

# Kinetics and Mechanism of the Reduction of Chromium(VI) with Dimethyl Sulfoxide†

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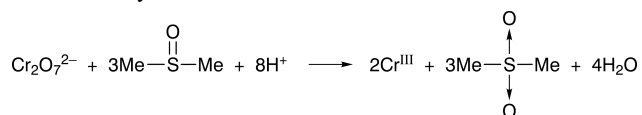
The kinetics of reduction of chromium(VI) by dimethyl sulfoxide has been studied in aqueous acid media.

The use of organosulfur compounds in organic synthesis is ever expanding.<sup>1,2</sup> Dimethyl sulfoxide (DMSO) is a compound of synthetic value. Various oxidants (organic peracids,<sup>3</sup> peroxodiphosphate<sup>4</sup> and potassium hydrogenpersulfate<sup>5,6</sup>) have been used for the oxidation of sulfides to sulfoxides or sulfones through free radical mechanisms. We now report the kinetics of oxidation of DMSO by the versatile oxidant chromium(VI) in aqueous HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> media.

The solvent water was twice distilled. The other reagents [potassium dichromate (Merck), DMSO (Fluka), perchloric acid (Merck, 70% reagent), sodium sulfate (Merck) and sodium perchlorate (Merck)] were used without further purification. The rate of formation of Cr<sup>III</sup>, d[Cr<sup>III</sup>]/dt, at 580 nm was followed by means of a UV–VIS spectrophotometer. All the kinetic runs were performed under pseudo-first-order conditions with [DMSO] ≫ [Cr<sup>VI</sup>] in aqueous acidic media at constant [HClO<sub>4</sub>] or [H<sub>2</sub>SO<sub>4</sub>] = 1.6 mol dm<sup>-3</sup> and ionic strength = 0.5 mol dm<sup>-3</sup> (NaClO<sub>4</sub> or Na<sub>2</sub>SO<sub>4</sub>). The first-order rate constants (*k*<sub>obs</sub>) were obtained from linear plots of ln(*A*<sub>∞</sub> - *A*) versus time (average linear correlation coefficient 0.989). A solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (0.1 mol dm<sup>-3</sup>, 5 cm<sup>3</sup>) in HClO<sub>4</sub> was added to a solution of 1.0 mol dm<sup>-3</sup> DMSO in 2.0 mol dm<sup>-3</sup> HClO<sub>4</sub> and 25% v/v acrylonitrile at 20 °C. No polymer (white precipitate) formation was observed. Furthermore, the addition of acrylonitrile had no effect on the rate. This indicates that a free radical mechanism is unlikely.

The product (Cr<sup>III</sup>) analysis was performed under kinetic conditions. After the reaction has proceeded to completion the two d-d bands ascribed to chromium(III) were observed at λ<sub>max</sub> = 410 and 580 nm. In a typical experiment, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was dissolved in H<sub>2</sub>O (50 cm<sup>3</sup>) to give a 10 × 10<sup>-3</sup> mol dm<sup>-3</sup> solution, H<sub>2</sub>SO<sub>4</sub> was then added until pH 2–3. To this was added 25 cm<sup>3</sup> of DMSO dropwise. The mixing of DMSO with an aqueous solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is exothermic and controlled addition of DMSO is advisable. The precipitate which appeared after keeping the mixture overnight at room temperature (20 °C) was filtered off, dried and then recrystallised with rectified spirit to give a white crystalline product. (mp = 107–108 °C; IR ν(S=O) at 1310 and 1140 cm<sup>-1</sup>, characteristic of sulfones) which was identified as dimethyl sulfone.

