Distribution of electron density in the methyltrioxorhenium molecule

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The effective charges on atoms in the methyltrioxorhenium molecule were determined on the basis of the correlation between the chemical shift of ^{17}O and the energy of electron transitions in absorption spectra.

Key words: methyltrioxorhenium, electronic structure.

The previously performed calculations of the effective charges q_0 on oxygen atoms in tetrahedral hydroxy anions with closed shells (MO_4^{2-}) showed that q_0 in anions of the 5d-period are higher than those in the corresponding anions of the 4d-period and decrease along the period[1—3] (Table 1).

At the same time, the chemical shifts of ^{17}O measured relative to H_2O in many hydroxy anions depend linearly on the lowest energy E of the electron transition in the absorption spectra.[4] The parameters of particles of other symmetry types ($Cr_2O_7^{2-}$, CrO_2Cl_2) (Table 2, Fig. 1) also obey this dependence.[4] Using the known value of $\delta(^{17}O)$ for ReO_3CH_3 (see Ref. 5) and the energies of charge-transfer bands E_{ct} proportional to the corresponding wave numbers ν_{ct} (see Ref. 6), we estimated the values of the effective charges on the oxygen and metal atoms on the basis of the q_0—$\delta(^{17}O)$[1,2] and $1/\nu_{ct}$—$\delta(^{17}O)$) dependences.

Table 1. Effective charges (in electron charge units) on oxygen atoms (by the data of Refs. 1—3)

Compound	q_0
MoO_4^{2-}	−0.56
WO_4^{2-}	−0.66
TcO_4^{2-}	−0.46
ReO_4^-	−0.55
OsO_4	−0.37

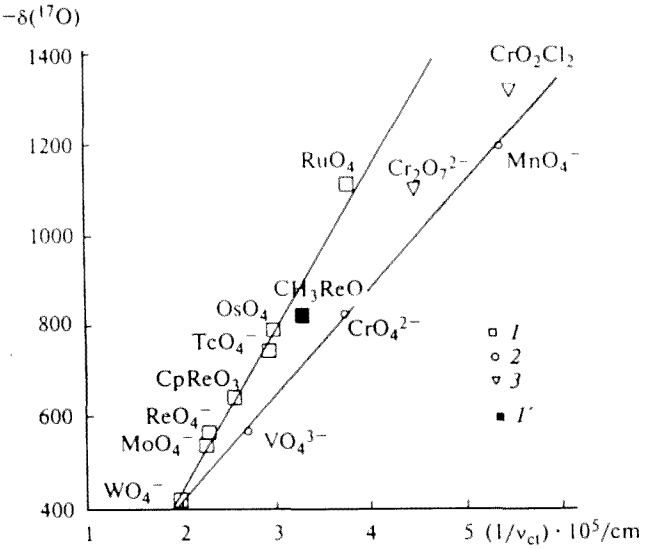

Fig. 1. Dependence of the chemical shift of ^{17}O nuclei in hydroxy anions on $1/\nu_{ct} \cdot 10^5$ (cm) $y = -a + bx$ ($a = -276.7$, $b = 355.8$, correlation coefficient $r = 0.987$, mean square deviation 37.5): *1*, *1′*, *2*, particles with symmetry C_{3v}; *3*, particles with different symmetry.

Table 2. Chemical shifts of oxygen atoms and lowest wave numbers ν_{ct} in absorption spectra

Compound	δ±0.1%/ppm	ν_{ct}/cm^{-1}
Na_3VO_4	−571	36900
Na_2CrO_4	−835	26800
K_2MoO_4	−540	44000
K_2WO_4	−420	50300
$NaMnO_4$	−1219	18300
$NaTcO_4$	−749	34000
$NaReO_4$	−569	43500
CH_3ReO_3	−829	29850
$CpReO_3$	−646	—
RuO_4	−1119	26400
OsO_4	−796	33500

The dependence between $\delta(^{17}O)$ and q_0 is shown in Fig. 2. It can be found from this dependence that

$$q_0(CH_3ReO_3) = -0.362 \quad \text{and} \quad q_0(CpReO_3) = -0.50$$

i.e., the oxygen atoms in CH_3ReO_3 are electron-deficient compared to those in $CpReO_3$ and ReO_4^-. The charge on the rhenium atom in perrhenate is equal to +1.2. Thus, the CH_3 group withdraws less electron

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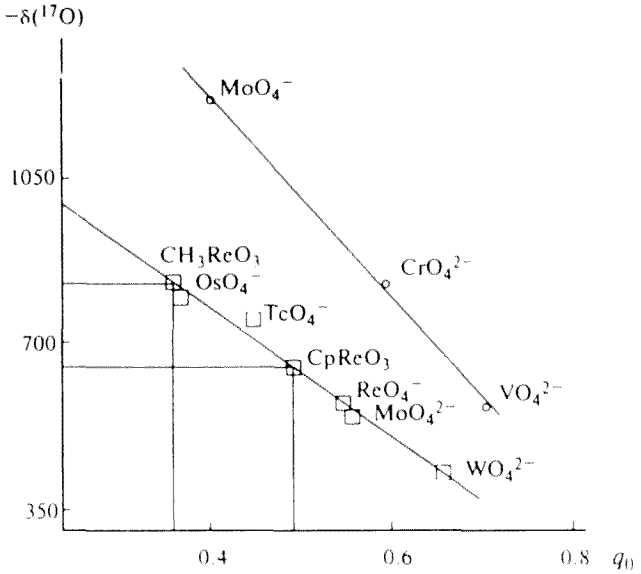
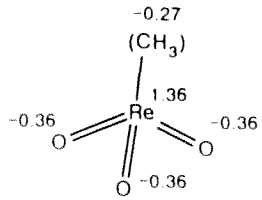


Fig. 2. Dependence of the chemical shift of ^{17}O nuclei in hydroxy anions on the charge (q_0, charge units) $y = a + bx$ determined by the least-squares method ($a = -1375.24$, $b = -0.996$, mean square deviation 20.2).

density than the O atom. The effective charges on the CH_3 group can be estimated as

$$q_{CH_3} = -0.362(9.84/13.614) = -0.27,$$

where $I(CH_3) = 9.84$ eV and $I(O) = 13.614$ eV are the ionization energies of the CH_3 group and the oxygen atom, respectively. Thus, the charges in CH_3ReO_3 are distributed as follows:



Experimental

Electronic absorption spectra were recorded on a Beckman DU-8 spectrophotometer in MeOH in cells with a 1-cm optical length. The solvent was used after dehydration.

Methyl(trioxo)rhenium was synthesized by the procedure described in Ref. 5 and characterized by ^{17}O and ^{1}H NMR (Bruker AMX 400) and IR Fourier spectroscopy (Bruker IFS 45).

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