

Thermodynamic study of an effective catalytic system, hydrogen peroxide and methyltrioxorhenium

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ABSTRACT

The thermodynamic of the known and very effective catalytic system, hydrogen peroxide (H_2O_2) and methyltrioxorhenium (MTO) is studied in different solvents using UV-Visible spectroscopic method. The thermodynamic parameters (ΔG , ΔH and ΔS) for two equilibrium reactions, $\text{MTO} + \text{H}_2\text{O}_2 \rightleftharpoons \text{A} + \text{H}_2\text{O}$ and $\text{A} + \text{H}_2\text{O}_2 \rightleftharpoons \text{B.H}_2\text{O}$ (A, $[\text{MeRe}(\text{O})_2(\text{O}_2)]$; **B.H₂O**, $[\text{MeRe}(\text{OH}_2)(\text{O})(\text{O}_2)_2]$), are determined. The obtained free energies of the reactions depend on dielectric constants of solvent, which are explained by Onsager's reaction field theory.

Keywords: Methyltrioxorhenium, Hydrogen peroxide, Thermodynamic study.

1. Introduction

In 1991, Herrmann and co-workers reported methyltrioxorhenium (VII) (CH_3ReO_3 , MTO) as an oxidation catalyst for the epoxidation of alkenes with hydrogen peroxide as the terminal oxidant [1]. For more than 3 decades, MTO and its derivatives have found many interesting applications in synthesis, catalysis and material chemistry [2-7]. The MTO/ H_2O_2 system has been investigated in a variety of reactions mostly oxidation of substrates such as alkenes [8-10], conjugated dienes [11], aromatic [12], sulfur [13], and phosphine [14] compounds. The importance of MTO/ H_2O_2 system is due to its ease of synthesis, availability, stability and high solubility of MTO in many polar and non-polar solvents and also non-hazardous byproduct of hydrogen peroxide formed during the oxidation process, i.e. H_2O .

On the basis of experimental [15-18] and theoretical [19-21] studies, it was shown that in solution, on treatment of methyltrioxorhenium in water or organic solvents with hydrogen peroxide, MTO undergoes peroxidation to afford mono- and bisperoxo complexes that are in equilibrium with the initial MTO (Scheme 1). In MTO/ H_2O_2 system used for oxygen transfer to the olefinic double bond, the involved active species are monoperoxo (A, $[\text{MeRe}(\text{O})_2(\text{O}_2)]$)

and bisperoxo (**B.H₂O**, $[\text{MeRe}(\text{OH}_2)(\text{O})(\text{O}_2)_2]$) complexes.

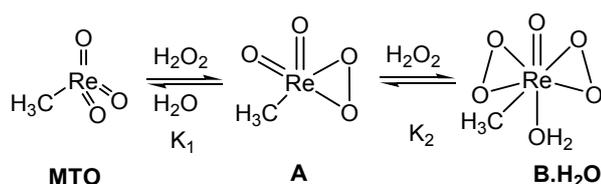
Although several experimental and theoretical studies about different aspects of MTO have been published [20,22,23], it is surprising that the information about the thermodynamics of the reactions presented in the MTO/ H_2O_2 system in different solvents is scarce.

In this report we have investigated the thermodynamic of the reactions shown in Scheme 1 in different solvents. The results obtained in the present work are particularly significant because of the importance of MTO/ H_2O_2 system in catalytic chemistry. These parameters also allow the chemists to optimize the best conditions needed for an ideal oxidation catalytic system.

2. Experimental

The compound methyltrioxorhenium (MeReO_3 or MTO) was prepared as reported [24]. Equilibrium studies were carried out by using a Perkin Elmer Lambda 25 spectrophotometer with temperature control using an EYELA NCB-3100 constant temperature bath. Solutions of hydrogen peroxide were standardized iodometrically and their concentrations were determined by standard method. Typically, a 3.6 mM solution of the MTO in solvent contained in a quartz cuvette with a 1 cm path length was treated with successive aliquots of a known concentration solution of H_2O_2 in the same solvent at 25 °C.

