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Lack of Linear Free Energy Relationships in the *p*-Toluenesulfonic Acid Mediated Chromium(VI) Oxidation of Organic Sulfides

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Summary. The oxidation of methylphenyl sulfide by imidazolium dichromate in acetonitrile mediated by *p*-toluenesulfonic acid is first order in *IDC* and *Ts*OH and zero order in MeSPh in the concentration range studied. The *IDC* oxidation of 14 *para*-, *meta*-, and *ortho*-substituted phenylmethylsulfides at 20–45°C conforms to the isokinetic relationship but not to any of the linear free energy relationships; the isokinetic temperature lies within the experimental temperature range.

Keywords. 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. Substituent constants represent inductive and resonance effects which influence the potential energies of the molecules and hence the activated complexes [1]. Kinetic studies on the oxidation of organic sulfides are numerous, and the reactions conform to the linear free energy relationships [2–6].

Chromium(VI) complexes of heterocyclic bases are mild oxidants soluble in organic solvents and are used under anhydrous conditions [7]. Kinetic and mechanistic studies on oxidations by chromium(VI) complexes are numerous. The oxidations are first order in chromium(VI) reagents and are catalyzed by mineral acids. The reactions are of either first order or fractional order with respect to the substrates. The mechanism of oxidation is of two types: one involves the rapid formation of a substrate – protonated oxidant complex followed by its slow decomposition, and the other one is characterized by slow complex formation and fast decomposition. Recently we have shown that the oxidation by chromium(VI) complexes follows a common mechanism [8, 9]. Chromium(VI) has the largest reduction potential in acetonitrile (acetonitrile: 1632 mV, acetic acid: 1533 mV, water: 875 mV, dimethyl sulfoxide: 541 mV [7]), and therefore the oxidation was studied in this solvent. Imidazolium dichromate (*IDC*) is an effective oxidant

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[10], and the IDC oxidation of organic sulfides in acetonitrile is catalyzed by *p*-toluenesulfonic acid (*Ts*OH).

Results and Discussion

Reaction order

The oxidation of MeSPh by *IDC* is first order in the oxidant. A plot of log(absorbance) *vs*. time is linear up to about one-half life of the oxidation. The reaction is zero order with respect to the sulfide; the *pseudo*-first order rate constant remains constant at different concentrations of MeSPh. Table 1 presents representative rate data. The oxidation proceeds only in the presence of *p*-toluenesulfonic acid (*Ts*OH), and mineral acids such as perchloric acid and carboxylic acids such as chloroacetic acid do not mediate the oxidation. The oxidation is first order with respect to *Ts*OH. The oxidation rate increases with increasing *Ts*OH concentration, and a plot of k' *vs*. [*Ts*OH] is linear and passes through the origin (correlation coefficient: $r = 0.986$; standard error: $s = 4.8 \times 10^{-5}\,\mathrm{s}^{-1}$; slope: $5.3 \times 10^{-2}\,\mathrm{dm}^3 \cdot \mathrm{mol}^{-1} \cdot \mathrm{s}^{-1}$).

Mechanism

The activation enthalpy and activation entropy of the title reaction vary with the substituents at the benzene ring (*vide infra*). This demonstrates that the substrate is encountered in the reaction prior to the rate-limiting step; it is involved such that the rate is independent of the substrate concentration. The oxidation proceeds under anhydrous condition, and hence hydrolysis of the dichromate ion can be ruled out. In non-aqueous media, chromium(VI) reagents form complexes with the sulfides, and the reactions obey *Michaelis-Menten* kinetics with respect to the sulfide [8, 11, 12]. If the formation constant K of the *IDC*-sulfide complex is large, the oxidation exhibits zero order dependence with respect to sulfide concentration (Scheme 1). Rate-limiting decomposition of the *IDC*-sulfide complex mediated by *p*-toluenesulfonic acid accounts for the observed kinetic orders.

