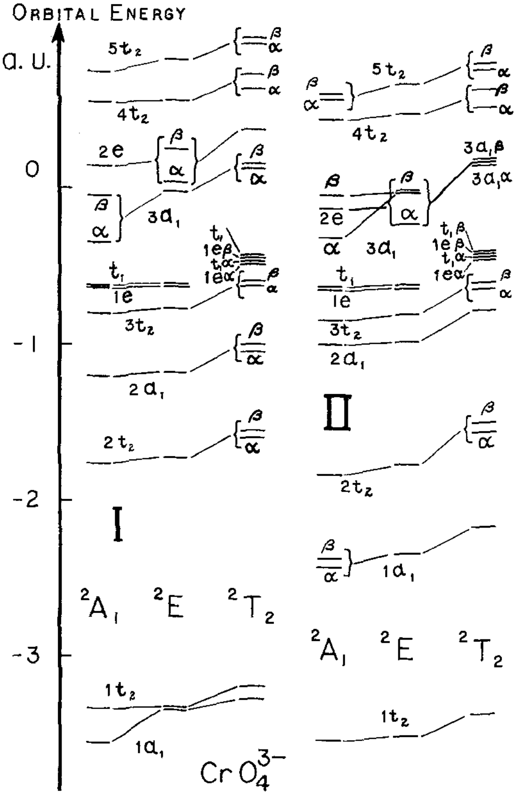

Fig. 2. Orbital energies for CrO_4^{3-}. (I) Those obtained for minimum total valence energy. The optimum atomic (or ionic) orbitals corresponding to Cr $3d(d^8)$, $4s(s^2d^3)$ and $4p(d^4p^1)$ and $O(s^2p^5)$. (II) Orbital energies for Cr with $4s(s^2d^4)$. All other valence orbitals were optimized and correspond to $O(s^2p^5)$ and Cr $4p(d^4p^1)$ with $3d(d^8)$ for the $^2A_1$ and ^2E states and $3d(d^7)$ for the $^2T_2$ state

indicates that the lone electron should occupy the $3a_1$ molecular orbital. It should also be noted that unlike the VCl_4 result, the $2e$ orbital energy is always below the $4t_2$ orbital energy and therefore is in accord with crystal field theory.

Since the results given above are not in accord with the experimental result [4, 5] of having the lone electron occupying the $2e$ molecular orbital of MnO_4^{2-}, we must conclude that the minimization of E may not be entirely justified for the method under investigation. Having varied only the atomic radial functions and nothing else, we considered our variations to determine if and under what conditions could be experimental results be obtained. Only under two types of variations was it found that the experimental results could be produced. By using the oxygen atomic radial functions for the neutral atom, $O(s^2p^4)$, instead of $O(s^2p^5)$ which corresponds to the O^- ion there is a drastic increase in E of about 16 a.u. and an inversion of the E's for the $^2A_1$ and ^2E states. The other variation that produced a similar result is by using a $4s(s^2d^5)$ ground state atom radial function for the Mn atom instead of the $4s(s^2d^4)$ plus one oxidation state functions. The E's

Table 1. Molecular orbitals for the ^2E state of MnO_4^{2-}, corresponding to the orbitals $3d(d^9)$, $4s(s^2d^5)$, $4p(d^5p^1)$, and $O(s^2p^5)$

Symmetry	Eigenvalue (eV)	Eigenvectors				
a_1		s	σ_s	σ_p		
α and β	−0.842	0.4473	0.3722	0.8133		
	−32.941	0.4359	0.7033	−0.5616		
	−69.329	0.7810	−0.6057	−0.1523		
e		d	π			
α	−17.077	0.9074	0.4202			
	−24.722	−0.4202	0.9074			
β	−10.785	0.9524	0.3048			
	−24.467	−0.3048	0.9524			
t_2		p	d	σ_p	σ_s	π_p
α	9.707	−0.4356	−0.3663	0.5617	0.0346	0.5996
	4.629	0.2743	−0.6609	0.2882	0.3968	−0.4973
	−30.457	−0.0380	0.3780	0.7078	−0.4052	−0.4364
	−53.786	0.0948	0.5346	0.2469	0.7939	0.1183
	−98.603	0.8512	−0.0170	0.1986	−0.2167	0.4344
β	9.730	−0.4364	−0.3639	0.5603	0.0333	0.6017
	4.645	0.2725	−0.6622	0.2907	0.3967	−0.4953
	−30.445	−0.0385	0.3781	0.7079	−0.4054	−0.4360
	−53.786	0.0949	0.5347	0.2470	0.7938	0.1182
	−98.591	0.8513	−0.0170	0.1987	−0.2168	0.4342
t_1		π				
α	−23.799	1.0000				
β	−23.734	1.0000				

for this calculation are -199.12 a.u., -199.23 a.u. and -195.47 a.u. for the $^2A_1$, ^2E, and $^2T_2$ states respectively. Since the ^2E state has only a 2.35 a.u. increase in total valence energy with the 4*s* metal variation as compared with about 16 a.u. in the oxygen orbital variation, we must conclude that the method does not adequately take the contraction of the 4*s* metal orbital into consideration and that the *E* minimization is not an entirely good criteria. The orbital energy results for the *E* minimization with the ground state metal atom radial functions being used are given in Part II of Figs. 1 and 2 for MnO_4^{2-} and CrO_4^{3-} respectively. The total valence energies for CrO_4^{3-} are -188.551 a.u., -188.553 a.u., and -184.83 a.u. for the $^2A_1$, ^2E, and $^2T_2$ states respectively.