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Scheme 1. Reaction of MTO with H_2O_2 .

The values of equilibrium constants were determined by fitting the equilibrium absorbances to Eq. 1 [25] by the method of non-linear least squares using KaleidaGraph program.

$$\bar{\varepsilon} = \frac{\text{Abs}}{[\text{MTO}]_T} = \frac{\varepsilon_A K_1 [\text{H}_2\text{O}_2] + \varepsilon_B K_1 K_2 [\text{H}_2\text{O}_2]^2}{1 + K_1 [\text{H}_2\text{O}_2] + K_1 K_2 [\text{H}_2\text{O}_2]^2} \quad (1)$$

Here, Abs is the absorbance of a solution at equilibrium; $[\text{MTO}]_T$ is total concentration of MTO in solution, ε_A and ε_B are molar absorptivities for **A** and **B.H₂O** species, respectively at corresponding wavelength; K_1 and K_2 are equilibrium constants for the reactions presented in solution (Scheme 1) and $[\text{H}_2\text{O}_2]$ represents the equilibrium H_2O_2 concentration. The calculated equilibrium constants for the reaction shown in Scheme 1 are collected in Table 1. The same method was used at other temperatures and solvents and thermodynamic parameters were obtained from the van't Hoff equation (Eq. 2).

$$\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (2)$$

3. Results and Discussion

3.1. Equilibrium Studies

On mixing of MTO in water (or organic solvents) with hydrogen peroxide, a yellow solution is obtained according to Scheme 1 that is more intense at higher peroxide concentrations. The absorbance-concentration titration diagram is shown in Fig. 1. As is clear from the Figure, upon increasing of more H_2O_2 , the absorbance continues to rise until finally a plateau is reached, suggesting the existence of equilibrium in solution. The UV spectral scans at various H_2O_2 concentrations are illustrated in Fig. 2.

The Absorbance (at 360 nm)- $[\text{H}_2\text{O}_2]$ data were analyzed based on two equilibriums (Scheme 1) presented in solution. The nonlinear least-squares fit of Abs- $[\text{H}_2\text{O}_2]$ data according to Eq. 1 gave the values of the equilibrium constants K_1 and K_2 and the data are collected in Table 1. The binding constant for the second equilibrium in MTO/ H_2O_2 system (K_2) is considerably larger than that obtained for the first step (K_1). For example in acetone at 25 °C, the values of K_1 and K_2 are 550 and 2007 L mol^{-1} , respectively. The same behavior was observed in other solvents and temperatures.

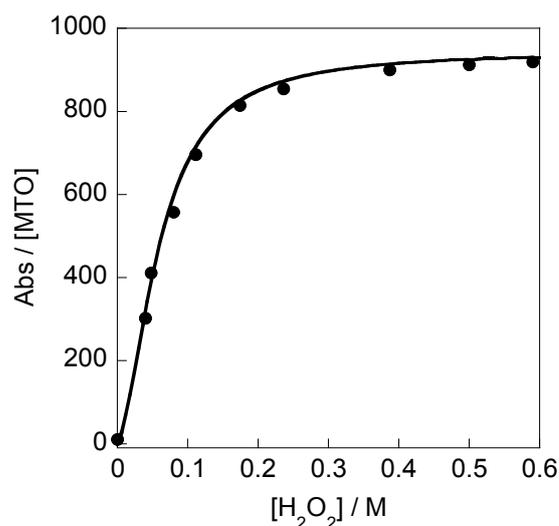


Fig. 1. Changes in absorbance (at 360 nm) on addition of H_2O_2 to MTO in THF at 30 °C. The solid line is the fit of the data to Eq. 1.

