

Effect of γ -irradiation on the oxidation of decyl sulphoxide (DSO) with Ce(IV) in acetic acid-water medium

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Influence of γ -irradiation (5.0×10^2 K Gy) on the oxidation of decyl sulphoxide (DSO) with Ce(IV) in acetic acid-water medium is studied in the temperature range 308-323 K. The data reveal that the rate of the reaction is enhanced with increase in temperature as well as with increase in concentration of the substrate in both the cases of unirradiated and irradiated samples. The rate limiting step involves the decomposition of the complex, generating free radical species which then give rise to sulphone in subsequent stages. Irradiation, decelerates the rate of reaction and lowers the activation enthalpy and entropy values marginally.

During extraction of highly active materials in nuclear technology, the solvent undergoes radiolysis, and the species generated complicate the extraction process¹. Sulphoxides on the other hand, are relatively simple compounds and form no undesirable radiolytic degradation products, hence may be used as good extractants for actinides, lanthanides and transition elements. Extraction of americium(III) and neptunium(IV) from nitric acid solution is poor at higher acid concentration probably due to oxidation of sulphoxides to sulphones². It is pertinent therefore, to study the role of γ -irradiation on the oxidation of long chain alkyl sulphoxides in order to explore their suitability to be used as extractants. The present investigations throw light on the role of γ -irradiation on the oxidation of decyl sulphoxide (DSO) with Ce(IV) in acetic acid-water media.

Experimental

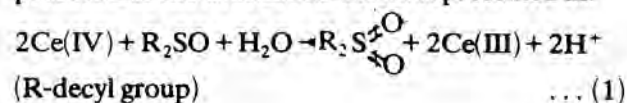
Analytical reagent grade chemicals were employed for all experimental purposes. Organic solvents were freshly distilled at the temperature range of $\pm 1^\circ\text{C}$ and DSO was synthesized by following the procedure reported earlier³ taking the corresponding alcohol as the starting material and the product was characterized⁴ by melting point data (obs: $82-83^\circ\text{C}$, lit: 83°C) as well as by

molecular weight determination (330). Decyl sulphoxide (≈ 5 g), was sealed in glass ampoules and exposed to 1.5×10^2 K Gy of γ -rays at the dose rate of 1.1 K Gy h^{-1} as determined by Fricke dosimetry, $G(\text{Fe}^{3+}) = 15.5$. Kinetics of oxidation of both unirradiated and irradiated materials with Ce(IV) was carried out in acetic acid-water medium.

The experiment was undertaken with different [substrate] and [oxidant] at 303-323 K using a constant temperature bath under pseudo-first order conditions, $[\text{DSO}] = 0.5 - 1.5 \times 10^{-2}$ and $[\text{Ce}(\text{SO}_4)_2] = 0.5 - 2.0 \times 10^{-3}$ mol dm^{-3} . The reaction mixture was homogeneous throughout the experiment and the kinetics of the process was followed by monitoring the decrease in optical absorption of the oxidant at 375 nm using a Jasco-7800 UV/vis spectrophotometer. At this wavelength, the radiolytic products did not interfere as no absorption was observed in the case of irradiated sample. Duplicate kinetic runs indicated that the rate constant obtained by two different determinations agreed within $\pm 3\%$.

Stoichiometry and product analysis

The stoichiometry and product analysis of the reaction was found by taking known excess of Ce(IV) solution in H_2SO_4 to react with sulphoxide in binary mixture of acetic acid-water for 48 h. The product isolated from the reaction mixture by extracting with crushed ice was washed with distilled water and then recrystallised from petroleum ether ($60-80^\circ\text{C}$). Chromatographic separation of the samples was undertaken by thin layer technique (TLC). For a comparative study, known sample of decyl sulphone was also subjected to TLC and the spots were identified by exposure to iodine and the solvent system was benzene-ethanol (80:20 v/v) mixture. The R_f value obtained was the same as that of known sample of decyl sulphone which was further confirmed by IR spectra and molecular weight determination. A blank experiment without the substrate indicated that the solvent did not take part in the oxidation process and the overall reaction is represented as:



Results and discussion

Data on effects of temperature and [substrate] on the oxidation of both unirradiated and irradiated samples (Tables 1 and 2) indicate that in both type of crystals, the pseudo-first order rate constant (k_1) increases with increase in [substrate], whereas the second order rate constant ($k_2 = k_1 / [\text{substrate}]$) remains almost constant in all the cases indicating overall first order dependence on [sulphoxide] as well as on [oxidant]. The rate of the reaction in both the type of substrates also increases with increase in temperature. Plots of k_1 versus [sulphoxide] are linear passing through the origin indicating that the reaction is first order in [sulphoxide]. Oxidation of both unirradiated and irradiated crystals exhibit identical kinetic behaviour under the present experimental conditions showing that same mechanism operates in both the categories of substrates. It is also evident from the data (Table 1) that irradiation retards the rate of reaction, the effect being marginal at lower concentration but appreciable at higher concentration of the sulphoxide.

