Journal of the Serbian Chemical Society

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J. Serb. Chem. Soc. 73 (7) 735–744 (2008)
JSCS–3756

UDC 547.466.24+547.831:544.35:531.3
Original scientific paper

Effect of excess free energy of solvents on the oxidation of methionine by quinolinium fluorochromate. A kinetic study

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(Received 18 October 2007, revised 5 May 2008)

Abstract: The oxidation of methionine by quinolinium fluorochromate (QFC) was studied in the presence of chloroacetic acid, in water/organic solvent mixtures of varying excess molar free energy function. The reaction is first order with respect to both QFC and acid. The reaction rates were determined at different temperatures and the activation parameters computed. The rate data was correlated with different solvent parameters using linear multiple regression analysis. From the results, information on the solvent–reactants and the solvent–transition state interactions was obtained.

Keywords: solvent effect; kinetics; methionine.

INTRODUCTION

Studies of the kinetics of the oxidation of organic compounds in non-aqueous and aqua–organic solvent mixtures[1–6] revealed the important role of non-specific and specific solvent effects on the reactivity. It is of great interest to study the kinetics of oxidation of methionine in binary solvent mixtures, which are more complex than pure solvents, due to the varying degrees of solute–solvent interactions. In a pure solvent, the composition of the microsphere of solvation of a solute, the so-called cybotatic region, is the same as in the bulk solvent but in binary mixtures, the composition in this microsphere can be different. The solute can interact to a different degree with the components of the mixture and this difference in the interactions is reflected in the composition of the microsphere of solvation. The effect of varying the composition of a mixture from the bulk solvent to the solvation sphere is called preferential solvation.[7]

It was shown that the reactivity is influenced by the preferential solvation of the reactants and/or transition state through non-specific and specific solvent–solvent–solute interactions. Furthermore, it was established that the technique of

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doi: 10.2298/JSC0807735B

correlation analysis might be used well to separate and quantify such solvent–solvent–solute interactions on reactivity. Extensive studies on the mechanism of oxidation of methionine (Met) by several oxidants have been reported. This sulphur containing essential amino acid is reported to behave differently, in comparison to other amino acids, towards many oxidants.[8–12] This may well be due to the presence of an electron-rich sulphur centre, which is easily oxidisable.

Quinolinium fluorochromate (QFC) was reported to be a mild, stable and selective oxidant.[13] A perusal of the literature showed that there seems to be a very few reports using QFC. Blandamer and Burgess[14] classified aqueous mixtures based on their thermodynamic properties, particularly their molar excess functions, X^E. Thus, in this article, the kinetics and mechanism of the oxidation of methionine by QFC in water/1,4-dioxane (apolar, aprotic, hydrogen bond acceptor solvent), water/DMF (polar, aprotic, hydrogen bond acceptor solvent), water/acetonitrile, water/acetone (both dipolar aprotic non-hydrogen bond donor solvent), and water/*t*-BuOH (protic, hydrogen bond donor solvent) mixtures of varying mole fractions, with the view of comprehending the utility of studies of solvent variation in the understanding of the mechanism of this biologically important amino acid, as it may reveal the mechanism of amino acid metabolism. Furthermore, solvent mixtures are very useful for studying solvent effects upon reactions, since the properties of various mixed solvents can be adjusted continuously by changing the composition of the mixture.

EXPERIMENTAL

Materials

All the employed chemicals and solvents were of analytical grade. Methionine (SRL, India) was used as supplied. Quinolinium fluorochromate (QFC) was prepared by a reported method[13] and its purity was checked by the iodometric method. Doubly distilled water was used for all purposes.

Kinetic measurements

The reactions were performed under pseudo-first order conditions by keeping the substrate in excess over QFC. The progress of the reactions was monitored by estimating the unreacted oxidant iodometrically at 25±0.2 °C. The rate constants were determined by the least squares method, from the linear plots of log titre *versus* time. Duplicate runs showed that the rate constants were reproducible to within ±3 %. The stoichiometry and product analysis were performed as reported earlier.[11,12]

Data analysis

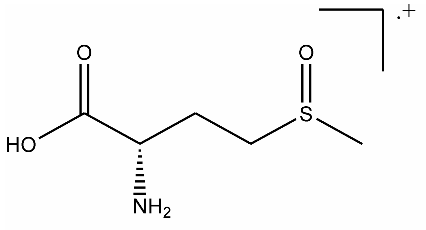
Correlation analyses were performed using Microcal Origin (version 6.0) computer software. The goodness of the fit is discussed using the correlation coefficients and standard deviations.