Linear free energy relationships

The measurement of the rates of oxidation of 14 *para*-, *meta*-, and *ortho*-substituted phenylmethyl sulfides at different temperatures (20–45°C) yields the activation

Table 1. *IDC* oxidation of methylphenyl sulfide in acetonitrile ($[IDC]_0 = 4.9 \times 10^{-4}\,\mathrm{mol} \cdot \mathrm{dm}^{-3}$, 35°C)

$\frac{10^2 \cdot [\mathrm{MeSPh}]_0}{\mathrm{mol} \cdot \mathrm{dm}^{-3}}$	$\frac{10^2 [Ts\mathrm{OH}]_0}{\mathrm{mol} \cdot \mathrm{dm}^{-3}}$	$\frac{10^4 k'}{\mathrm{s}^{-1}}$
3.8	2.9	15
7.7	2.9	15
15	2.9	14
3.8	2.3	12
3.8	2.6	14
3.8	3.2	16
3.8	3.5	18

$$IDC + \mathrm{MeSPh} \rightleftharpoons \mathrm{IDC\text{-}MeSPh} \qquad K$$

$$IDC\text{-}\mathrm{MeSPh} + Ts\mathrm{OH} \rightarrow \mathrm{MeSOPh} + \mathrm{HCrO_4^-} + \mathrm{CrO_2} + Ts\mathrm{O^-} + 2\,\mathrm{C_3H_5N_2^+} \qquad k$$

$$\mathrm{Cr(IV)} + \mathrm{Cr(VI)} \rightarrow 2\mathrm{Cr(V)} \qquad \text{fast [7–9]}$$

$$\mathrm{Cr(V)} + \mathrm{MeSPh} \rightarrow \text{products} \qquad \text{fast [8]}$$

Scheme 1. $-\mathrm{d}[IDC]_\mathrm{T}/\mathrm{d}t = k[IDC\text{-}\mathrm{MeSPh}][Ts\mathrm{OH}] = Kk[IDC]_\mathrm{T}[\mathrm{MeSPh}][Ts\mathrm{OH}]/(1 + K[\mathrm{MeSPh}])$ where $[IDC]_\mathrm{T} = [IDC\text{-}\mathrm{MeSPh}] + [IDC]$; if $K[\mathrm{MeSPh}] \gg 1$, the rate law of the suggested mechanism is $-\mathrm{d}[IDC]_\mathrm{T}/\mathrm{d}t = k[IDC]_\mathrm{T}[Ts\mathrm{OH}]$ with a *pseudo*-first order rate constant of $k' = k[Ts\mathrm{OH}]$

parameters (Table 2). The reaction is neither isoenthalpic nor isoentropic but conforms to the compensation law $\partial E_\mathrm{a}/\partial \ln A = R\beta$, $\partial(\Delta H^\#)/\partial(\Delta S^\#) = \beta$, also known as isokinetic relationships, where E_a is the energy of activation, A is the frequency factor, $\Delta H^\#$ is the enthalpy of activation, $\Delta S^\#$ is the entropy of activation, R is the gas constant, and β is the isokinetic temperature, *i.e.* the temperature at which all substrates react at equal rate. In other words, at the isokinetic temperature the substituent has no influence on the free energy of activation. In an isoentropic reaction, the isokinetic temperature is infinity, and only the enthalpy of activation determines the reactivity. The isokinetic temperature is zero for an isoenthalpic series, and the reactivity depends on the activation entropy. In the title reaction the activation energy varies linearly with log(frequency factor) ($r = 0.999$, slope $= 2.58\,\mathrm{kJ \cdot mol^{-1}}$, intercept $= 13.9\,\mathrm{kJ \cdot mol^{-1}}$), and the enthalpy of activation is linearly related to the entropy of activation (Fig. 1; $r = 0.999$, $s = 1.22\,\mathrm{kJ \cdot mol^{-1}}$, slope $=$ 310 K). The maximum possible errors in activation enthalpy (δ) and activation entropy are $3\,\mathrm{kJ \cdot mol^{-1}}$ and $10\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. The error criterion is satisfied in the

Table 2. Activation parameters for the *IDC* oxidation of *para*-, *meta*-, and *ortho*- substituted phenylmethyl sulfides in acetonitrile