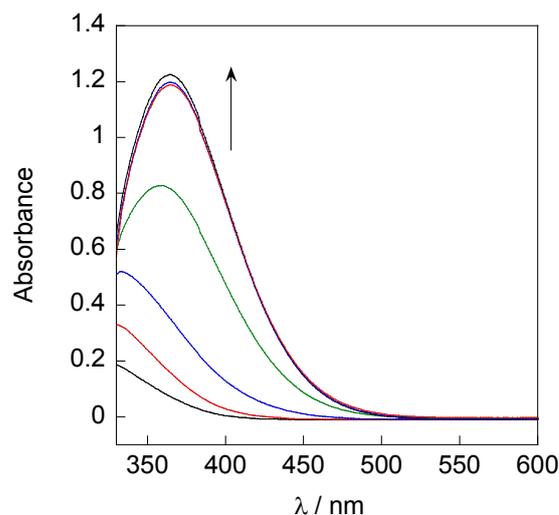


Fig. 2. Changes in UV-vis spectra of equilibrated MTO- H_2O_2 mixtures in acetone at 20 °C. The total MTO concentration is 3.6 mM and the concentrations of H_2O_2 (reading upward) are 20.5-45.0 mM. Successive spectra were recorded at intervals of at least 45 min.

In order to have a better understanding of the thermodynamics of equilibrium reactions between MTO and H_2O_2 , it is useful to consider the enthalpic and entropic contributions to these reactions. The ΔH and ΔS values for the reactions in different solvents were evaluated from the corresponding temperature data by applying a linear $\ln K_1$ (or $\ln K_2$) least squares analysis according to the van't Hoff equation. Plots of $\ln K$ vs. $1/T$ for the MTO/ H_2O_2 system at different solvents were linear for all cases studied (Fig. 3). The enthalpies and entropies of equilibrium reactions were determined in the usual manner from the slopes and

Table 1. Equilibrium constants and thermodynamic parameters for the formation of compounds **A** and **B.H₂O** according to the reactions shown in Scheme 1 in different solvents.

Solvent	K_1 (L mol ⁻¹) ^a for MTO + H ₂ O ₂ ⇌ A + H ₂ O					ΔH_1 / kJmol ⁻¹	ΔS_1 / JK ⁻¹ mol ⁻¹	ΔG_1^b / kJmol ⁻¹
	10 °C	20 °C	25 °C	30 °C	40 °C			
Water	150.0	33.4	17.7	10.2	3.5	-83.9±1.0	-257.6±3.5	-7.1±0.1
Acetone	1930.0	999.8	550.0	420.1	210.4	-55.4±3.0	-132.6±10.0	-15.9±0.3
THF	2859.6	1389.1	755.2	599.7	249.3	-60.1±3.2	-145.7±10.8	-16.7±0.2
CH ₃ OH	829.8	435.1	281.8	228.4	135.3	-44.9±2.0	-103.1±7.0	-14.2±0.2
CH ₃ CN	725.4	340.1	219.4	123.9	66.1	-60.4±3.0	-155.3±9.9	-14.1±0.3
Ethyl acetate	3307.7	1609.3	915.5	716.2	310.7	-58.2±2.7	-138.0±9.0	-17.1±0.3
Solvent	K_2 (L mol ⁻¹) ^a for A + H ₂ O ₂ ⇌ B.H ₂ O					ΔH_2 / kJmol ⁻¹	ΔS_2 / JK ⁻¹ mol ⁻¹	ΔG_2^b / kJmol ⁻¹
	10 °C	20 °C	25 °C	30 °C	40 °C			
Water	654.1	285.2	149.8	79.7	30.1	-77.3±4.4	-218.2±14.7	-12.2±0.2
Acetone	3440.1	2380.0	2006.8	1598.9	1090.5	-28.3±1.0	-32.0±3.5	-18.8±0.1
THF	9936.2	3852.4	2688.4	1843.6	1150.3	-53.5±3.8	-112.8±13.0	-19.9±0.2
CH ₃ OH	1650.0	996.3	784.6	512.2	285.0	-43.6±3.0	-91.7±10.0	-16.3±0.2
CH ₃ CN	1783.2	928.1	639.9	365.4	180.2	-57.4±3.6	-139.8±12.0	-15.7±0.2
Ethyl acetate	10541.0	4529.3	2886.4	2219.5	1330.8	-51.2±3.4	-104.6±11.5	-20.1±0.2

^aEstimated errors in K values are ± 7%.