The stoichiometry of the reaction was determined by taking a known excess of Cr<sup>VI</sup> over DMSO. The reaction was allowed to go completion in aqueous HClO<sub>4</sub> by keeping it overnight and the remaining Cr<sup>VI</sup> estimated iodometrically. The reaction took place according to the following stoichiometry:



The effect of [DMSO] on the reaction rate is shown in Table 1; as [DMSO] increases, *k*<sub>obs</sub> increases but non-linearly. The slope of a plot of log *k*<sub>obs</sub> vs. log[DMSO] is approximately 2.0, corresponding to a second-order dependence on [DMSO]. The *k*<sub>obs</sub> were obtained at various [Cr<sup>VI</sup>]<sub>0</sub> but at constant [HClO<sub>4</sub>], [DMSO] and temperature. The rate was found to be constant with increasing [Cr<sup>VI</sup>]<sub>0</sub>, indicating that the total [Cr<sup>VI</sup>] must be used in the rate law. The rate equation is, therefore,

$$\frac{d[\text{Cr}^{\text{III}}]}{dt} = -\frac{d[\text{Cr}^{\text{VI}}]_{\text{T}}}{dt} = k_{\text{obs}}[\text{Cr}^{\text{VI}}]_{\text{T}} \quad (1)$$

To investigate the effect of acid concentration on the rate, the reaction was studied as a function of [HClO<sub>4</sub>] and [H<sub>2</sub>SO<sub>4</sub>] at fixed [DMSO] (3.0 mol dm<sup>-3</sup>) and [Cr<sup>VI</sup>] (2.8 × 10<sup>-3</sup> mol dm<sup>-3</sup>) at 20 °C. The values of *k*<sub>obs</sub> are shown in Table 1. A plot of *k*<sub>obs</sub> against [HX] was a curve passing through the origin. Further, when log *k*<sub>obs</sub> was plotted vs. log[HX] a straight line with slope of ca. 2.0 was obtained indicating the order with respect to [HClO<sub>4</sub>] and [H<sub>2</sub>SO<sub>4</sub>] to be second at lower acid concentrations (0.26 to 0.70 mol dm<sup>-3</sup>). The second-order kinetics shifted to higher order at higher [HClO<sub>4</sub>].

Carrington and Symons<sup>7</sup> reported the formation of HOCrO<sub>2</sub>OClO<sub>3</sub> and HOCrO<sub>2</sub>OSO<sub>3</sub>H by the interaction of Cr<sup>VI</sup> and HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>, respectively, according to the following reaction



where X = ClO<sub>4</sub> and HSO<sub>4</sub>.

Before attempting to propose a mechanism, it is necessary to discuss the chromium(VI) species existing in acidic media. In an aqueous solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, UV–VIS studies showed that the Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ion is the predominant species.<sup>8</sup> Spectra of mixtures containing the same [Cr<sup>VI</sup>] and [HClO<sub>4</sub>] in different molar ratios exhibited different absorbances with the same λ<sub>max</sub> (=450 nm); the absorbance decreased with increasing [HClO<sub>4</sub>] indicating that Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ion is converted into HOCrO<sub>2</sub>OClO<sub>3</sub>.<sup>7,9–13</sup>

