

## Linear Free Energy Relationships near Isokinetic Temperature. Oxidation of Organic Sulfides with Nicotinium Dichromate

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The nicotinium dichromate (NDC) oxidation of methyl phenyl sulfide (MeSPh) in acetonitrile, brought about by *p*-toluenesulfonic acid (TsOH), is first order in NDC and TsOH, and is zero order with respect to MeSPh in the concentration range investigated. The NDC oxidation of 14 *para*-, *meta*- and *ortho*-substituted phenyl methyl sulfides at 293–318 K complies with the isokinetic relationship but not to any of the linear free energy relationships; the isokinetic temperature lies within the experimental temperature range.

*Key words:* linear free energy relationships, activation parameters, isokinetic temperature.

### INTRODUCTION

Linear free energy relationships are empirical relationships between thermodynamic quantities and are known as extrathermodynamic equations. The substituent constants represent inductive and mesomeric effects which influence the potential energies of the molecules and hence the activated complexes.<sup>1</sup> Kinetic studies on the oxidation of organic sulfides are many and the oxidation conforms to the linear free energy relationships.<sup>2–6</sup>

Chromium(VI) complexes of heterocyclic bases are mild oxidants, soluble in organic solvents and are used under anhydrous condition.<sup>7</sup> Nicotinium dichromate (3-carboxypyridinium dichromate, NDC), a new oxidant, is a non-

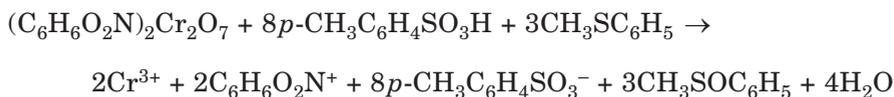
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hygroscopic, non-photosensitive, stable, yellow-orange solid,<sup>8</sup> and this is the first kinetic study on the NDC oxidation. Kinetic and mechanistic studies on oxidation by chromium(VI) complexes like pyridinium fluorochromate (PFC), quinolinium fluorochromate (QFC), pyridinium chlorochromate (PCC), quinolinium chlorochromate (QCC), 2,2'-bipyridinium chlorochromate (BPCC), pyridinium bromochromate (PBC) and 2,2'-bipyridinium chromate (BPC) are numerous. The oxidation is first order in chromium(VI) reagents and is catalyzed by mineral acid. The reaction is first order or fractional order with respect to substrates. The mechanism of oxidation is of two types; one involves rapid formation of substrate-protonated oxidant complex followed by slow decomposition of the complex, and in the other, the complex formation is slow, its decomposition is fast. Similar studies with dimers (*viz.* pyridinium dichromate, PDC and quinolinium dichromate, QDC) are also many; the monomer is the proffered oxidizing species.<sup>9-15</sup> The NDC oxidation of organic sulfides in acetonitrile is brought about by *p*-toluenesulfonic acid (TsOH) and the isokinetic temperature falls within the experimental temperature range. The kinetic results reveal that the oxidation does not conform to any of the linear free energy relationships at the isokinetic temperature; but at a temperature that is a little away from the isokinetic temperature the reaction conforms to linear free energy relationship.

## EXPERIMENTAL

Nicotinium dichromate (NDC),  $(C_6H_6O_2N)_2Cr_2O_7$ , was prepared by the reported procedure.<sup>8</sup> The *para*-, *meta*-, and *ortho*-substituted phenyl methyl sulfides were prepared using standard methods and purified by distillation. Solution of NDC in acetonitrile (HPLC grade) was prepared and standardized iodometrically. *p*-Toluenesulfonic acid (TsOH) was dissolved in acetonitrile and standardized. The kinetics of the oxidation at constant temperature was studied under pseudo-first order condition:  $[TsOH]$  and  $[MeSPh] \gg [NDC]$ . Chromium(VI) has the largest reduction potential in acetonitrile (acetonitrile: 1632 mV, acetic acid: 1533 mV, water: 875 mV, dimethyl sulfoxide: 541 mV)<sup>7</sup> and hence the oxidation was studied in acetonitrile. The reaction was initiated by the addition of substrate and the progress of the oxidation was monitored spectrophotometrically (UVIDEC-7800, Jasco) at 350 nm. The pseudo-first order rate constants ( $k'$ ) were obtained from the least squares slopes of log absorbance *versus* time plots. The oxidation stops at the sulfoxide stage itself; under the experimental condition, further oxidation of sulfoxide is slow. The oxidation product is sulfoxide, identified by its IR spectrum. The reduction product of NDC is chromium(III), identified by the UV-visible spectrum of the reaction solution after completion of the oxidation. Hence the reaction is represented as:



## RESULTS AND DISCUSSION

*Reaction Order*

The NDC oxidation of MeSPh is first order with respect to the oxidant. Plot of log absorbance *versus* time is linear up to about one-half life of the reaction. The oxidation is zero order in the sulfide; the pseudo-first order rate constant remains constant at different  $[\text{MeSPh}]_0$ . Table I presents representative rate data. The oxidation occurs only in the presence of *p*-toluenesulfonic acid (TsOH), and mineral acids such as perchloric acid and carboxylic acids such as chloroacetic acid do not bring about the oxidation. The oxidation is first order in TsOH. The oxidation rate increases with increasing  $[\text{TsOH}]$  and plot of  $k'$  *versus*  $[\text{TsOH}]$  is a straight line passing through the origin (correlation coefficient,  $r = 0.999$ , standard error of estimate,  $s = 2.0 \times 10^{-4}$ , slope =  $0.47 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ).

TABLE I

NDC oxidation of methyl phenyl sulfide in acetonitrile at 308 K  
 $[\text{NDC}]_0 = 1.3 \times 10^{-4} \text{ mol dm}^{-3}$

$\frac{[\text{MeSPh}]_0 \times 10^3}{\text{mol dm}^{-3}}$	$\frac{[\text{TsOH}]_0 \times 10^3}{\text{mol dm}^{-3}}$	$\frac{k' \times 10^3}{\text{s}^{-1}}$
8.5	8.2	4.3
17	8.2	4.5
26	8.2	4.5
34	8.2	4.5
8.5	11	5.6
8.5	14	6.5
8.5	55	26

*Mechanism*

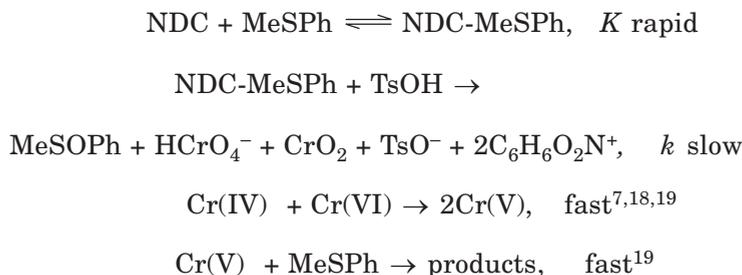
The title oxidation is in acetonitrile and under the reported anhydrous condition hydrolysis of the dichromate anion to monomer is unlikely. The energy of activation of the oxidation is susceptible to the substituent present in the benzene ring (*vide infra*). This indicates the involvement of substrate in or prior to the rate-limiting step in such a way that the rate is independent of [substrate]. In non-aqueous medium chromium(VI) reagents complex with the sulfides and the reaction exhibits Michaelis-Menten kinetics with respect to the sulfide.<sup>16,17</sup> If the formation constant ( $K$ ) of the NDC-sulfide complex is large the oxidation is to exhibit zero order dependence on [sulfide] (Scheme 1).

$$[\text{NDC-MeSPh}] = K[\text{NDC}]_T [\text{MeSPh}]/(1 + K[\text{MeSPh}])$$

where  $[\text{NDC}]_T = [\text{NDC-MeSPh}] + [\text{NDC}]$ .

If  $K[\text{MeSPh}] \gg 1$ ,  $[\text{NDC-MeSPh}] \approx [\text{NDC}]_T$ .

*p*-Toluenesulfonic acid catalyzed rate-limiting decomposition of the NDC-sulfide complex accounts for the observed kinetic orders.



Scheme 1.

Scheme 1 yields the rate law:

$$-d[\text{NDC}]_T/dt = k[\text{NDC}]_T[\text{TsOH}].$$

The pseudo-first order rate constant,  $k' = k[\text{TsOH}]$ .

### *Linear Free Energy Relationships*

Kinetic study on the oxidation of 14 *para*-, *meta*- and *ortho*-substituted phenyl methyl sulfides at 293–318 K affords the activation parameters (Table II). The oxidation is neither isoenthalpic nor isoentropic but complies with the compensation law also known as isokinetic relationship:

$$\partial E_a / \partial \ln A = R\beta$$

$$\partial(\Delta H^\ddagger) / \partial(\Delta S^\ddagger) = \beta$$

where  $E_a$  is the energy of activation,  $A$  is the frequency factor,  $\Delta H^\ddagger$  is the enthalpy of activation,  $\Delta S^\ddagger$  is the entropy of activation,  $R$  is the gas constant and  $\beta$  is the isokinetic temperature. The isokinetic temperature is the tem-

TABLE II

Activation parameters for NDC oxidation of *para*-, *meta*- and *ortho*-substituted phenyl methyl sulfides in acetonitrile