^bAt 298 K.

intercepts of the plots and the results are collected in Table 1. The ΔG values, calculated from $\Delta G = \Delta H - T\Delta S$ at 298 K are also included in Table 1.

3.2. Correlation between free energies and solvent parameters

Different solvent parameters have been proposed over the years to give various solvent properties [26]. They have been used to explain discrepancies observed between various properties of a given solute as the solvents are changed.

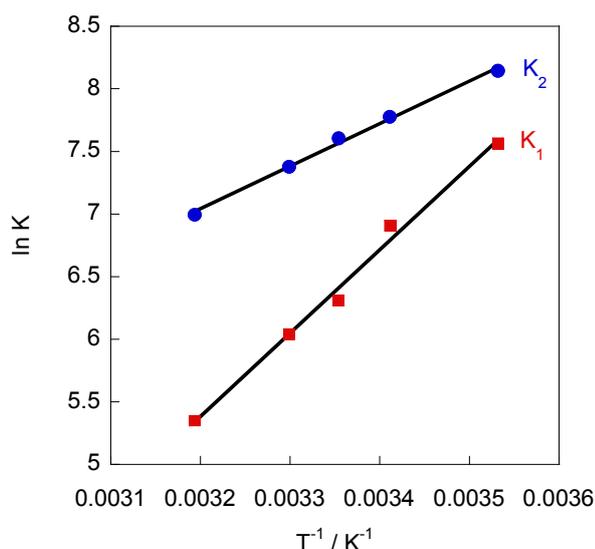


Fig. 3. van't Hoff plots for reactions of MTO + H₂O₂ ⇌ A + H₂O (K_1) and A + H₂O₂ ⇌ B.H₂O (K_2) in acetone.

In many cases, it has been demonstrated that solute properties are dependent on more than one solvent parameter [27,28]. A method was applied for the treatment of the results in which the obtained free energies of the reactions shown in Scheme 1 in different solvents were first correlated separately with each one of the solvent parameters to evaluate them for their ability to provide a reasonable explanation (the solvents used and their parameters are given in Table 2). Then, to give an independent interpretation of the free energies in different solvents, the linear solvation energy relationship (LSER) multi-parameter method, based on that of Kamlet et al. [29,30] was performed using two solvent parameters according to multi-parametric correlations expressed by:

$$\Delta G = \Delta G^\circ + aX_1 + bX_2 \quad (3)$$

where ΔG° is the value of ΔG in a solvent for which the properties X_i are zero for all i values, X_1 and X_2 are different solvent parameters, and a and b are the coefficients of X_1 and X_2 , respectively, which can be obtained by multiple linear regression analysis.

The change of the free energy values for the reactions studied in this work was correlated at first with each of the solvent parameters as follows: ϵ_r , dielectric constant of the solvent; $E_T(30)$, its polarity; DN , donor number of solvent; α , the hydrogen bond donation (HBD) ability; β , its hydrogen bond acceptance (HBA) or electron pair donation ability to form a coordinative bond and π^* , its polarity/polarizability parameter. For ΔG of two reactions presented in MTO/H₂O₂ system (Scheme 1), the best correlation was found for ϵ_r

Table 2. The property parameters of solvents.^a

Solvent	ϵ_r ^b	$E_T(30)$ ^c	DN ^d	α ^e	β ^e	π^* ^e
Water	78.5	63.1	18.0	1.17	0.47	1.09
Acetone	20.6	42.2	17.0	0.08	0.43	0.71
THF	7.3	37.4	20.0	0.00	0.55	0.58
MeOH	32.7	55.4	30.0	0.98	0.66	0.60
CH ₃ CN	36	45.6	14.1	0.19	0.40	0.75
Ethyl acetate	6	38.1	17.1	0.00	0.45	0.55

^aData from ref. [26].^b ϵ_r = dielectric constant.^cPolarity.^dDonor number.^eKamlet–Taft parameters.