RESULTS AND DISCUSSION

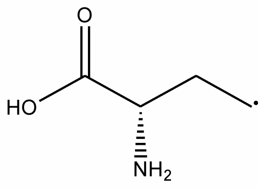
The kinetics of oxidation of methionine by QFC was studied in water at 25±0.2 °C in the presence of chloroacetic acid. The effect of added organic co-solvent, *viz*. DMF, 1,4-dioxane, acetone, *t*-BuOH and MeCN on the kinetics of oxidation was also investigated at varying mole fractions of the co-solvents. The stoichiometry of the reaction between methionine and QFC was found to be 1:1, corresponding to the following equation:

$$\mathrm{Me{-}S{-}R} + \mathrm{O_2CrFOQuH} \rightarrow \mathrm{Me{-}S(O){-}R} + \mathrm{OCrFOQuH}$$

The product analysis was carried out under kinetic conditions. The oxidation of methionine resulted in the formation of the corresponding sulphoxide, which was confirmed using GC–MS (*m*/*z* 166) and its fragmentation at *m*/*z* 102, as well from the IR spectra (S=O stretching frequency at 1066 $\mathrm{cm^{-1}}$):



m/z 166



m/z 102

The reactions were of first order with respect to QFC. Furthermore, the values of k_{obs} were independent of the initial concentration of QFC (Table I). The reaction was catalyzed by hydrogen ions and the order with respect to $\mathrm{H^+}$ was one. The reaction rate increased linearly with increasing concentration of Met. The order of the reaction with respect to Met was also one. Furthermore, the plot $1/k_{\mathrm{obs}}$ *versus* $1/c(\mathrm{Met})$ was linear ($r = 0.982$, slope = 4.519±0.48) with a positive intercept on the rate ordinate, which indicates that the reaction follows a Michalies–Menten type mechanism. Therefore, the rate law can be represented as:

$$-\mathrm{d}c(\mathrm{QFC})/\mathrm{d}t = k\, c(\mathrm{Met})\, c(\mathrm{QFC})\, c(\mathrm{H^+})$$

The oxidation of Met in a nitrogen atmosphere failed to induce the polymerization of acrylonitrile. Furthermore, the rate of oxidation decreased with the addition of Mn(II), indicating the involvement of a two-electron reduction of Cr(VI) to Cr(IV). Therefore, a one-electron oxidation, giving rise to free radicals, is unlikely. The rate of oxidation of Met was determined at different temperatures and the activation parameters were calculated at 35 °C: $\Delta H^{\#} = 19.8\ \mathrm{kJ\ mol^{-1}}$, $\Delta S^{\#} = -211\ \mathrm{J\ K^{-1}\ mol^{-1}}$ and $\Delta G^{\#} = 84.7\ \mathrm{kJ\ mol^{-1}}$. These activation parameters are comparable with those for the oxidation of Met by other halochromates.[11,12,15]

The influence of solvent on the rate of the reaction was studied in water–organic solvent mixtures at different mole fractions of organic co-solvent, *viz*. 1,4-dioxane, DMF, acetonitrile, acetone and *t*-BuOH. The results in Table II indicate that the rate constants (k_2) are remarkably sensitive to the nature and the composition of the mixed solvent.

Solvent variations may effect the kinetics and the energy of the electron transfer processes in a complex manner, particularly in mixed solvent media as the physico–chemical properties of mixed solvent media are often quite different form those of the pure solvents or of their ideal mixtures.[16] The dependence of the kinetic parameters for reactions on the composition of mixed aqueous solvents often affords complicated patterns. In aqueous solutions, at least, it has become clear that an important aspect of the activation process is the reorganization of the solvent surrounding the reacting solute(s). Not surprisingly, such reorganizations will be profoundly affected by the addition of a co-solvent to these aqueous solutions. Indeed, it is now clearly recognized that the action of the non-aqueous component of a mixture is more than that of a simple diluent of water or a modifier of its dielectric properties.[14]