Substituent	$E_a$	$\ln A$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$
	$\text{kJ mol}^{-1}$		$\text{kJ mol}^{-1}$	$\text{J K}^{-1} \text{mol}^{-1}$	$\text{kJ mol}^{-1}$
					308 K
H	76	25	69	-61	88
<i>p</i> -CH <sub>3</sub>	98	33	95	24	88
<i>p</i> -OCH <sub>3</sub>	95	32	93	16	88
<i>p</i> -Cl	103	35	100	34	89
<i>p</i> -Br	71	23	69	-62	88
<i>p</i> -NO <sub>2</sub>	77	24	74	-54	91
<i>m</i> -CH <sub>3</sub>	94	32	92	11	89
<i>m</i> -Cl	103	35	101	37	90
<i>m</i> -NO <sub>2</sub>	30	7	28	-199	89
<i>o</i> -CH <sub>3</sub>	83	28	80	-24	87
<i>o</i> -OCH <sub>3</sub>	106	35	103	41	90
<i>o</i> -Cl	76	23	73	-62	92
<i>o</i> -Br	82	26	80	-39	92
<i>o</i> -NO <sub>2</sub>	72	22	69	-70	91

perature at which all the compounds of the series react equally fast. Also, at the isokinetic temperature the variation of substituent has no influence on the free energy of activation. In an isoentropic oxidation the isokinetic temperature lies at infinity and only enthalpy of activation determines the reactivity. The isokinetic temperature is zero for an isoenthalpic series and the reactivity is determined by the entropy of activation. In the present oxidation the activation energy varies linearly with the logarithm of frequency factor ( $r = 0.997$ , slope =  $2.54 \text{ kJ mol}^{-1}$ , intercept =  $14.5 \text{ kJ mol}^{-1}$ ) and the activation enthalpy is linearly related to activation entropy ( $r = 0.997$ , slope =  $306 \text{ K}$ ). The maximum possible errors in activation enthalpy ( $\delta$ ) and activation entropy are  $3 \text{ kJ mol}^{-1}$  and  $10 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively. The errors in  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  result in the maximum possible error in  $\Delta G^\ddagger$  as  $6 \text{ kJ mol}^{-1}$ . The error criterion is satisfied in the present study, *i.e.*,  $\Delta\Delta H^\ddagger$  ( $75 \text{ kJ mol}^{-1}$ )  $\gg 2\delta$  ( $6 \text{ kJ mol}^{-1}$ ) and hence the correlation between  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  is significant. The operation of isokinetic relationship reveals that all the substituted phenyl methyl sulfides examined are oxidized through a common mechanism.

The free energies of activation of the NDC oxidation of *para*- and *meta*-substituted phenyl methyl sulfides, calculated from the activation enthalpies and activation entropies, were analyzed using the linear free energy re-

lationships. The linear free energy relationship is based on the ionization of benzoic acids; hence the correlation of the activation free energy, enthalpy and entropy of the NDC oxidation with the free energy, enthalpy and entropy of ionization of benzoic acids,<sup>1</sup> respectively, should be meaningful. But the correlation is poor in all the cases. The influence on the free energy of activation by the substituent is through the enthalpic and entropic components.<sup>1</sup> But the biparametric correlation of the activation free energy of the NDC oxidation with the enthalpic ( $\sigma_H$ ) and entropic ( $\sigma_S$ ) substituent constants is unsatisfactory; the activation enthalpy and entropy also fail to correlate with  $\sigma_H$  and  $\sigma_S$  substituent constants, respectively. Further more, the free energy of activation does not correlate with the usual Hammett substituent ( $\sigma$ ) constant. The *p*-nitro group is likely to enter into conjugation with the reaction center. Also, expansion of the valence shell of sulfur beyond the octet enables conjugation with *p*-methoxy group.<sup>20</sup> As "cross-conjugation", conjugation involving the *para*-substituents and the reaction center, is likely the  $\sigma^+$  and  $\sigma^-$  constants were employed in the single parameter correlation but also without success. The failure of all the single parameter equations to correlate the free energy of activation leads to the possibility of operation of dual substituent parameter (DSP) equations. All the biparametric equations including the Swain *et al.* equation fail to correlate the activation free energy with the substituent. The  $\sigma_I$ ,  $\sigma_R^0$ ,  $\sigma_{R(BA)}$ ,  $\sigma_R^-$  and  $\sigma_R^+$  values used are those reported by Dayal *et al.*<sup>21</sup> The *F* and *R* values are those of Swain *et al.*<sup>22</sup> The possible reason for the lack of any linear free energy relationship is that the isokinetic temperature falls within the experimental temperature (293–318 K); the isokinetic temperature calculated from the isokinetic plots is  $306 \pm 7$  K. It is pertinent to note that the compensation law may lead to artefact.<sup>23,24</sup> But the reversal of the order of reactivity on transgressing the calculated isokinetic temperature (electron releasing groups accelerate but on crossing the reported isokinetic temperature decelerate the reaction; electron withdrawing substituents also show similar results) confirms the isokinetic relationship.