(ϵ_r =dielectric constant) with R^2 values of 0.96-0.98 for both reactions (see Table 3). Then the ΔG values were correlated with two solvent parameters. Correlations of ΔG of the reactions in MTO/H₂O₂ system with the solvent parameters of Kamlet et al. are given in Table 3 with multiple correlation coefficients R^2 in the range 0.97–0.98. As is clear from the Table 3, multi-parameter correlations using two parameters gave no

further improvement, with the following form:

$$\Delta G = \Delta G^\circ + a\epsilon_r + bX_2 \quad (X_2 = E_T(30), DN, \alpha, \beta \text{ and } \pi^*) \quad (4)$$

Therefore from the results presented in Table 3, it can be concluded that the dielectric constant of the solvent is the most important parameter in this system ($R^2=0.98$ for ΔG versus ϵ_r plot, Fig. 4). Water, with the highest dielectric constant, shows the negative smallest

Table 3. Parametric solvent coefficients of free energy of the reactions in the MTO/H₂O₂ system obtained from the different multi-parametric equations (LSER).^a

LSER equation	MTO+H ₂ O ₂ ⇌ A+H ₂ O				A+H ₂ O ₂ ⇌ B.H ₂ O			
	ΔG°	a	b	R^2	ΔG°	a	b	R^2
$\Delta G = \Delta G^\circ + a\epsilon_r$	-18.30 (0.42)	0.14 (0.01)	---	0.98	-20.54 (0.41)	0.11 (0.01)	---	0.96
$\Delta G = \Delta G^\circ + aE_T(30)$	-29.6 (3.6)	0.33 (0.07)	---	0.83	-30.14 (2.59)	0.28 (0.05)	---	0.87
$\Delta G = \Delta G^\circ + aDN$	-14.03 (6.65)	-0.01 (0.33)	---	0.01	-17.61 (5.49)	0.02 (0.27)	---	0.01
$\Delta G = \Delta G^\circ + a\alpha$	-16.54 (1.20)	5.84 (1.91)	---	0.70	-19.13 (0.96)	4.88 (1.53)	---	0.72
$\Delta G = \Delta G^\circ + a\beta$	-13.29 (9.61)	-1.81 (19.17)	---	0.01	-16.82 (7.94)	-0.71 (15.84)	---	0.00
$\Delta G = \Delta G^\circ + a\pi^*$	-26.60 (2.21)	17.41 (3.00)	---	0.89	-26.68 (2.68)	13.34 (3.64)	---	0.77
$\Delta G = \Delta G^\circ + a\epsilon_r + bE_T(30)$	-17.73 (3.05)	0.14 (0.03)	-0.02 (0.08)	0.98	-22.10 (2.98)	0.10 (0.03)	0.04 (0.08)	0.97
$\Delta G = \Delta G^\circ + a\epsilon_r + bDN$	-18.27 (1.22)	0.14 (0.01)	-0.01 (0.06)	0.98	-21.09 (1.19)	0.11 (0.01)	0.03 (0.06)	0.97
$\Delta G = \Delta G^\circ + a\epsilon_r + b\alpha$	-18.28 (0.48)	0.13 (0.02)	0.16 (1.12)	0.98	-20.50 (0.48)	0.11 (0.02)	0.43 (1.11)	0.97
$\Delta G = \Delta G^\circ + a\epsilon_r + b\beta$	-18.73(1.73)	0.14 (0.01)	0.86 (1.32)	0.98	-21.28 (1.72)	0.11 (0.01)	1.48 (3.30)	0.97
$\Delta G = \Delta G^\circ + a\epsilon_r + b\pi^*$	-19.59 (2.28)	0.12 (0.03)	2.59 (4.46)	0.98	-17.56 (1.70)	0.15 (0.03)	-5.94 (3.33)	0.98

^aValues in parentheses are standard deviations.