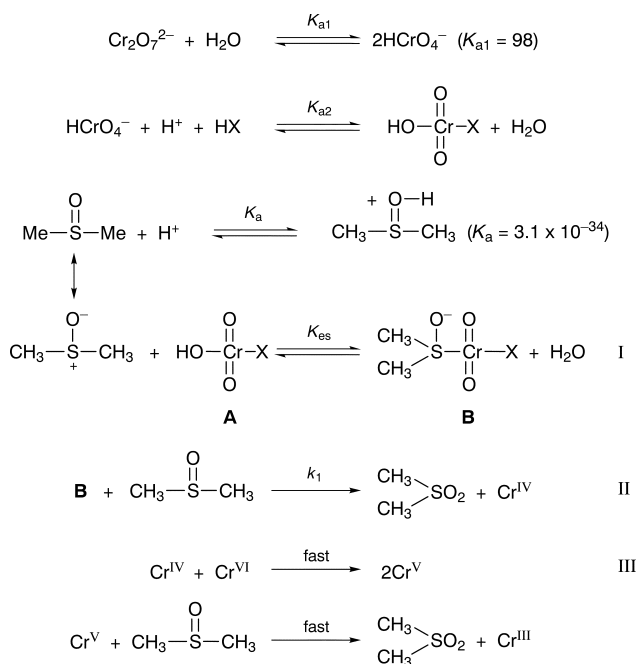
A mechanism consistent with all experimental data is given in Scheme 1. DMSO is a resonance hybrid of the forms >S=O ↔ >S<sup>+</sup>–O<sup>-</sup>; in view of the back-donation resonance of the non-bonding electrons of oxygen with the empty d orbitals of sulfur, the availability of electrons on oxygen can be considered to be less compared to that on sulfur. The oxidation of DMSO involves the formation of an S=O bond. Therefore, chromium(VI) (oxidant) would lose its oxygen. In Scheme 1 the first step represents the formation of an ester between chromic acid and DMSO which decomposes to chromium(IV) and dimethyl sulfone. The reaction Cr<sup>IV</sup> + Cr<sup>VI</sup> → 2Cr<sup>V</sup> has an extremely favourable reduction potential.<sup>14</sup> Therefore, the third reaction in Scheme 1 indicates the formation of Cr<sup>V</sup>. In analogy with previous studies<sup>15</sup> we assume that Cr<sup>V</sup> is converted into Cr<sup>III</sup> after the reaction with DMSO.

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**Table 1** Rate constants at various concentrations of chromium(vi), DMSO, HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> for the reduction of chromium(vi) by DMSO at 20 °C

10 <sup>3</sup> [Cr <sup>VI</sup> ]/ mol dm <sup>-3</sup>	[DMSO]/ mol dm <sup>-3</sup>	[HClO <sub>4</sub> ]/ mol dm <sup>-3</sup>	[H <sub>2</sub> SO <sub>4</sub> ]/ mol dm <sup>-3</sup>	10 <sup>5</sup> k <sub>obs</sub> / s <sup>-1</sup>	(k <sub>obs</sub> -k <sub>calc</sub> )/ k <sub>obs</sub>
2.8	3.0	0.35	0.00	7.1	
3.2				7.1	
3.8				7.2	
4.2				7.2	
4.6				7.3	
5.0				7.1	
2.8	2.0	0.00	0.35	6.0	
	3.0			12.0	
	4.0			22.0	
	4.5			30.0	
	5.0			36.0	
2.8	3.0	0.00	0.26	6.7	+0.23
			0.35	10.0	0.00
			0.40	13.0	0.00
			0.50	19.0	-0.05
			0.60	29.0	+0.02
			0.70	41.0	
2.8	3.0	0.26	0.00	4.8	-0.20
		0.35		7.1	-0.04
		0.40		9.2	-0.06
		0.50		11.0	-0.30
		0.60		20.0	-0.10
		0.70		31.0	0.00
		0.80		40.0	+0.02
		0.90		90.0	-0.03
		1.0		110.0	+0.04



**Scheme 1**

The rate law derived from Scheme 1 is

$$\begin{aligned}
 \text{Rate} &= d[\text{Cr}^{\text{III}}]/dt \\
 &= K_{a1}K_{a2}K_{es}k_1[\text{HX}]^2[\text{Cr}_2\text{O}_7^{2-}][\text{DMSO}]^2 \quad (2)
 \end{aligned}$$