The Hammett equation and its different modified forms fail when applied to the reactions of *ortho*-substituted benzene derivatives. In addition to the well known inductive and resonance effects caused by the *para*- and *meta*-substituents, the *ortho*-substituents exert steric effect. The Charton method of analysis is to correlate with (1a)  $\sigma_I$  &  $\sigma_R^0$ , (1b)  $\sigma_I$ ,  $\sigma_R^0$  &  $\nu$ , (2a)  $\sigma_I$  &  $\sigma_{R(BA)}$ , (2b)  $\sigma_I$ ,  $\sigma_{R(BA)}$  &  $\nu$ , (3a)  $\sigma_I$  &  $\sigma_R^-$ , (3b)  $\sigma_I$ ,  $\sigma_R^-$  &  $\nu$ , (4a)  $\sigma_I$  &  $\sigma_R^+$ , (4b)  $\sigma_I$ ,  $\sigma_R^+$  &  $\nu$ , (5a) *F* & *R* and (5b) *F*, *R* &  $\nu$  where  $\nu$  is the steric substituent constant.<sup>25</sup> Analysis of the activation free energies of the *ortho*-substituted phenyl methyl sulfides by the Charton method reveals that the NDC oxidation does not conform satisfactorily to any of the linear free energy relationships.

Correlation analysis of the activation free energy at a temperature that is a little away from the isokinetic temperature confirms the operation of linear free energy relationships in the NDC oxidation of organic sulfides (Tables III and IV). The substituent constants  $\sigma_I$  and  $\sigma_R^-$  explain better than the rest the variation of activation free energy with the substituent.

TABLE III

Multiple linear correlation of activation free energy of NDC oxidation at 318 K: *para*-substituted phenyl methyl sulfides

Explanatory variables	$R^2$	$s$
$\sigma_I, \sigma_R^0$	0.95	0.37
$\sigma_I, \sigma_{R(BA)}$	0.92	0.48
$\sigma_I, \sigma_R^-$	0.96	0.33
$\sigma_I, \sigma_R^+$	0.91	0.51
$F, R$	0.92	0.49

$R$ , multiple correlation coefficient;  $100R^2$ , percentage of variation explained.

TABLE IV

Multiple linear correlation of activation free energy of NDC oxidation at 293 K: *ortho*-substituted phenyl methyl sulfides

Explanatory variables	$R^2$	$s$
$\sigma_I, \sigma_R^0$	0.96	0.50
$\sigma_I, \sigma_R^0, v^a$	0.98	0.52
$\sigma_I, \sigma_R^0, v^b$	0.97	0.59
$\sigma_I, \sigma_{R(BA)}$	0.93	0.74
$\sigma_I, \sigma_{R(BA)}, v^a$	0.95	0.76
$\sigma_I, \sigma_{R(BA)}, v^b$	0.94	0.78
$\sigma_I, \sigma_R^-$	0.99	0.23
$\sigma_I, \sigma_R^-, v^a$	0.99	0.28
$\sigma_I, \sigma_R^-, v^b$	0.99	0.29
$\sigma_I, \sigma_R^+$	0.89	0.88
$\sigma_I, \sigma_R^+, v^a$	0.94	0.82
$\sigma_I, \sigma_R^+, v^b$	0.91	0.97
$F, R$	0.89	0.87
$F, R, v^a$	0.94	0.81
$F, R, v^b$	0.92	0.96

<sup>a</sup> NO<sub>2</sub>, planar; <sup>b</sup> NO<sub>2</sub>, orthogonal.

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**SAŽETAK****Linearni odnosi slobodne energije u blizini izokinetičke temperature.  
Oksidacija organskih sulfida nikotinijevim dikromatom**

*Chockalingam Karunakaran i Vaithiyalingam Chidambaranathan*

Oksidacija metil-fenil-sulfida (MeSPh) nikotinijevim dikromatom (NDC) i *p*-toluensulfonskom kiselinom (TsOH) u acetonitrilu, reakcija je prvog reda s obzirom na NDC i TsOH te nultog reda s obzirom na MeSPh u istraženom koncentracijskom području. Oksidacija 14 *para*-, *meta*- i *ortho*-supstituiranih fenil-metil-sulfida s NDC, pri 20–40 °C, slijedi izokinetički odnos ali ne i linearne odnose slobodne energije. Izokinetička temperatura nalazi se u temperaturnom području pokusa.