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Evidence of a Common Mechanism in the Oxidation by Chromium(VI) Complexes: Kinetics of Oxidation of Diphenyl Sulfide

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Summary. The oxidation of diphenyl sulfide by dichromate and seven chromium(VI) complexes in glacial acetic acid is first order in the oxidants and exhibits *Michaelis-Menten* kinetics with respect to the sulfide. UV/Vis spectroscopic studies confirm the formation of an oxidant-sulfide complex. Oxidations by dichromate and chromium(VI) complexes follow a common mechanism.

Keywords. Chromium(VI) complexes; Oxidation; Kinetics.

Hinweise auf einen gemeinsamen Mechanismus bei der Oxidation durch Chrom(VI)-Komplexe: Kinetik der Oxidation von Diphenylsulfid

Zusammenfassung. Die Oxidation von Diphenylsulfid in Eisessig mit Dichromat und sieben Chrom(VI)-Komplexen verläuft nach erster Ordnung und gehorcht einer *Michaelis-Menten*-Kinetik in bezug auf das Sulfid. UV/Vis-spektroskopische Studien bestätigen die Bildung eines Oxidans-Sulfid-Komplexes. Die Oxidation durch Dichromat und Chrom(VI)-Komplexe folgt einer isokinetischen Beziehung, was auf einen gemeinsamen Mechanismus hinweist.

Introduction

Reports on the kinetics of oxidation of a variety of organic substrates by chromium(VI) complexes are numerous [1, 2], and so are studies on the influence of substituents on the rates of oxidation by chromium(VI) complexes. However, there seems to be no investigation on a comparison of the mechanism of oxidation by chromium(VI) complexes. Chromium(VI) complexes are suitable for oxidation under anhydrous conditions; therefore, we studied their behaviour in glacial acetic acid using UV/Vis spectroscopy to investigate the kinetics of the reaction.

Results and Discussion

The oxidation of diphenyl sulfide in glacial acetic acid by potassium dichromate (dichromate), pyridinium dichromate (*PDC*), quinolinium dichromate (*QDC*),

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Table 1. Oxidation of PhSPh by chromium(VI) complexes[1]

$10^4[\mathrm{Cr(VI)}]_o$/ gatom · dm^{-3}	$10^2[\mathrm{PhSPh}]_o$/ mol · dm^{-3}	$10^3k'/\mathrm{s}^{-1}$							
		Dichromate	*PDC*	*QDC*	*IDC*	*PFC*	*QFC*	*PCC*	*QCC*
1.0	1.0	5.3	3.0	2.2	3.1	4.1	3.7	2.9	3.0
1.5	1.0	4.9	3.2	2.1	3.2	3.8	3.5	2.7	3.0
2.0	1.0	4.9	3.2	2.0	3.0	3.9	3.6	2.8	2.8
1.0	0.2	2.0	1.0	0.75	1.2	1.6	1.0	0.92	0.92
1.0	0.5	4.0	2.0	1.5	2.3	2.8	2.2	1.9	1.9
1.0	2.0	7.4	4.2	3.0	4.2	5.4	5.4	4.0	4.2

[1] 100% HOAc, 35°C

imidazolium dichromate (*IDC*), pyridinium fluorochromate (*PFC*), quinolinium fluorochromate (*QFC*), pyridinium chlorochromate (*PCC*), and quinolinium chlorochromate (*QCC*), studied under the condition: $[\mathrm{Cr(VI)}] \ll [\mathrm{PhSPh}]$, is first order with respect to the oxidant; plots of log(absorbance) *vs.* time are linear up to about 50% of the oxidation. The *pseudo*-first order rate constants (k') are independent of the initial concentration of the oxidants (Table 1). However, the oxidation slows down after about 60% completion, and the log(absorbance)/time trace deviates from linearity, a behaviour which is not unknown in the context of oxidation by Cr(VI) complexes [3, 4]. The title oxidation exhibits *Michaelis-Menten* kinetics with respect to the sulfide; the oxidation rate increases only marginally with increasing [PhSPh], and the k'-[PhSPh] profile (not shown) displays a typical *Michaelis-Menten* dependence. Representative rate data are given in Table 1. Double reciprocal plots of k' *vs.* [PhSPh] and also the statistically balanced *Hanes* plots of [PhSPh]/k' *vs.* [PhSPh] are linear with positive slopes and *y*-intercepts. Addition of acetonitrile to the reaction solution suppresses the oxidation; the oxidation is sluggish in aqueous acetic acid (70% (v/v) aq. HOAc). The rate measurements at 25–45°C yield the energy of activation and the frequency factor. The linear variation of activation energy with log(frequency factor) (correlation coefficient: $r = 0.998$; standard deviation: $sd = 0.164$) refers to the comparison of the various systems under consideration [5].

Mechanism

In aqueous and partly aqueous media, dichromate is hydrolyzed; at low concentration it exists predominantly as monomer which acts as the oxidizing species [6].

$$\mathrm{Cr_2O_7^{2-}} + \mathrm{H_2O} \rightleftharpoons 2\mathrm{HCrO_4^-} \quad K_1 = 2.8 \times 10^{-2}\,\mathrm{mol \cdot dm^{-3}}$$

However, absence of even traces of water in the reaction medium was confirmed with anhydrous copper sulfate for the title oxidation. This rules out the hydrolysis of dichromate. Moreover, the value of the equilibrium constant (K_1) demands that the monomer exists as dimer under anhydrous conditions. Existence of chromium(VI) as a dimer in glacial acetic acid was confirmed by UV/Vis spectroscopy (445 nm).