Tables 1 and 2 contain the ^2E state orbital energies and MO coefficients. As shown in these tables, the 4*s* and 4*p* metal orbitals have a heavy involvement in bonding. This is in accord with the results of Dahl and Johansen [11, 12] for MnO_4^- and CrO_4^{2-} but does not agree with the MnO_4^- results of Viste and Gray [8]. The MnO_4^{2-} results (Table 1) suggests about 18% ligand participation for the

Table 2. Molecular orbitals for the ^2E state of CrO_4^{3-}, corresponding to the orbitals $3d(d^8)$, $4s(s^2d^4)$, $4p(d^4p^1)$, and $\mathrm{O}(s^2p^5)$

Symmetry		Eigenvalue (eV)	Eigenvectors				
a_1			s	σ_s	σ_p		
	α and β	-0.7748	0.4687	0.3908	0.7922		
		-26.450	0.3882	0.7144	-0.5822		
		-63.433	0.7935	-0.5804	-0.1831		
e			d	π			
	α	-6.116	0.9960	-0.0893			
		-16.973	0.0893	0.9960			
	β	-0.350	0.9972	-0.0751			
		-16.962	0.0751	0.9972			
t_2			p	d	σ_p	σ_s	π_p
	α	17.945	0.1883	0.7154	-0.5463	-0.2911	-0.2639
		13.000	-0.4587	0.3445	0.1101	-0.3292	0.7419
		-21.920	-0.0281	0.3027	0.7776	-0.3468	-0.4271
		-48.028	0.0939	0.5268	0.2299	0.8016	0.1350
		-95.211	0.8629	-0.0205	0.1780	-0.2100	0.4234
	β	17.946	0.1884	0.7153	-0.5463	-0.2910	-0.2641
		13.004	-0.4586	0.3447	0.1099	-0.3292	0.7419
		-21.919	-0.0281	0.3027	0.7778	-0.3468	-0.4271
		-48.028	0.0939	0.5268	0.2300	0.8016	0.1350
		-95.210	0.8629	-0.0205	0.1780	-0.2100	0.4233
t_1			π				
	α	-16.907	1.000				
	β	-16.900	1.000				

$2e$ orbital and is in reasonable accord with Schonland's ESR results [4] which suggest not more than 10% participation. Viste and Gray [8] indicate 63% for MnO_4^- in their calculation while Dahl and Johansen [11] obtain about 5%.

In Table 2 we have about 1% ligand participation indicated for the $2e$ orbital of CrO_4^{3-}. This sizable decrease in going from MnO_4^{2-} to CrO_4^{3-} is not consistant with the results of Dahl and Johansen [12] of about 27% participation for CrO_4^{2-}. Since our unrestricted calculation and the restricted calculation of Dahl and Johnsen [12] are very similar, the differences in the results probably are caused by their choice of radial functions and that they did not vary these functions.

The strong covalent bonding of the occupied MO's that is experimentally indicated [4, 5] is suggested by our results and those of Dahl and Johansen [11, 12]. This type of bonding is not indicated by Viste and Gray [8].

Considering the lower placement of the $3a_1$ orbital could give a fuller explaination of MnO_4^{2-} and CrO_4^{3-} spectra. With a lower placement of this level it would allow transitions from (or to) this level. This reasoning is in essence the same as that of Fenske and Sweeney [2] for indicating a preference for the Wolfsberg and Helmholz energy level scheme for spectral interpretation. Although electronic transitions are forbidden as electric dipole transitions between the t_2 and the $3a_1$ levels, these transitions would be analogous to $d-d$ bands and would probably be of comparable intensity [14].

4. Conclusions

In an unrestricted CNDO–MO calculation it is found possible to obtain results which are consistent with experimental ESR data [4, 5]. A slight relaxation of the valence energy minimization criteria is required since the calculation scheme apparently does not account adequately for contracted 4s metal orbitals. The molecular electronic configuration for MnO_4^{2-} and CrO_4^{3-} is suggested to be $(1t_2)^6(1a_1)^2(2t_2)^6(2a_1)^2(3t_2)^6(1e)^4(t_1)^6(2e)^1(3a_1)^0(4t_2)^0(5t_2)^0$ where the lone electron occupies the $2e$ orbital with the first virtual orbital being the $3a_1$ orbital.

Reconsidering the results for VCl_4 would suggest only slight changes of the molecular orbital configuration since ground state 4s metal orbitals would favor a lower $3a_1$ orbital energy as is shown in Fig. 4 of Paper I. Consequently we still conclude that the lone electron occupies the $3a_1$ orbital in VCl_4 and that the $4t_2$ orbital is below the $2e$ orbital.

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Dr. D. A. Copeland
Department of Chemistry
University of Tennessee at Martin
Martin, Tennessee 38237, USA