TABLE I. Pseudo-first order rate constants for the oxidation of Met by QFC in water at 25±0.2 °C

c(Met) / 10^{-2} mol dm^{-3}	c(QFC) / 10^{-3} mol dm^{-3}	c(Acid) / mol dm^{-3}	k_{obs} / 10^{-4} s^{-1}
2.0	1.00	0.30	4.28
2.0	1.25	0.30	4.31
2.0	1.50	0.30	4.28
2.0	1.75	0.30	4.29
2.0	2.00	0.30	4.12
1.0	1.00	0.30	2.20
1.5	1.00	0.30	2.85
2.0	1.00	0.30	4.28
2.5	1.00	0.30	5.29
3.0	1.00	0.30	6.12
2.0	1.00	0.30	2.85[a]
2.0	1.00	0.10	1.57
2.0	1.00	0.20	2.94
2.0	1.00	0.30	4.28
2.0	1.00	0.40	6.24
2.0	1.00	0.50	7.23

[a]Contained 5×10^{-4} M Mn(II)

TABLE II. Effect of added organic co-solvents on the rate constant (k_{obs} / 10^{-4} s^{-1}) of the oxidation of methionine by QFC at 25 °C

Mole fraction of organic co-solvent	DMF	1,4-Dioxane	Acetone	*t*-BuOH	MeCN
0	4.28	4.28	4.28	4.28	4.28
0.10	1.01	3.86	4.23	4.25	3.63
0.20	0.50	3.48	4.24	4.25	3.50
0.30	0.36	3.42	4.34	4.36	3.85
0.40	0.27	3.51	4.45	4.52	3.91
0.50	0.23	3.84	4.51	4.64	4.11
0.60	0.18	4.38	4.60	4.73	4.28
0.70	0.15	5.32	4.67	4.84	4.36

The binary aqueous mixtures chosen for the present study represent various classes of solvent mixtures according to Blandamar and Burgess.[14] Aqueous mixtures have been classified based on their thermodynamic properties, particularly their molar excess functions, X^E. Water/1,4-dioxane, water/acetone and water/ /*t*-BuOH mixtures are examples of the typical aqueous (TA) class, for which the excess Gibbs function, G^E, is positive. Water/MeCN is classified as a typical non-aqueous positive (TNAP) mixture (G^E is positive). Water/DMF falls into the typical non-aqueous negative (TNAN) category, for which G^E is negative.

The properties of TA mixtures are particularly sensitive to the mole fraction of the non-aqueous co-solvent, x_2. At low mole fractions, TA solvents exerts a water structure-forming action, the solvent co-spheres around each solute molecule overlap and mutually enhance water–water interactions. As more co-solvent is added, the mole fraction exceeds a critical mole fraction, x_2*, where there is insufficient water to maintain a three-dimensional hydrogen-bonded network of water molecules. In the TNAP mixtures, the co-solvent exerts a depolymerising effect on water and in this sense is a structure breaker. In TNAN mixtures, intercomponent association occurs which leads to a breakdown of the water–water interactions. Further, an extra-thermodynamic analysis indicates that, at least qualitatively, if G^E is positive, the solute should be more soluble in the mixture than predicted from its solubility in the individual pure solvents.[14]

A plot of log k_{obs} *versus* the mole fraction of organic co-solvent, x_2, is depicted in Fig. 1, from which it is evident that in these aqueous organic solvent mixtures, the rate initially decreased with increasing mole fraction of the organic co-solvent up to ≈ 0.3. With further increase in the amount of co-solvent, in the case of the TAP and TNAP mixtures, the rate of oxidation markedly increased with increasing x_2, while in the TNAN mixtures, the rate decreased very slightly. In other words, when a TAP/TNAP co-solvent was added the rate increased as G^E increased and when a TNAN co-solvent was added, it decreased as G^E decreased. This may be because the transition state was stabilized by the addition of a TAP/TNAP co-solvent; consequently, the rate increased with increasing mole fraction of co-solvent. However, in the water/DMF mixture, the transition state was not stabilized largely, as it is less soluble in the mixtures, as predicted by the negative value of G^E, hence the rate of the reaction decreased. This decrease in the rate, however, was very small. This may be due to the stabilization of the transition state through other specific/non-specific solute–solvent–solvent interactions.

