Electronic absorption spectra of rhenium(VII) compounds: the effect of the coordination number

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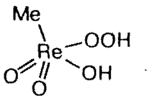
Changes in electronic absorption spectra in the following series:

$MeRe(L_2)O_3 \leftarrow MeReO_3 \leftarrow ReO_4^- \rightarrow ReO_6^{5-}$,

have been studied in terms of the qualitative MO scheme.

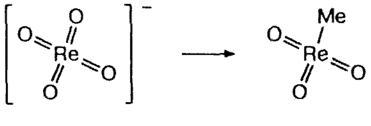
Key words: methyltrioxorhenium; electronic absorption spectra; molecular orbitals.

Methyltrioxorhenium $MeReO_3$ is a highly efficient catalyst for epoxidation, metathesis, and polymerization of olefins and cyclic hydrocarbons, and hydrolysis of epoxides.[1–3] In the course of these reactions, intermediate complexes form, which changes the color of the initial solutions. In particular, the appearance of the yellow color of the solution of methyltrioxorhenium in t-C_4H_9OH in the presence of hydrogen peroxide is caused by the formation of a complex of the following type[3]



Previously,[4] based on the data of IR spectroscopy, it was suggested that the oxirane cycle is coordinated by the $MeReO_3$ molecule in the alkylation of cyclohexane oxide. In this case, the colorless initial solution of methyltrioxorhenium in isopropyl alcohol turns light brown, and then the color disappears. Because intermediate complexes were not isolated, they were not well characterized.

Compounds of Re^{VII} are mainly perrhenates, salts of perrhenic acid, and their derivatives containing ReO_4^-, ReO_5^{3-}, or ReO_6^{5-} anions. The $MeReO_3$ compound under consideration is an analog of the ReO_4^- perrhenate anion in which the O atom is replaced by a Me group.



(1)

An interesting feature of the Re^{VII} compounds is the fact that they change color when the coordination number changes. Previously, it has been established[5] that ReO_4^- has a tetrahedral structure (the Re—O distance is 1.77 Å). Salts containing the ReO_4^- anion, as well as perrhenic acid, are colorless. However, when the structure changes from tetrahedral to octahedral or distorted octahedral, the color changes.[6] Thus, $Ba(ReO_4)_2$ is colorless, $Ba_3(ReO_5)_2$ is yellow, and $Ba_5(ReO_6)_2$ is orange. It may be suggested that the change in color of the solution of the metal complex in the course of the catalytic reaction is associated with an increase in the coordination number, as in the case with the ReO_4^- perrhenate ion. If a compound, such as a dimer, contains two Re^{VII} atoms, one of which is tetrahedrally coordinated and the other of which is octahedrally coordinated, a yellow color, which is typical of the ReO_6^{5-} anion, appears (see Ref. 7).

In this work, electronic absorption spectra in the following series of compounds

$$MeRe(L_2)O_3 \leftarrow MeReO_3 \leftarrow ReO_4^- \rightarrow ReO_6^{5-}.$$

were studied in terms of the qualitative MO scheme.

Molecules of hydrogen peroxide[3] or cyclohexane oxide[4] may act as ligands (L).

Results and Discussion

In the Re^{VII} compounds, all seven valence electrons are involved in chemical bonding. In these complexes, only one type of electron transition, which corresponds to the transfer of charge from the ligands to the central atom, is possible. Analysis of the energies of the charge transfer bands (E_{ct}) in complexes of transition metals with the d^0 electronic configuration (Table 1) demonstrates that, first, in going from ReO_4^- to $MeReO_3$ and ReO_6^{5-}, E_{ct} decreases, *i.e.*, the maxima of the corresponding bands in the electronic absorption spectra shift to the long-wave region; second, in $MeReO_3$ and ReO_4^-, transitions with close energy values occur (41800 and 44000 cm^{-1}); third, in $MeReO_3$, new electron transitions in the long-wave region appear because of the decrease in the symmetry.