Substituent	E_a / $\mathrm{kJ \cdot mol^{-1}}$	$\ln A$	$\Delta H^\#$ / $\mathrm{kJ \cdot mol^{-1}}$	$\Delta S^\#$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\Delta G^\#$ / $\mathrm{kJ \cdot mol^{-1}}$ (308 K)
H	42	11	39	−157	87
p-$\mathrm{CH_3}$	80	26	78	−37	89
p-$\mathrm{OCH_3}$	74	23	72	−61	91
p-Cl	85	28	82	−22	89
p-Br	69	21	66	−80	91
p-$\mathrm{NO_2}$	49	13	47	−145	92
m-$\mathrm{CH_3}$	35	8	32	−184	89
m-Cl	45	13	43	−148	89
m-$\mathrm{NO_2}$	42	10	39	−169	91
o-$\mathrm{CH_3}$	69	22	66	−73	89
o-$\mathrm{OCH_3}$	106	36	104	45	90
o-Cl	91	30	89	−7	91
o-Br	92	30	89	−2	90
o-$\mathrm{NO_2}$	65	19	62	−92	90

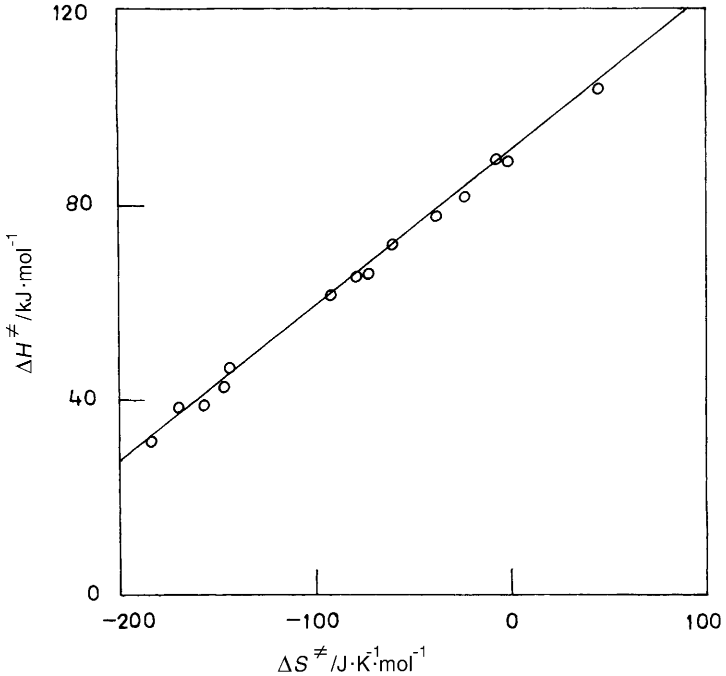

Fig. 1. Isokinetic plot of $\Delta H^{\neq}$ *vs.* $\Delta S^{\neq}$

present study, *i.e.* $\Delta\Delta H^{\#}$ ($72\,\mathrm{kJ\cdot mol^{-1}}$) $\gg 2\delta$ ($6\,\mathrm{kJ\cdot mol^{-1}}$), and hence the correlation between $\Delta H^{\#}$ and $\Delta S^{\#}$ is significant. The existence of isokinetic relationship suggests that all substituted phenylmethyl sulfides studied are oxidized *via* a common mechanism.