The influence of relative permittivity, ε_r, on the rate can be described by the equation of Laidler and Eyring:[17]

$$\frac{\mathrm{d}\ln k}{\mathrm{d}\,(1/\varepsilon_\mathrm{r})} = e^2 Z^2 \left(\frac{1}{r} - \frac{1}{r^*}\right) / \, 2kT \tag{1}$$

where k is the rate, Z the net charge, r the effective radius and r^* the radius of the activated species. A plot of log k_{obs} *versus* $1/\varepsilon_r$ was nonlinear in all the studied aqua–organic solvent mixtures. A representative plot is shown in Fig. 2, from which it is evident that in the TNAN mixture, the rate of the reaction decreased curvi-linearily with decreasing relative permittivity of the medium. However, in the case of TAP and TNAP mixture, with decreasing relative permittivity, the rate of the reaction initially decreased and after a certain point, it increases.

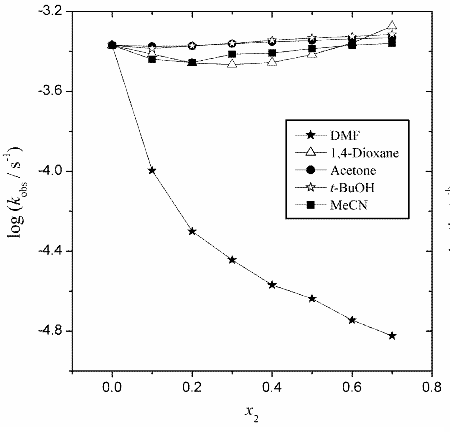


Fig. 1. Plot of log k_{obs} *vs*. mole fraction of the co-solvent, x_2, for the oxidation of methionine by QFC.

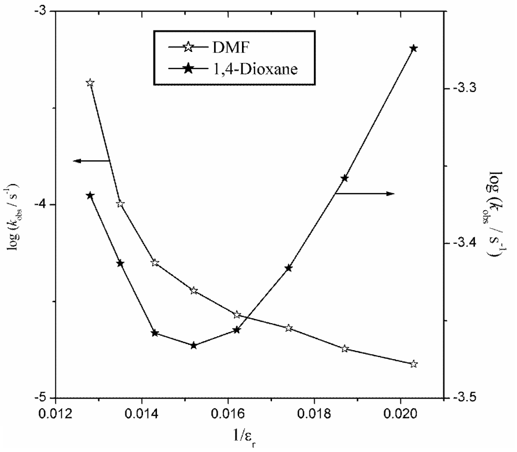


Fig. 2. Plot of log k_{obs} *vs*. $1/\varepsilon_r$ for the studied aqua/organic mixtures.

The solvent effect was also analyzed using the Reichardt solvent parameter $E_T(30)$, which is defined as the solvent micropolarity.[18] Plots of log k_{obs} *versus* $E_T(30)$ for all the water/organic co-solvent mixtures were also nonlinear. This observation, together with the dependence of the rate on the relative permittivity of the medium is parallel to the previously discussed variation of the rate with G^E. These results indicate that the correlations between log k_{obs} and the macroscopic solvent parameters, such as relative permittivity and micropolarity, are poor, *i.e.*, no single solvent parameters can completely explain the effect of the solvent on the reactivity.

The simplicity of idealized electrostatic models for the description of solvation of ions and dipolar molecules, considering solvents as non-structured continua, has led to the use of physical constants, such as relative permittivity, ε_r, refractive index, n, and functions thereof, as macroscopic solvent parameters for the evaluation of medium effects. However, solute–solvent interactions occur on a molecular microscopic level within a structured discontinuum consisting of individual solvent molecules, capable of mutual solvent–solvent interactions. For this reason and because they neglect specific solute–solvent interactions, the electrostatic approach to medium effects often failed in the correlation of the observed solvent effects with physical solvent parameters. In reality, satisfactory quantitative descriptions of medium effects have taken into account all non-specific and specific solvent–solvent–solute interactions. The separation of the solvent polarity into the non-specific and specific solvent–solvent–solute interaction mechanism is purely formal, but, if this separation can be reasonably realised, the resultant parameters may be used to interpret solvent effects through such multiple correlations, thus providing information about the type and magnitude of the interactions with the solvent.[18]