In the qualitative MO scheme, the t_1 and t_2 ligand levels in ReO_4^- and ReO_6^{5-} (Fig. 1) are occupied by

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Table 1. Energies (in 10^3 cm^{-1}) of the charge transfer bands in complexes with the d^0-electronic configuration of the metal[8,9,10]

Complex	E_{ct}	References
VO_4^{3-}	36.9	8,9
CrO_4^{2-}	26.82	8,9
MoO_4^{2-}	44.5	8,9
TcO_4^-	34.9	8,9
RuO_4	26.0	8,9
WO_4^{2-}	50.3	8,9
OsO_4	33.5	8,9
MnO_4^-	18.32	8,9
ReO_4^-	44.0; 49.0	8,9
ReO_6^{5-}	23.26	10
$MeReO_3$	41.84; 37.04; 29.85	This work

electrons, while the d levels of the central atom are free. In ReO_6^{5-}, the highest occupied molecular orbital is a nonbonding orbital with the participation of the π orbitals of the oxygen atom.[9]

In Fig. 1, the splitting of the energy terms of the d electron by the ligand crystal field in the cases of tetrahedral and octahedral coordinations are denoted by Δ_t and Δ_o. It is known[9] that

$$\Delta_t = 4/9\Delta_o, \tag{2}$$

if R_{Re-O} are equal in the cases of octahedral and tetrahedral coordination. However, even in Re_2O_7 (see Ref. 7), the average values of R_{Re-O} are 1.75 Å and 1.905 Å in the tetrahedral and octahedral coordination polyhedra, respectively; in ReO_6^{5-} the Re—O distance is even larger. Because of the different values of R_{Re-O}, the coefficient in (2) is not equal to 4/9; however, the ratio

$$\Delta_t < \Delta_o \tag{3}$$

is retained. It is apparent that two factors, namely, a larger value of Δ_o and a lower energy of the 2p-AO of the oxygen atom in the molecule with octahedral coordination, should decrease the value of the energy gap between the ligand MO and the d-AO.

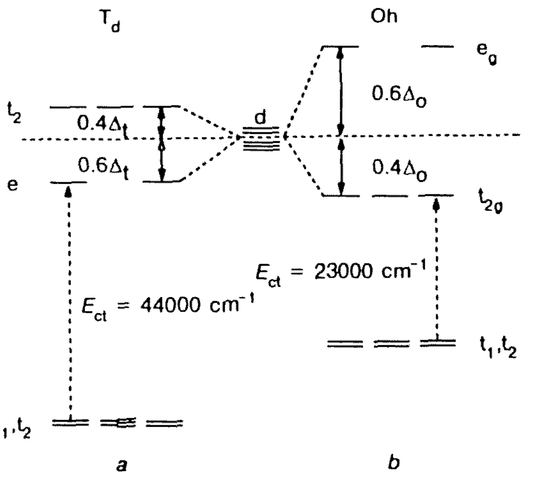


Fig. 1. Splitting of the energy terms of the d electron in (*a*) the tetrahedral ligand field in ReO_4^- and in (*b*) the octahedral ligand field in ReO_6^{5-}.

To make a quantitative estimation, let us define E_{ct} as the difference between the energy of the donor AO of the oxygen atom (E_0) and the energy of the acceptor AO of the metal (E_m):

$$E_{ct} = E_0 - E_m. \tag{4}$$

It is evident that

$$E_0 = E_{2p} - E'_{2p}, \tag{5}$$

where E_0 is the energy of the 2p-AO of the free oxygen atom and E'_{2p} is the change in this energy in the molecule owing to the negative charge on the oxygen atom. Therefore,

$$E_M = E_{5d} - E'_{5d} + E_{CT} \equiv E_{5d} - \delta E_{5d}, \tag{6}$$

where E_{5d} is the energy of the 5d-AO of the Re atom and δE_{5d} is the change in this energy in the molecule. As a result, we obtain

$$E_{ct} = (E_{2p} - E'_{2p}) - (E_{5d} - \delta E_{5d}). \tag{7}$$

The parameters of the free atoms were determined previously:[11] E_{2p} = 13.614 eV. The energies of the 5d-AO of the rhenium atom were calculated[12] by the Hartree—Fock—Slater method including the relativistic correction: $E_{5d(-3/2)}$ = 9.278 eV and $E_{5d(-5/2)}$ = 8.246 eV.

