

On the Chemistry of MeO_2^{n+} Oxycation Compounds*

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In the case of CrO_2X_2 chromyl compounds it was possible to demonstrate by methods of molecular spectroscopy that the CrO_2^+ group has features of an oxycation group and its individual characteristics depend on the type of bonds with the remaining X. This is clearly evident from the reaction mechanism of chromyl compounds with hydrocarbons, which is different for chromyl chloride and chromyl acetate.

New data, concerning the physico-chemical properties of molybdenum(VI) complexes containing an MoO_2^+ group, were obtained. The following compounds were investigated: MoO_2Cl_2 , MoO_2Br_2 and complexes with acetyl acetone, 8-hydroxyquinoline and tri-phenylarsenic oxide. On this basis, among other facts, the spectroscopic characteristics of the MoO_2^+ group were obtained.

The results of investigations of compounds with the vanadyl group VO_2^+ also corroborate the opinion that the basic structure and the mechanism of light absorption is closely related to that of the above mentioned oxyocations.

The literature concerning the chemical and physical properties of the compounds with oxycation groups of the MeO_2^{n+} type is not very extensive. The chemistry of uranyl compounds is an exception as it was remarkably developed. As a result, the uranyl group was sufficiently characterized and its significance for the properties determined. This applies also in a certain degree to some other compounds containing the actinyl groups (for example PuO_2^{2+}). Much less attention was devoted to the groups of d^0 electronic configuration, such as chromyl or vanadyl entities.

This paper gives new research data on the chemistry of compounds containing such a grouping.

Scarce informations are found in literature on the properties of CrO_2^+ chromyl compounds (except chromyl chloride). This is due to serious experimental difficulties resulting from strong oxidizing properties of these compounds.

The chromyl compounds may be divided into two principal types. The first contains solids and the second covers liquid compounds. Table 1 shows some chromyl compounds that have been obtained so far or whose existence is assumed.

Both these groups of chromyl compounds differ in the type of bonding.

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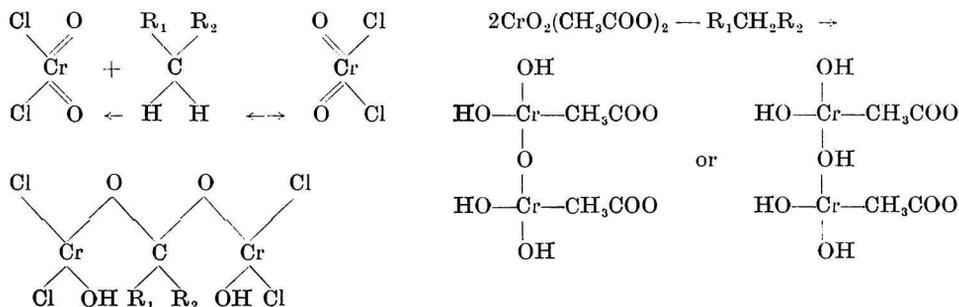
The first is supposed to have a strong ionic bond and the second a strong covalent bonding. Although such a differentiation is certainly only a schematic one, it may explain to some extent the differences observed by us in chemical behaviour of these compounds. An essential difference is revealed in the mechanism of Étards reaction between chromyl compounds and hydrocarbons [1, 2].

Table 1
Chromyl compounds

Solid	Liquid	Solution
CrO_2F_2 CrO_2Br_2 $\text{CrO}_2(\text{CH}_3\text{COO})_2$	CrO_2Cl_2 $\text{CrO}_2(\text{NO}_3)_2$	$\text{CrO}_2(\text{CNS})_2$ $\text{CrO}_2(\text{CNO})_2$ CrO_2J_2 ?

It was known for a long time that chromyl chloride (in CCl_4 solution) reacts readily with various types of hydrocarbons (paraffines, cyclic and aromatic hydrocarbons) forming as a result solid amorphous products. At the Wrocław Symposium [3], I reported on the existence of Cr(IV) in these compounds, assumed on the basis of magnetic studies, and the reaction mechanism was partly discussed. This has been further confirmed by spectroscopic measurements as well as by calculations based upon the ligand field theory [4].