This kind of dual dependency of the reactivity on the solvent composition is illustrated by the Kamlet–Taft solvatochromic comparison method.[19] This method may be used to unravel, quantify, correlate and rationalize multiple interacting solvent effects on reactivity. Thus, the rate data were correlated with solvatochromic parameters in the form of the following linear solvation energy relationship (LSER):

$$\log k = \mathrm{A}_0 + s\pi^* + a\alpha + b\beta \tag{2}$$

where π^* is an index of the solvent dipolarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect, α is the solvent hydrogen bond donor (HBD) acidity, which describes the ability of the solvent to donate a proton, β is the solvent hydrogen bond acceptor (HBA) basicity, which provides a measure of the ability of the solvent to accept a proton (donate an electron pair), in a solute to solvent hydrogen bond, and A_0 is the regression value of the solute property in the reference solvent cyclohexane. The regression coefficients, s, a and b, measure the relative susceptibilities of the solvent dependent solute property $\log k_{\mathrm{obs}}$ to the indicated solvent parameter. These solvatochromic parameters for the aqueous organic mixtures used in the present study were obtained from the literature.[20] The rate of oxidation in the solvent mixture studied show good correlations with solvent *via* the above LSER. The correlation results obtained are given below.

In water/DMF mixtures:

$$\log k_{\mathrm{obs}} = -2.806\pm1.92 - (0.414\pm0.55)\pi^* + (0.888\pm0.45)\alpha - (2.468\pm1.72)\beta$$
$$(N = 8;\ R = 0.999;\ R^2 = 0.998;\ Sd = 0.02;\ P_\alpha = 24\ \%;\ P_\beta = 65\ \%;\ P_{\pi^*} = 11\ \%)$$

In water/1,4-dioxane mixtures:

$$\log k_{\mathrm{obs}} = -0.874\pm0.83 - (1.330\pm0.89)\pi^* + (0.122\pm0.72)\alpha - (1.889\pm0.85)\beta$$
$$(N = 8;\ R = 0.974;\ R^2 = 0.953;\ Sd = 0.04;\ P_\alpha = 4.0\ \%;\ P_\beta = 57\ \%;\ P_{\pi^*} = 39\ \%)$$

In water/acetone mixtures:

$$\log k_{\mathrm{obs}} = -2.041\pm0.78 - (0.782\pm0.25)\pi^* + (0.007\pm0.21)\alpha - (0.911\pm0.58)\beta$$
$$(N = 8;\ R = 0.945;\ R^2 = 0.894;\ Sd = 0.01;\ P_\alpha = 0\ \%;\ P_\beta = 54\ \%;\ P_{\pi^*} = 46\ \%)$$

In water/*t*-BuOH mixtures:

$$\log k_{\text{obs}} = -3.165\pm0.01 - (0.121\pm0.05)\pi^* - (0.023\pm0.04)\alpha - (0.096\pm0.03)\beta$$
$$(N = 8;\ R = 0.997;\ R^2 = 0.994;\ Sd = 0.002;\ P_\alpha = 10\ \%;\ P_\beta = 40\ \%;\ P_{\pi^*} = 50\ \%)$$

In water/MeCN mixtures:

$$\log k_{\text{obs}} = -2.645\pm0.20 - (0.028\pm0.22)\pi^* - (0.252\pm0.25)\alpha - (0.847\pm0.26)\beta$$
$$(N = 8;\ R = 0.940;\ R^2 = 0.882;\ Sd = 0.02;\ P_\alpha = 22\ \%;\ P_\beta = 76\ \%;\ P_{\pi^*} = 2.0\ \%)$$

Such good correlations, with an explained variance of 94–99 % in the aqua–organic solvent mixtures, indicate the existence of non-specific and specific solvent–solute interactions. From the values of the regression coefficients, the contribution of each parameter (P_x), on a percentage basis, to the reactivity were calculated.[21] The following conclusions were drawn from the systematic correlation studies:

i) In all the investigated solvent mixtures, except MeCN, the contribution of both specific and non-specific solute–solvent interactions play dominant roles, as indicated by the percentage contributions of the α, β and π^* terms. In case of MeCN, the contribution of the specific property is dominant.

ii) The contribution of the solvent HBA term is dominant in all the mixtures, except *t*-BuOH, as indicated by the percentage contributions of this term, P_β compared to P_α and P_{π^*}. This may be because all the co-solvents are typical HBA solvents. Hence, increasing the mole fraction of these solvents in the mixture increases the solute–solvent interactions through the HBA property.

iii) The sign of the coefficient of the α term is positive in the water/DMF, water/1,4-dioxane and water/acetone mixtures, suggesting that the transition state–solvent interactions, through specific HBD property, dominate over the reactant–solvent interactions.

