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COMPARISON OF E_a VALUES OBTAINED BY THERMAL ANALYSIS WITH ENERGY OF 'CHARGE-TRANSFER' SPECTRA FOR POTASSIUM AND SILVER PERMANGANATES

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Abstract

The activation energy, E_a taken from the thermal decomposition of $KMnO_4$ and $AgMnO_4$ was compared with the energy of the longest wavelength O→Mn 'charge transfer' (CT) transition. The E_a and CT correlation was found in these systems. However, such relationship can be valid when in the dissociation process the electron transfer is assumed to be the rate determining step. Thus, the permanganates as well as the previously studied chromates, are positive examples showing that in some cases, the energies derived from both methods can be comparable.

Keywords: activation energy, $AgMnO_4$, 'charge transfer', $KMnO_4$

Introduction

This work is an extension to our previous attempt to correlate the spectral and thermal data for potassium and silver chromates and permanganates [1]. The present investigation is concerned with the detail description of both spectral properties and the thermal decomposition mechanisms of these compounds.

There are two reasons for which a search for a relationship between the activation energy calculated from the thermal decomposition study and e.g. spectroscopic parameters seems to be useful.

– Firstly, it is the aim to understand the micromechanism of the thermal decomposition of a studied solid phase.

– Secondly, the agreement between the E_a value determined from the thermal decomposition stage and the energy of the charge transfer transition in the electronic absorption spectrum can testify the reality of the former. On the other hand, the assignment of a particular transition can sometimes be verified by data obtained from a thermal analysis. However, this is true when in thermal

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decomposition the process of an electron transfer is assumed to be the rate determining step.

Determining the kinetic parameters from the thermal decomposition is not a trivial task and there are numerous doubts as for their reality.

According to Boldyrev [2, 3] all thermal decomposition reactions for solids can be divided into two groups:

– the first group includes the dissociation reactions issuing from the bond breaking inside an anionic or cationic sublattices not assisted by an electron transfer. The decomposition of metal ions formates and/or oxalates (I_a and II_a groups of periodic table) as well as dissociation of the II_a group carbonates may serve as examples here.

– the second group involves reactions that occur as a result of an interionic bond breaking caused by an electron transfer inside the anionic or cationic sublattice or by an electron transfer from the anion to the cation with radicals formation as an intermediate.

The decomposition of permanganates, chromates and perchlorates can be given as an example of the first sub-group in the second group. The second subgroup can be represented by the decomposition mechanism of $Ag_2C_2O_4$, AgCl and AgN_3.

From a spectroscopic point of view the permanganates seem to be an ideal species for such studies. The investigation of the electronic and molecular structure of the MnO_4^- ion has been an extensive field of both theoretical and experimental endeavour. The energy order is thus firmly established [4]. Moreover, this system has a simple chemical formula, which is an important parameter in the task for understanding the complementarity between spectral and thermal methods.

Experimental

Potassium permanganate (spectrally pure) has been used as purchased. Silver permanganate was prepared from mixing of 50 cm^3 $AgNO_3$ (0.35 *M*) and 75 cm^3 $KMnO_4$ (0.35 *M*) and allowed to stay overnight. Small crystallites of $AgMnO_4$ were collected and dried several days in the darkness. The diffuse reflectance spectra of $KMnO_4$ and $AgMnO_4$ were measured in the range 12500–47000 cm^{-1} with a Hitachi model 356 UV/Vis spectrophotometer interfaced to IBM/PC computer. The diffuse reflectance spectra of $KMnO_4$ and $AgMnO_4$ (5% weight) were recorded in Li_2CO_3, MgO, Ag_2SO_4 and K_2SO_4 matrices.

The band position has been established applying the digital filter method [5].

The thermal data for $KMnO_4$ and $AgMnO_4$ were taken from the literature [6–23].