The reaction of CrO_2Cl_2 with hydrocarbon results in formation of a binuclear complex with the $\text{Cr}(\text{OH})\text{Cl}_2\text{O}$ -grouping as a structural unit and two such groups are linked through a C atom of the hydrocarbon molecule:



A similar reaction with chromyl acetate takes a different course. Unexpectedly it was found that it leads to the formation of products which do not contain hydrocarbon molecules at all. Although the structure of this compound could not yet be considered as finally determined, it seems that it is a binuclear complex with oxygen or hydroxide bridge.

The magnetic measurements and the analysis of absorption spectra show that in both cases a reduction of Cr(VI) to Cr(IV) takes place, but in chromyl chloride the reduction is weaker and involves an intramolecular rearrangement of hydrogen atoms which is accompanied by displacement of charges towards Cr atoms. In the case of chromyl acetate the reduction is much stronger and its mechanism corresponds to an ordinary redox reaction.

In view of the above differences it may be assumed that the chromyl entity is a stronger oxidizer in chromyl acetate than in chromyl chloride. This would also affect the spectroscopic properties. Although no direct data concerning the infra-red spectra of chromyl acetate are available, the difference between the values of ν_1 Cr—O stretching frequencies in fluoride and chloride are concordant with the weaker ionic character of chloride. Therefore it is assumed that ν_1 for chromyl acetate is intermediate between chloride and fluoride values.

Spectroscopic studies supplied also new evidence that the chromyl grouping may be really considered as an oxycation group. We have calculated the force constants for the CrO_2^{2+} entity on the basis of known frequencies [5] by applying the valence forces model for the C_{2v} symmetry. A comparison with data given by Stammreich [5] for CrO_2Cl_2 molecule (Table 2) shows a full agreement provided that the interaction force constant is taken into account. On the

Table 2
Force constants of CrO_2Cl_2

System	Kind of vibration or interaction	Symbol	Value 10^5 dyn/cm
CrO_2^{2+}	Cr—O str.	k_1	6.71
CrO_2^{2+}	O—Cr—O bend.	k/l^2	0.50
CrO_2Cl_2	Cr—O str.	f_1	7.18
CrO_2Cl_2	Cr—O—Cr—O $f_1 = k_1 - f_{RR}$	f_{RR}	0.47

basis of these data and of the results of spectrographic studies of electronic spectra [6, 7] in which the vibrational structure may with all probability be accepted, it would be possible to conclude that an essential component of chromyl compounds is the chromyl group, around which the remaining atoms vibrate. The character of bonding between these atoms and the chromyl group affects Cr—O bond strength and, hence, its chemical and physical properties.

Almost no data are available on the spectroscopy and general properties of compounds containing the MoO_2^{2+} group. Beside the simple compounds such as molybdenyl chloride and molybdenyl bromide and complexes like

$\text{MeMoO}_2\text{Cl}_3$, many complexes with organic ligands were obtained, in which the presence of the MoO_2^{2+} group is assumed. There are, however, no sufficient data to determine the character of this entity in particular compounds, or even to find out whether they all contain such a grouping.

The results shown below concern the following compounds: MoO_2Cl_2 , MoO_2Br_2 , their complexes with triphenylarsine oxide and dioxane as well as the complexes with acetylacetone and 8-hydroxyquinoline.

The absorption spectra of the said compounds (Table 3) exhibit many characteristic features for which their molybdenyl entity is responsible.