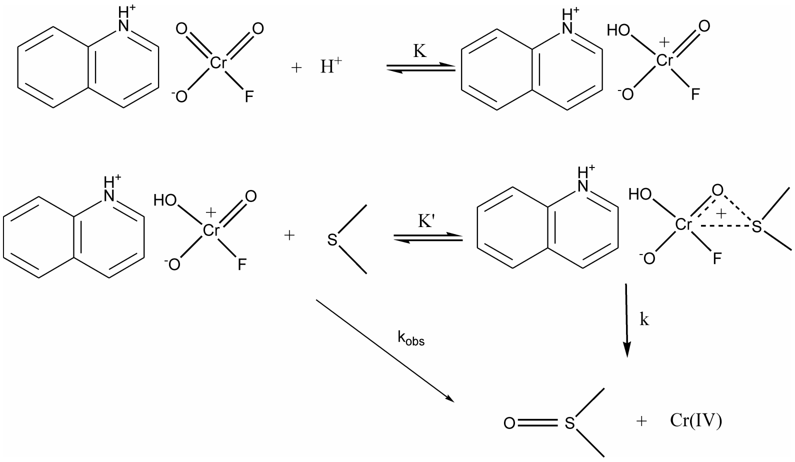
iv) In water/*t*-BuOH and water/MeCN mixtures, the sign of the coefficient of the α term is negative, indicating the reactants are solvated through HBD property to a larger extent than the transition state.

v) The sign of the coefficient of the β and π^* terms in all the investigated mixtures is negative, indicating the reactants are solvated to a larger extent than the transition state through the HBA and dipolarity/polarizability properties.

Therefore, it is concluded that both specific (microscopic) and non-specific (macroscopic) solute–solvent–solvent interactions play a dominant role in governing the reactivity of the substrate under investigation.

Mechanism

Under the experimental conditions employed in the present study, methionine is oxidized to the corresponding sulphoxide stage only. Based on the above kinetic observations, *i.e.*, the first order dependence on *c*(Met), *c*(QFC) and *c*(Acid), the following mechanism is proposed for the oxidation of methionine by QFC. The linear increase in the rate with acidity suggests the involvement of protonated QFC in the rate-determining step. In the first step, QFC becomes protonated. The protonated QFC attacks the substrate to form a complex, in a pre-equilibrium step, which subsequently decomposes to give the products in a slow step. The proposed scheme envisages an oxygen atom transfer from the oxidant, which is in agreement with earlier observations involving the oxidation of sulphur-containing compounds with halochromates. The electrophilic attack on the sulphide sulphur can be viewed as an S_N2 reaction. An S_N2-like transition state (more hydrophobic) is supported by the observed solvent effects:



The above mechanism leads to the following rate law:

$$\text{Rate} = kc(\text{Complex})$$

$$c(\text{Complex}) = k'c(\text{Met})c(\text{QFCH}^+)$$

$$c(\text{QFCH}^+) = k''c(\text{QFCH})c(\text{H}^+)$$

$$c(\text{Complex}) = k'k''c(\text{Met})c(\text{QFCH})c(\text{H}^+)$$

$$-\text{d}c(\text{QFCH})/\text{d}t = kk'k''c(\text{Met})c(\text{QFCH})c(\text{H}^+)$$

The rate law in its final form accounts for the observed kinetics. The negative entropy of activation suggests complex formation in the transition state. The linear increase in rate with acidity suggests the involvement of protonated QFC in the rate-determining step.

ИЗВОД

УТИЦАЈ ВИШКА ГИБСОВЕ ЕЕНРГИЈЕ РАСТВАРАЧА НА ОКСИДАЦИЈУ МЕТИОНИНА ХИНОЛИНИУМ-ФЛУОРОХРОМАТОМ. ИСПИТИВАЊЕ КИНЕТИКЕ РЕАКЦИЈЕ

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Оксидација метионина хинолинијум-флуорохроматом (QFC) испитивана је у присуству хлор-сирћетне киселине, у смеши воде и органских растварача са различитим функцијама вишка моларне Гибсове енергије. Реакција је првог реда у односу на QFC и киселину. Брзина реакције је одређена на различитим температурама и израчунати су параметри активације. Подаци за брзину реакције корелисани су са различитим параметрима растварача методом линеарне вишеструке регресије. На основу резултата добијене су информације о интеракцијама растварач–реактанти и растварач–прелазно стање.

(Примљено 18. октобра 2007, ревидирано 5. маја 2008)

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