Results and discussion

$KMnO_4$

The decomposition of potassium permanganate [6, 13] is one of the first solid state reactions for which an elucidation of the reaction mechanism has been attempted [6–23]. The variety of suggested decomposition sequences [6–9, 15–17, 19, 20, 23] are collected in Table 1, although the characterization of the residual decomposition products is still at present incomplete [20]. However, it appears to be an agreement in the literature that an electron transfer within the anion sublattice is an essential step in the decomposition of the solid permanganates [7, 9, 10, 13, 20, 23].

$$2MnO_4^- \rightleftarrows MnO_4^{2-} + MnO_4 \rightarrow MnO_4^{2-} + MnO_2 + O_2 \qquad (1)$$

The activation energy is identified with the electron transfer step:

$$2MnO_4^- \rightleftarrows Mn\ O_4^{2-} + MnO_4 \qquad (2)$$

In contrast to the silver chromate [1] where the first decomposition step connected with the change Cr(VI)→Cr(V) of the oxidation state is obscure, the decomposition process of potassium permanganate is significantly resolved.

The first stage of decomposition of whole crystals of $KMnO_4$ takes place in three substages: a slow reaction, followed by a rapid acceleration which in turn passes into a decay stage.

In the case of $KMnO_4$ crushed crystals the slow reaction does not take place. The acceleratory and decay stages usually obey the Prout–Tompkins (*P-T*) equation [6, 7, 24]. The variations in the reported kinetic obediences during the acceleratory period, i.e.

(i) the Prout-Tompkins equation: $\ln[\alpha/1-\alpha] = kt+C$ [6, 7] (3)
(ii) the power law equation $\alpha^{1/n} = kt$ [11] (4)
(iii) the Avrami–Erofe'ev equation: $[-\ln(1-\alpha)]^{1/2} = kt$ [7, 12] (5)
(iv) the exponential law equation $\ln\alpha = kt$ [7] (6)

can be traced to sample age and pretreatment [7] (α – the degree of conversion, k – the rate constant, t – the isothermal time, n – the exponent).

Table 1 The proposed sequences of the thermal decomposition of $KMnO_4$

Sequence	T /°C	Atmosphere	Ref.
$2KMnO_4 \rightarrow MnO_2 + K_2MnO_4 + O_2$	200–225	vacuum	[6]
$10KMnO_4 \rightarrow 3K_2MnO_4 + 2K_2O{\cdot}7MnO_2 + 6O_2$	180–300	air	[8]
$10KMnO_4 \rightarrow 2.65K_2MnO_4 + (2.35K_2O,\ 7.35MnO_{2.05}) + 6O_2$	220–250	air	[9, 20]
$10KMnO_4 \rightarrow 3K_2MnO_4 + K_4Mn_7O_{16} + 6O_2$	200	air	[15]
$5KMnO_4 \rightarrow K_2MnO_4 + K_3MnO_4 + 3MnO_2 + 3O_2$	240	nitrogen	[16]
$KMnO_4 \rightleftarrows K_3(MnO_4)_2 \rightleftarrows K_2MnO_4$	210–220	air	[17, 18]
$K_{9.6}{\cdot}(H_3O)_{0.4}{\cdot}10[MnO_{3.7}{\cdot}(OH)_{0.21}{\cdot}(H_2O)_{0.09}] = \{3K_2[MnO_{3.91}{\cdot}0.09HO] +$ $+ 7MnO_{1.8}{\cdot}1.8K_2O{\cdot}0.7HO{\cdot}1.3H_2O\} + 0.8H_2O + 6O_2$	220	air	[19]
$2MnO_4^- \rightarrow (1\text{–}x)MnO_4^{2-} + MnO_2^0{\cdot}xMnO_3^{2-} + (1 + 0.5x)O_2^0$ where $x \leq 2.5$	200–300		[23]

Table 2 The activation energy values of the thermal decomposition of $KMnO_4$

Sample	E_a / kJ·mol^{-1}(cm^{-1})	Equation	Ref.	Remarks
freshly prepared crystals				
ground	161.2 (13463)	(1)	[6]	the acceleratory period (chain branching reaction; P-T* Eq.)
whole	162.5 (13572)	(1)	[6]	the acceleratory period (chain branching reaction; P-T* Eq.)
recrystallized	155 (12946)	(4)	[7]	the acceleratory period (exponential law Eq.)
	130 (10858)		[7]	the reaction at the interface
	210 (17539)		[7]	the nucleation within the crystal

**P-T*, Prout-Tompkins equation (3)

The activation energies taken from the literature are shown in Table 2. The discrepancies in the magnitude of E_a (130–210 kJ/mole i.e. 10800–17600 cm^{-1}) are probably due to various experimental conditions, i.e. sample preparation, gas atmosphere, etc.