Table 3
Electronic absorption spectra of MoO_2^{2+} compounds

Compound	Solvent	Maxima nm (Shoulder)
MoO_2Cl_2	Dioxane	224 (258) 366
MoO_2Br_2	Dioxane	264 (365)
$\text{MoO}_2\text{Br}_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{AsO}$	Dioxane	264 270 (360)
$\text{MoO}_2\text{Br}_2 (\text{C}_6\text{H}_5)_3\text{AsO } \text{C}_4\text{H}_8\text{O}_2$	Dioxane	264 271 (360)
$\text{MoO}_2(\text{C}_5\text{H}_6\text{O}_2)_2$	Acetylacetone	343 (373) 496 765
$\text{MoO}_2(\text{C}_9\text{H}_6\text{OH})_2$	Methylformamide	336 380 (540)

This conclusion was arrived at by comparing the absorption spectra of chromyl compounds. It should be stressed that the triatomic MoO_2^{2+} entity has a similar geometric structure and angular configuration in which the Mo—O distances and O—Mo—O angles are approximately equal to distances and angles of the CrO_2^{2+} group. The bands at 27 000—30 000 cm^{-1} may be therefore ascribed to a transition in the molybdenyl group from oxygen to an empty molybdenum orbital, analogously to the transition at 24 000 cm^{-1} for CrO_2Cl_2 . This is in general agreement with the hypsochromic shifting:

of bands concordant with the increasing Z number in a given group of the periodic table. The long-wave bands in the spectra of acetylacetone and 8-hydroxyquinoline complexes should also be assigned to this transition type in full agreement to the chromyl compounds [8].

There is a considerable decrease of intensity in the spectra of molybdenyl compounds as compared to the chromyl compounds. The molar absorptivity in MoO_2Cl_2 and MoO_2Br_2 for the band considered are 140 and 400 respectively, while in the case of CrO_2Cl_2 it is equal to about 2000.

Two essential differences between chromyl and molybdenyl compounds should be taken into account in this connection. The first concerns the possible participation of molybdenum f -orbitals in the chemical bond. The second one results from a tendency of Mo to form octahedral complexes also on the VI oxidation state, while Cr(VI) forms only tetrahedral structures (pure or disturbed).

The chemical properties of molybdenyl compounds are in good agreement with physico-chemical considerations. In contradistinction to the chromyl compounds they do not react with hydrocarbons but owing to their tendency to reach coordination number 6, they easily form complexes with β -diketones, quinoline, phenols, organic oxides and other ligands. It should be pointed out that it was possible to obtain during these investigations a mixed complex with one molecule of dioxane and one of triphenylarsine oxide.

Investigations were also carried out on acid solutions (pH ab. 1) of vanadium pentoxide in sulphuric acid. These solutions contain (at appropriate vanadium concentration) only vanadyl ions [9] to which the form VO_2^+ or $\text{V}(\text{OH})_4^+$ may be assigned. The absorption spectrum was not yet examined in the entire range. Our measurements indicate that in the long-wave region a typical transition inside the oxycationic group occurs (the band at about $13\,000\text{ cm}^{-1}$). Beside this band there are maxima in the ultraviolet region at ab. $35\,000\text{ cm}^{-1}$ which are almost identical with the spectrum of vanadyl perchlorate [9]. It should be therefore assumed that under the above conditions vanadium(V) forms an oxycationic entity VO_2^+ .

Our studies on compounds containing an oxycationic group of MeO_2^{n+} type ($n = 1$ or 2) clearly show that this entity is an essential factor for their physical and chemical properties. The electronic structure is formally identical in all cases since there are no unpaired electrons and the configuration is d^0 and f^0 . The geometric structure of the oxycationic group may be either linear as in the uranyl group or angular as in other cases discussed here. This geometry seems to be due to the participation of proper orbitals in the chemical bonding. It was pointed out [10] that the linearity of the uranyl cation is most probably caused by the participation of f orbitals in bonds (both equatorial and axial ones). But the uranyl group is most probably bent in chelate complexes and

this fact was connected with the additional participation of d orbitals in the bonds. Hence, the uranyl group becomes similar to other groups with d^0 electronic configuration and in particular to the MoO_2^{2+} entity where a certain participation of f orbitals is suggested.

As far as 30 years ago the uranyl group was called "radical" This term is certainly right from the point of view of its exceptional stability and individuality (in the spectroscopic sense). However, it seems to us that a better term would be "chromophore". The presence of a π -electron cloud is essential for an organic chromophore. The π -electron of the oxygen atoms of an oxy-cation group should be taken into account in this connection. In our opinion this term applies more or less to other oxycations discussed in the present paper.

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