Comparing (1) and (2) we get

$$k_{\text{obs}} = K_{a1}K_{a2}K_{es}k_1[\text{HX}]^2[\text{DMSO}]^2 \quad (3)$$

Eqn. (2) is consistent with the results, since the kinetic orders in oxidant and reductant concentrations are first and second, respectively. According to eqn. (3), plots of  $k_{\text{obs}}$  vs.  $[\text{H}_2\text{SO}_4]^2$  or  $[\text{HClO}_4]^2$  at constant  $[\text{DMSO}]$  should be linear with intercept = 0 and slope =  $K_{a1}K_{a2}K_{es}k_1[\text{DMSO}]^2$ . This has been found to be the case, thus supporting the proposed mechanism. From slope, the values of  $k_1K_{es}$  have been calculated as  $9.5 \times 10^{-7}$  and  $7.0 \times 10^{-7} \text{ s}^{-1}$  for H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub>, respectively, at constant  $[\text{DMSO}]$  (3.0 mol dm<sup>-3</sup>). Substituting the values of  $k_1K_{es}$  and  $K_a$  in eqn. (3), the rate constants ( $k_{\text{calc}}$ ) have been calculated for various kinetic runs and compared with the experimentally determined values (Table 1). The close agreement between the observed and calculated values provides supporting evidence for the proposed mechanism.

At higher  $[\text{HClO}_4]$  the formation of another complex cannot be ruled out. The kinetic equation derived including the additional steps will have the same dependence on  $[\text{DMSO}]$  and explains the higher-order behaviour with respect to HClO<sub>4</sub> at higher concentration.

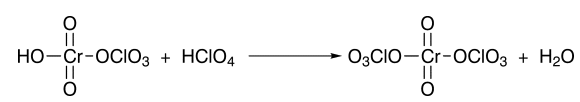


Table 1 indicates that the rate of reduction of chromium(vi) by DMSO depends on the acidity as well as on the identity of the mineral acid (H<sub>2</sub>SO<sub>4</sub> or HClO<sub>4</sub>). The reaction may be explained by considering the electron-withdrawing ability of ClO<sub>3</sub> and SO<sub>3</sub>H which decrease the ease of protonation of the chromate ester but increase the tendency of chromium(vi) to accept electrons from the reducing agent. The oxidising ability of the ester A decreases in the order HO-CrO<sub>2</sub>OSO<sub>3</sub>H > HO-CrO<sub>2</sub>OCIO<sub>3</sub> for a given concentration.

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**References**

- 1 B. M. Trost, *Chem. Rev.*, 1978, **78**, 363.
- 2 P. D. Mangnus, *Tetrahedron*, 1977, **33**, 2019.
- 3 H. H. Szmant, H. F. Harnserger and F. J. Krahe, *J. Am. Chem. Soc.*, 1954, **76**, 2185.
- 4 P. Maruthamuthu and M. Santappa, *Indian J. Chem.*, 1978, **16A**, 43.
- 5 R. J. Kennedy and A. M. Stock, *J. Org. Chem.*, 1960, **25**, 1901.
- 6 B. M. Trost and D. P. Curran, *Tetrahedron Lett.*, 1981, **22**, 1287; A. McKillop and J. A. Tarkin, *Tetrahedron Lett.*, 1983, **24**, 1505.
- 7 A. Carrington and M. C. R. Symons, *Chem. Rev.*, 1963, **63**, 443.
- 8 M. Creslak-Golonka, *Coord. Chem. Rev.*, 1991, **109**, 223.
- 9 Z. Khan, A. A. Hashmi and Kabir-ud-Din, *Transition Met. Chem.*, 1988, **23**, 147.
- 10 Z. Khan, A. A. Hashmi, L. Ahmad and M. M. Haq, *Int. J. Chem. Kinet.*, 1998, **30**, 335.
- 11 H. C. Mishra and M. C. R. Symons, *J. Chem. Soc.*, 1962, 4411.
- 12 F. Holloway, *J. Am. Chem. Soc.*, 1952, **74**, 224.
- 13 D. G. Lee and R. Stewart, *J. Am. Chem. Soc.*, 1964, **86**, 3051.
- 14 F. H. Westheimer, *Chem. Rev.*, 1949, **45**, 419; W. Watanabe and F. H. Westheimer, *J. Chem. Phys.*, 1949, **17**, 61.
- 15 J. F. Perez-Benito, C. Arias and D. Lamrhari, *J. Chem. Soc., Chem. Commun.*, 1992, 472.