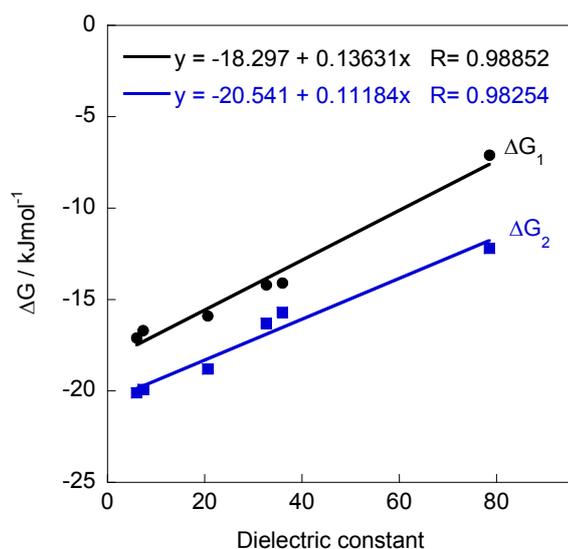


Fig. 4. Plots of ΔG versus ϵ_r for the reactions presented in the MTO/H₂O₂ system. Data are taken from Table 3.

values of ΔG for both reactions studied in the present work and ethyl acetate with the lowest dielectric constant shows the negative largest ΔG values.

It is possible to use Onsager's reaction field model [31, 32] for the interpretation of solvent effects by considering that the free energy change for the reactions presented in MTO/H₂O₂ system may be described by a one-parameter equation that contains the term for the dielectric constant. The reaction field model expresses solvation energy as shown in the following equation:

$$\Delta E_{sol} = \frac{2\mu^2}{r^3} \left(\frac{\epsilon_r - 1}{\epsilon_r + 2} - \frac{n^2 - 1}{n^2 + 2} \right) \quad (5)$$

where ϵ_r and n are the dielectric constant and the refractive index of the solvent, respectively. μ and r also represent the dipole moment and the diameter of the solute, respectively. Since the refractive indexes are constant ($n = 1.4$) for all of the solvents, the second term of parenthesis will be constant. Therefore, solvation energy depends only on the parentheses term and will be a function of dielectric constant. According to Table 1 and Fig. 4, when the solvent has an insignificant and small ϵ_r , the free energy changes of solvation for the reactants and the product are unimportant and the solvent molecules are not tightly bonded to the reactants and the products. Therefore, the solvent molecules are not closely associated with the reactants or with the products. It means the reactivity of the reactants in this solvent is more than the other solvent and therefore the equilibrium constant of the reaction is larger (i.e. more negative ΔG value). In contrast, in the polar solvent having large ϵ_r , the solvation energy becomes much larger according to Onsager's reaction field model, resulting less negative

ΔG value and the reactants and the products are tightly trapped by the solvent molecules. Hence, the solvent molecules are well aligned with the reactants and with the products.

4. Conclusions

The two equilibrium reactions presented in the MTO/H₂O₂ system were studied in different solvents using Uv-vis spectroscopy. The thermodynamic parameters for the reactions MTO + H₂O₂ \rightleftharpoons A + H₂O and A + H₂O₂ \rightleftharpoons B.H₂O were determined and solvent effects on these parameters were investigated. It was found that the dielectric constant of the solvent is the most important parameter in this system. The values of free energies correlate with dielectric constants of the solvents. Water, with the highest dielectric constant, showed the largest values of ΔG for both reactions studied in the present work and ethyl acetate with the lowest dielectric constant showed the smallest ΔG values.

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