Dichromate in acidic solution undergoes protonation [6]:

$$Cr_2O_7^{2-} + H^+ \rightleftharpoons HCr_2O_7^- \quad K_2 = 1.2\,\mathrm{dm^3 \cdot mol^{-1}}$$

A calculation using the protonation constant of dichromate (K_2) and the dissociation constant of acetic acid indicates that dichromate exists predominantly as dichromate anion and not as acid dichromate in glacial acetic acid.

The observed *Michaelis-Menten* kinetics reveals the complex formation between sulfide and oxidant. This is further confirmed by UV/Vis spectroscopy; UV/Vis spectra of the oxidant, the sulfide, and a mixture of both reveal the formation of a dichromate-sulfide complex. The results indicate a rapid precursor complex formation, followed by a slow and, therefore, rate-determining breakdown of the complex (Scheme 1).

$$\begin{array}{rcll}
Ph_2S + Cr_2O_7^{2-} & \rightleftharpoons & Ph_2SCr_2O_7^{2-} & K_3\text{, rapid} \\
Ph_2SCr_2O_7^{2-} & \rightarrow & Ph_2SOCrO_2 + CrO_4^{2-} & k_4\text{, slow} \\
Ph_2SOCrO_2 & \rightarrow & Ph_2SO + CrO_2 & \text{fast} \\
\mathrm{Cr(IV)} + \mathrm{Cr(VI)} & \rightarrow & 2\mathrm{Cr(V)} & \text{fast} \\
\mathrm{Cr(V)} + Ph_2S & \rightarrow & \text{products} & \text{fast}
\end{array}$$

Scheme 1

The rate law for the suggested mechanism is

$$\frac{-\mathrm{d}[\text{oxidant}]}{\mathrm{dt}} = \frac{K_3 k_4 [\text{PhSPh}][\text{oxidant}]}{1 + K_3[\text{PhSPh}]}$$

with a *pseudo*-first order rate constant of

$$k' = \frac{K_3 k_4 [\text{PhSPh}]}{1 + K_3[\text{PhSPh}]}$$

The rate law agrees with the experimental results. The formation constant (K_3) and disproportionation constant (k_4) are listed in Table 2. A possible explanation for the slowdown of the oxidation beyond 60% completion is hydrolysis of dichromate to chromate by water which is formed as a product. This proposition stems from the fact that addition of water renders the oxidation sluggish. Examination of the oxidation rates reveals that potassium dichromate is the most powerful oxidant

Table 2. Thermodynamic and kinetic parameters at 35°C

	Dichromate	*PDC*	*QDC*	*IDC*	*PFC*	*QFC*	*PCC*	*QCC*
$E_a/\mathrm{kJ \cdot mol^{-1}}$	49	98	101	85	78	44	92	82
$\ln A$	14	33	34	27	25	12	30	26
$\Delta H^{\#}/\mathrm{kJ \cdot mol^{-1}}$	47	95	99	82	75	42	89	79
$\Delta S^{\#}/\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	−136	17	26	−25	−46	−156	−3	−37
$K_3/\mathrm{dm^3 \cdot mol^{-1}}$	119	89	97	126	124	54	83	77
$k_4/\mathrm{s^{-1}}$	10	6.5	4.6	5.8	7.6	11	6.4	6.9

among the complexes studied. Complexing of chromium(VI) with heterocyclic bases moderates the reactivity of chromium(VI). Among the chromium(VI) complexes, oxidation by fluorochromates are faster than those effected by the rest. This may be explained by the electron withdrawing power of fluorine.

Experimental

Pyridinium dichromate (*PDC*) [7], quinolinium dichromate (*QDC*) [8], imidazolium dichromate (*IDC*) [9], pyridinium fluorochromate (*PFC*) [10], quinolinium fluorochromate (*QFC*) [11], pyridinium chlorochromate (*PCC*) [12], and quinolinium chlorochromate (*QCC*) [13] were prepared as reported. Diphenyl sulfide (Fluka) was distilled before use. All other chemicals were of analytical grade. Acetic acid AR was refluxed for 6 h over chromium(VI) oxide and distilled through a column. Acetonitrile was also distilled before use.

Rate studies at constant temperature were performed under *pseudo*-first order conditions with a large excess of sulfide in glacial acetic acid. Solutions of chromium(VI) reagents in acetic acid were prepared and standardized iodometrically. Required volumes of the reagents of desired concentrations were mixed, and the progress of the oxidation was followed spectrophotometrically at 350 nm (UVIDEC-340, Jasco). The *pseudo*-first order rate constants were computed from the least squares slopes of the linear plots of log(absorbance) *vs*. time. *Arrhenius* plots afforded activation energies and frequency factors.

Chromium(VI) reagents (5 mmol) were allowed to react with diphenyl sulfide (15 mmol) in glacial acetic acid (15 cm^3) at 45°C. Acetic acid was evaporated, the residue extracted with diethyl ether, and identified as diphenyl sulfoxide by its IR spectrum. Chromium(III) was identified as the reduction product by its UV/Vis spectrum. Hence the reaction has to be written as

$$Cr_2O_7^{2-} + 3Ph_2S + 8H^+ \rightarrow 2Cr^{3+} + 3Ph_2SO + 4H_2O.$$

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