The electronic spectra of the potassium permanganate measured in solution and in solid state in various environment, are shown in Figs 1 and 2. The solid state spectra were resolved with digital filtration in order to obtain precise position of the bands, and the results are presented in Table 3. It was found that the position of the bands depends only slightly upon matrix applied. (We did not measure the spectra of $KMnO_4$ in Ag_2SO_4 matrix since a significant replacement of the potassium ions into silver ones takes place in this case [27].)

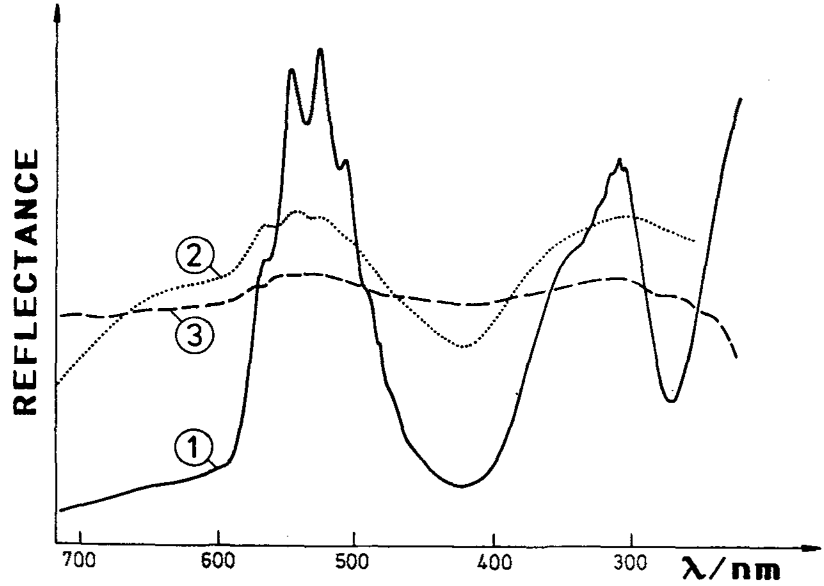

Fig. 1 Electronic spectra of the studied permanganates; 1- $KMnO_4$ in water; 2- $KMnO_4$ in Li_2CO_3 (diffuse reflectance spectrum); 3- $AgMnO_4$ in Ag_2SO_4 (diffuse reflectance spectrum)

Similarly to the solution case, the most prominent 'color' band (absorption in the green region), appears to be centered at ca 18800 cm^{-1} in both matrices. It possesses a vibronic character [4]. It was established that this band involves the intraionic transfer of an electron from t_1 molecular orbital, which is predominantly oxygen centered in character, to the $2e$ molecular orbital, predominantly metal in character i.e. $L\rightarrow M$ charge transfer. The antibonding $2e$ molecular orbitals are a combination of π oxygen orbitals and manganese $3d$ orbitals. This orbital excitation gives rise to four excited states: $^1T_2$, $^3T_2$, $^1T_1$ and

$^3T_1$. The $^1T_2 \leftarrow {}^1A_1$ transition was established to be responsible for the ca 18000 cm^{-1} band.

The vibrational fine structure of this band is due to the totally symmetric Mn–O vibration (735–768 cm^{-1}, according to various authors) [28]. The extend of band resolution is dependent upon the environment (Figs 1 and 2).

