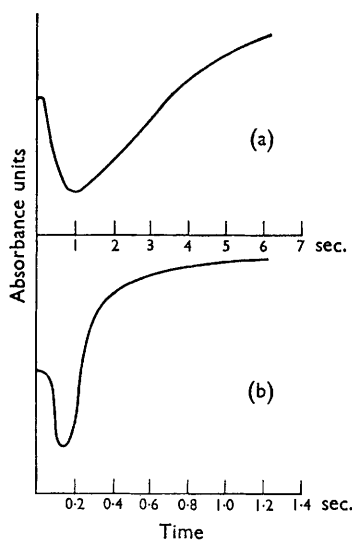


Spectral Evidence for Intermediates in the Oxidation of α -Mercaptans

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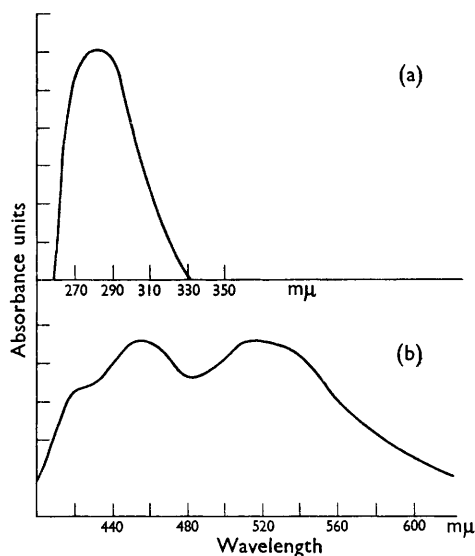
THE mechanism suggested for many inorganic redox reactions includes as a first step the formation of short-lived intermediates which subsequently decompose in the rate-determining step of the oxidation. The initial complex or ion-pair formation can involve both cationic¹ and anionic² oxidants. In most cases, however, the nature of the intermediate has been postulated from kinetic studies with little physical evidence for its existence. This can be attributed mainly to the speed with which these species decompose. In the oxidation of thiosulphate by iron(III) the lifetime of the intermediate can be measured in seconds enabling the spectrum of the intermediate to be obtained.^{1d} We have employed a stopped-flow technique to obtain direct evidence for the existence of transient species with half-lives of formation of the order of milliseconds.

FIGURE 1. Stopped-flow traces, $T = 10^\circ$.

- (a) $4.5 \times 10^{-4}M\text{-Co}^{3+}$ and $2.8 \times 10^{-2}M\text{-thiomalic acid}$, $\lambda = 280 m\mu$.
 (b) $10^{-3}M\text{-VO}_3^-$ and $5 \times 10^{-2}M\text{-thiomalic acid}$, $\lambda = 450 m\mu$.

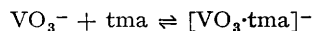
When an aqueous solution of an α -mercaptan is mixed (within a few msec.) with one containing vanadate, dichromate, molybdate, cobaltic, or ferric ions, a change in the ultraviolet or visible spectrum occurs which is not attributable to

either the reactants or the final oxidation products. The effect of this on the stopped-flow trace is the appearance at certain wavelengths of an increase in optical density followed by a slower decrease. Figure 1 shows the formation and subsequent decomposition of the intermediate formed in the reactions of cobalt(III) and vanadate ions with thiomalic acid. The magnitude of the optical density change as a function of wavelength has been used to prepare the spectra of the transient species shown in Figure 2.

FIGURE 2. Spectral curves of transient intermediate species, $T = 10^\circ$.

- (a) $4.5 \times 10^{-3}M\text{-Co}^{3+}$ and $2.8 \times 10^{-2}M\text{-thiomalic acid}$.
 (b) $10^{-3}M\text{-VO}_3^-$ and $5 \times 10^{-2}M\text{-thiomalic acid}$.

The reaction of iron(III) with α -mercaptans produces blue intermediates, whilst in the corresponding dichromate oxidation the intermediates are brown. In the vanadate-thiomalic reaction the species is red-purple, and preliminary kinetic studies indicate a stability constant $K \sim 20$ at 15° for the reaction



where tma is thiomalic acid.

In the cobaltic oxidation, the charge-transfer band appears at 285 $m\mu$ in contrast to the 250 $m\mu$ for the Co^{3+} ion in aqueous perchloric acid. It is of interest that the corresponding maximum for the species produced in the cobalt(III)-malic acid

reaction occurs at 275 $m\mu$ reflecting the greater reducing power of the mercaptan over the oxygen analogue.³

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