Therefore, Eq. (7) can be written in the form:

$$E_{ct} = 39141\ (cm^{-1}) - E'_{2p} + \delta E_{5d}. \tag{8}$$

This equation is applicable to all Re compounds. From this equation, the change in E_{ct} for ReO_4^- and ReO_6^{5-} may be evaluated. According to the data previously reported,[8,9] the first charge transfer band in ReO_4^- has a maximum at 44000 cm^{-1}, although the maximum is at 41700 cm^{-1} (see Ref. 13). Then, for ReO_4^- we obtain

$$-E'_{2p} + \delta E_{5d} \cong 5000\ cm^{-1}.$$

For ReO_6^{5-}, this value changes sign (-15881 cm^{-1}). This occurs because of the large negative charge on the oxygen atom. It is evident that Eq. (8) gives results that closely approximate the experimental data.

For $MeReO_3$, the scheme of the levels corresponds to the C_{3v} point symmetry group (a distorted tetrahedron). Figure 2 shows splitting of the energy terms of the d electron in going from ReO_4^- to $MeReO_3$. In the

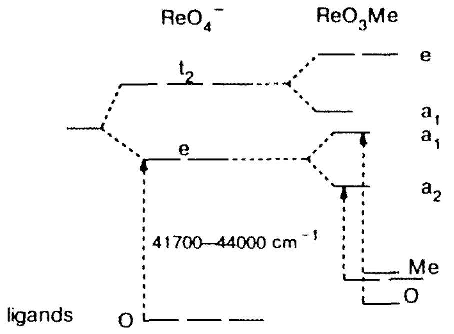
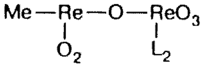


Fig. 2. Change in splitting of energy terms of the d electron in going from ReO_4^- to $MeReO_3$.

crystal field of the distorted tetrahedron of $MeReO_3$, the e level splits into a_1 and a_2, which results in the appearance of two charge transfer bands instead of one band. The t_2 level splits into e and a_1; however, the transition to these levels is, apparently, higher than 40000 cm^{-1}. Therefore, bands with maxima corresponding to transitions to the a_1 and a_2 levels will appear in the electronic absorption spectrum. The shift of the E_{ct} perrhenate band (43500—44000 cm^{-1}) to 42000 cm^{-1} in $MeReO_3$ is determined by splitting of the e level, and, apparently, by the lower charge on the oxygen atom.

Therefore, analysis of the electronic absorption spectra provide valuable data on the structures of the intermediate complexes that are formed in the course of reactions in which rhenium(VII) complexes participate. The appearance of new bands is indicative of the change in the coordination number of rhenium in its complexes. The method described using Eq. (8) makes it possible to characterize the structure of the intermediate complex. It is conceivable that formation of dimers with different coordination numbers of Re atoms of the type



$$\underset{O_2}{\underset{|}{Me—Re}}—O—\underset{L_2}{\underset{|}{ReO_3}}$$

will limit the use of Eq. (8).

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References

1. W. A. Herrmann, W. Wagner, J. G. Kuchler, *et al*, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 394.
2. W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1297.
3. W. A. Herrmann, W. Fisher, and D. Marz, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1638.
4. A. B. Kholopov, A. V. Nikitin, and V. L. Rubailo, *Kinet. Katal.*, 1995, **36**, 111 [*Kinet. Catal.*, 1995, **36** (Engl. Transl.)].
5. J. C. Moscow, *Acta Crystallogr.*, 1960, **13**, 443.
6. R. Scholder, K. L. Hupper, and P. P. Pfeifer, *Angew. Chem.*, 1963, **75**, 375.
7. H. Bayer et all, *Angew. Chem., (Int. Ed.)*, 1968, **7**, 295.
8. A. Carrington and McR. Symons, *Chem. Rev.*, 1963, **64**, 443.
9. C. K. Jorgensen, *Absorption Spectra and Chemical Bonding in Complexes*, Addition Wesley Publ., 1962.
10. E. J. Baran and A. Muller, *Z. Anorg. Allgem. Chem.*, 1969, **368**, 167.
11. C. E. Moore, *Atomic Energy Levels*, Ed. by National Burean standarts, 1958, **1**.
12. L. M. Dautov, Preprint of Institute of Nuclear Physics, Acad. Sci. of Kazakhstan, no. 5-82, Alma-Ata, 5, 1982.
13. G. C. Allen and K. Warren, *Structure and Bonding*, 1975, 108.

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