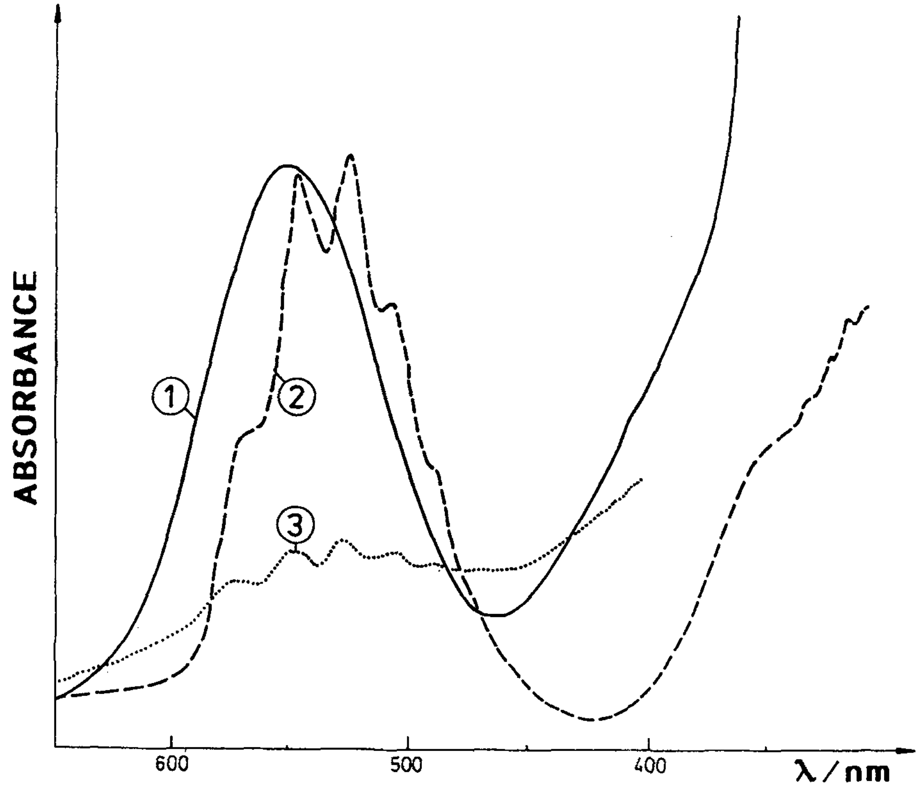

Fig. 2 Electronic spectra of $AgMnO_4$; 1- $AgNO_3$ solution; 2- water solution; 3- KBr pellet

According to the accumulated evidence the 'Teltow' red-band system was found in the electronic spectra of the MnO_4^- ion in the absorption range 13000–16000 cm^{-1} [29]. It can be ascribed to the forbidden electric-dipole $^1T_1 \leftarrow {}^1A_1$ transition in the parent T_d group. This absorption region can be seen more significantly under the influence of the solid state splitting at low temperature and polarization light spectra.

Our matrices are, thus, the source for the activation of the forbidden transitions. Moreover, in $KMnO_4$ crystal lattice the $^1T_2$ state possesses a lower symmetry C_s [30] and hence the lowest energy band can also be assigned to one of the component(s) of the tetrahedral states splitting. (A noticeable feature of the

Table 3 The band position after digital filtration and spectral assignment for potassium and silver permanganates in various matrices (Filter parameters applied: α = 200, N = 30; distances between measured points = 100 cm^{-1})

Matrix Compound	K_2SO_4	Li_2CO_3	Ag_2SO_4	Assignment
$KMnO_4$	15650 (s)	15800 (s)		$^1T_1 \leftarrow {}^1A_1$
	18850 (vs, as)	18800 (vs)		$^1T_2 \leftarrow {}^1A_1$
	26950 (s)	27000 (s)		$^1T_1 \leftarrow {}^1A_1$ or $^1T_2 \leftarrow {}^1A_1$
$AgMnO_4$	15180 (w)	15200 (w)	15200 (s)	$^1T_2 \leftarrow {}^1A_1$
	18500 (s)	18500 (s)	19700 (vw)	
	23400 (vw)	23600 (ms)		
	28500 (s, as)	29000 (s, br)	26800 (vs)	

s - strong, vs - very strong, as - asymmetric, w - weak, vw - very weak, ms - medium strong, br - broad filtered system is the vibrational fine structure which will be a subject of our future studies). The symmetry lowering can be additionally magnificated through using a diluter.

For comparison with the activation energy of the process taken from thermal analysis: Mn(VII)+$e(0)$ → Mn(VI) in $KMnO_4$ two candidates must be taken into account: 18000 cm^{-1} and 15000 cm^{-1} transitions. We favour the first candidate (Table 4) since the second one yields much weaker intensity (i.e. it is the less probable).