The free energies of activation of the *IDC* oxidation of *para-* and *meta-*substituted phenylmethyl sulfides, calculated from the activation enthalpies and activation entropies, were analyzed using the linear free energy relationships. The linear free energy relationship is based on the ionization of benzoic acids; hence, a correlation of free energy of activation, enthalpy of activation, and entropy of activation of the *IDC* oxidation with the free energy, enthalpy, and entropy of ionization of benzoic acids [1] should be meaningful. However, the correlation is poor in all cases. The substituent influence on the free energy of activation concerns the enthalpic and entropic components [1]. The biparametric correlation of the free energy of activation with the enthalpic (σ_H) and entropic (σ_S) substituent constants is nonetheless unsatisfactory and the activation enthalpy and entropy also fail to correlate with σ_H and σ_S. In addition, the free energy of activation does not correlate with the usual *Hammett* substituent (σ) constant (Fig. 2). The *p*-nitro group is likely to establish conjugation with the reaction center. Also, expansion of the valence shell of sulfur beyond the octet enables conjugation with the *p*-methoxy group [13]. Therefore, the σ^+ and σ^- constants were used in the single parameter correlation, but also without success. The failure of all single parameter equations to correlate the free energy of activation turned our interest towards dual substituent parameter (DSP) equations. However, all known DSP equations including that of *Swain* [14] failed to correlate the free energy of activation with the substituent constants σ_I, σ_R^0,

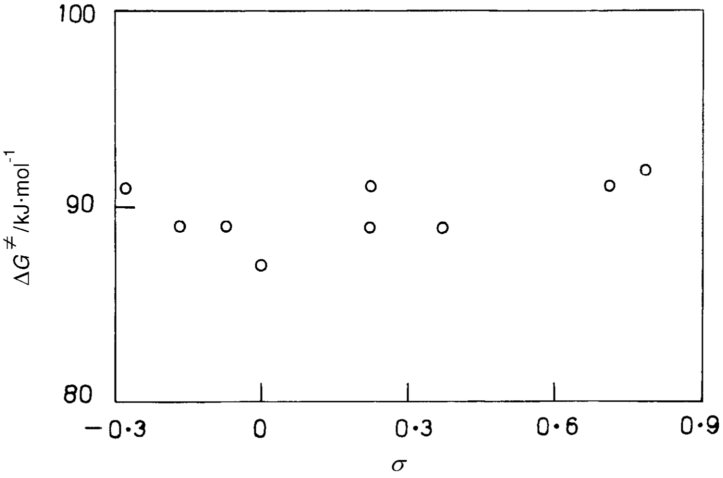

Fig. 2. Lack of linear relationship between $\Delta G^{\neq}$ and σ

$\sigma_{R(BA)}$, σ_R^-, and σ_R^+ [15] (*F*- and *R*-values: Ref. [14]). The possible reason for the lack of any linear free energy relationship is that the isokinetic temperature lies within the experimental temperature (293–318 K); the isokinetic temperature calculated from the isokinetic plots is 310 ± 5 K.

Experimental

The *para*-, *meta*-, and *ortho*-substituted phenylmethyl sulfides were prepared by standard methods [16] and distilled. Imidazolium dichromate ($(C_3H_5N_2)_2Cr_2O_7$) was prepared by a reported procedure [10], dissolved in acetonitrile (HPLC grade), and standardized iodometrically. A solution of *p*-toluenesulfonic acid (*Ts*OH) in acetonitrile was prepared and standardized. The kinetics of the oxidation were investigated under *pseudo*-first order conditions ([*Ts*OH] and [MeSPh] $\gg$ [*IDC*]) at constant temperature. The reaction was initiated by the addition of sulfides, and the progress of the oxidation was followed spectrophotometrically (UVIDEC-7800, Jasco) at 350 nm. The *pseudo*-first order rate constants (k') were calculated from the slopes of log(absorbance) *vs.* time plots (least squares fits). The oxidation stops at the sulfoxide; under the chosen experimental conditions, further oxidation of sulfoxide is slow. The reduction product of *IDC* is chromium(III), identified by the UV/Vis spectrum of the reaction solution after completion of the oxidation. Hence, the oxidation follows Eq. (1).

$$\begin{aligned}&(C_3H_5N_2)_2Cr_2O_7 + 8\,p\text{-}CH_3C_6H_4SO_3H + 3\,CH_3SC_6H_5\\&\quad\rightarrow 2\,Cr^{3+} + 2\,C_3H_5N_2^+ + 8\,p\text{-}CH_3C_6H_4SO_3^- + 3\,CH_3SOC_6H_5 + 4H_2O\end{aligned} \tag{1}$$

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