Table 4 A comparison of the activation energy and the electron transfer energy in various chromate and permanganate salts (1kJ = 83.52 cm^{-1})

Compound	Activation energy/ cm^{-1}	Energy of CT transition/ cm^{-1}	Ref.
$MgCrO_4$	27600 ± 1400	27000	[25]
$La_2(CrO_4)_3$	26900 ± 2800	26700	[25]
$Nd_2(CrO_4)_3$	27600 ± 1700	26700	[25]
$Sm_2(CrO_4)_3$	23100 ± 2100	23100	[25]
$CuCrO_4$	20730, 19130	23750	[26]
Ag_2CrO_4	16700	17000	[1]
$KMnO_4$	13500 ± 500	18800*	[6]
	17500		[7]
$AgMnO_4$	10300	15200*	[6]

* Present work

However, it seems to be premature to decide undoubtly which particular electronic transition is responsible for the rate determining step in the decomposition process of potassium permanganate.

$AgMnO_4$

It seems that the decomposition of other permanganates is less intense studied than the potassium salt. For example, the thermal decomposition of $AgMnO_4$ has been described through the following sequence [6]:

$$4AgMnO_4 \xrightarrow{105-120^\circ C} 2Ag_2O+4MnO_2+3O_2 \qquad (7)$$

The E_a value is equal to ca 124 kJ /mole (ca 10400 cm^{-1}) for the acceleratory period (chain branching reaction, P-T modified equation) [6, 7].

The electronic absorption spectra of $AgMnO_4$ in water, silver nitrate solutions and KBr pellet are presented in Fig. 2. Table 3 shows the filtration effect in various matrices. The dissolution of silver permanganate in solution containing silver ions was found to give the most reliable results. In the solid state some amount of replacement of the Ag^+ ions with the matrix cations takes place. This causes the blue shift of the band with some resemblance to $KMnO_4$ system. For example, the 18500 cm^{-1} band in $AgMnO_4/K_2SO_4$ and $AgMnO_4/Li_2CO_3$ is still the most intense band in the system although it is not as intense as in $KMnO_4$.

In silver sulphate matrix the 15200 cm^{-1} transition is the strongest one in the filtered spectrum and we may assume that this is the red-shifted ${}^1T_2 \leftarrow {}^1A_1$ transition. In the Ag_2CrO_4 spectra the shift of this transition in the silver salt in comparison to the potassium salt is about 10000 cm^{-1}. Hence, this transition can be assumed as comparable with the E_a thermal data for silver permanganate (Table 4).

Conclusion

We have studied two permanganate salts using thermal and spectroscopic methods. The thermal data are taken from the literature, and the spectral data from our own experiments. The ${}^1T_2 \leftarrow {}^1A_1$ ($t_1 \rightarrow 2e$) 'charge transfer' transition has been compared with the activation energy of the electron transfer. We realized that, similarly to the previously studied chromates, this energy is comparable (including discrepancies) in both methods. However, in our opinion, it is premature to discuss all the differences thoroughly explicitly. It is interesting enough, for example, that the energy obtained from the spectra in all cases is higher than the energy taken from thermal decomposition. Thus, the permanganate salts are another positive examples admitting that in some cases the energies derived with both methods can be compared.

We believe, that in our future studies on thermochemical and spectral relations, the role of such attempt will be shown more convincing. However, to do this, very careful experimental examples are necessary. Especially, the objects should possess firmly established mechanisms of thermal decomposition.

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Zusammenfassung — Die aus der thermischen Zersetzung von $KMnO_4$ und $AgMnO_4$ erhaltene Aktivierungsenergie E_a wurde mit der größten Wellenlänge des Chargetransfer(CT)-Überganges O→Mn verglichen. In diesen Systemen wurde eine Korrelation zwischen E_a und CT gefunden. Eine derartige Beziehung kann gelten, wenn man annimmt, daß die Elektronenübergabe der geschwindigkeitsbestimmende Schritt im Dissoziationsprozeß ist. Somit sind die Permanganate und auch die bereits früher untersuchten Chromate positive Beispiele dafür, daß die mittels beiden Methoden ermittelten Energien vergleichbar sind.