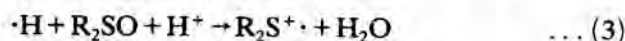
Induced polymerization of acrylamide is observed during the oxidation of both unirradiated and irradiated materials, conforming a free radical mechanism reported earlier⁵. Higher rate of polymerization in irradiated compound also gives additional evidence in favour of free radical mechanism.

Upon exposure of decyl sulphoxide to ^{60}Co γ -rays the molecules require excess energy from an electron impact and the following basic processes^{6,7} occur: (i) Formation of ions and excited molecules; (ii) generation of radicals either directly or on collision or from the ions or excited molecules; (iii) rearrangement of the molecules due to redistribution of the acquired energy among the bonds of the molecules, forming double bonds; (iv) transfer of excess energy from the ions or excited molecules to other molecules; and (v) rupture of C-C bonds may take place with the generation of free radicals, trapped electrons (e^-) and holes.

In addition to this, on dissolving the irradiated salt in aq. acetic acid, the trapped electrons (e^-) may undergo secondary reaction resulting^{8a} in $\cdot\text{H}$ atoms as shown in Eq. (2)



which are able to reduce sulphoxide to sulphide radical cation^{8(b)} (Eq. 3)



(R-decyl group)

Table 1—Dependence of velocity constant on [substrate] in unirradiated and irradiated decyl sulphoxide (DSO)

$[\text{Ce(IV)}] = 1.0 \times 10^{-3}$, $[\text{H}_2\text{SO}_4] = 3.5$, $[\text{AcH}] = 7.65 \text{ mol dm}^{-3}$, temp. = 308 K

$[\text{DSO}] \times 10^{-2}$ mol dm^{-3}	$k \times 10^4, \text{s}^{-1}$	
	Unirrad	Irrad
0.5	2.19	2.08
1.0	2.96	2.57
1.5	3.81	3.10
2.0	5.13	4.10

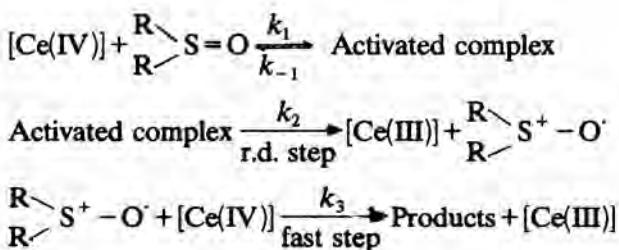
Table 2—Activation parameters of unirradiated and irradiated decyl sulphoxide (DSO) at different temperatures

$[\text{Ce(IV)}] = 1.0 \times 10^{-3}$, $[\text{R}_2\text{SO}] = 1.0 \times 10^{-2}$, $[\text{H}_2\text{SO}_4] = 3.5$, $[\text{AcH}] = 7.65 \text{ mol dm}^{-3}$

Temp. (K)	$k \times 10^4 \text{ s}^{-1}$	
	Unirrad.	Irrad.
303	4.37	3.33
308	5.13	4.10
313	6.20	4.85
318	7.02	5.03
$\Delta H^\ddagger$ (kJ/mol)	23.34 ± 1.168	18.779 ± 2.616
$\Delta S^\ddagger$ (JK ⁻¹ /mol)	-179.178 ± 3.763	-195.898 ± 8.437

Mechanism of oxidation

Though the presence of a number of species of Ce(IV) in H_2SO_4 has been suggested, under the present experimental conditions, the active oxidant species⁹ are $\text{Ce}(\text{SO}_4)_2^{2+}$, $\text{Ce}(\text{SO}_4)_2$ or higher sulphato complexes. Based on the data, the plausible mechanism is given by Scheme 1.



Scheme 1

Ce(IV) represents the reactive species; $\text{Ce}(\text{SO}_4)_2$, $\text{Ce}(\text{SO}_4)_2^{2+}$ or other sulphato complexes¹⁰.

Scheme 1 leads to rate law (4)

$$\begin{aligned}
 -\frac{d[\text{Ce(IV)}]_{\text{T}}}{dt} &= \frac{2k_1k_2f_1[\text{Ce(IV)}]_{\text{T}}[\text{Substrate}]}{k_{-1} + k_2} \\
 &= k[\text{Ce(IV)}]_{\text{T}}[\text{Substrate}]
 \end{aligned}$$

where

$$k = \frac{2k_1 k_2 f_1}{k_1 + k_2}, \quad (f \leq 1)$$

The concentration of reactive [Ce(IV)] species = $f_1[\text{Ce(IV)}]_T$, f_1 is the fraction defined by various equilibrium constants for sulphato Ce(IV) species in H_2SO_4 . In the present study, a pseudo-first order condition is maintained throughout the reaction as the experiment is undertaken at a given concentration of H_2SO_4 . Decomposition of complex is the rate determining step and the values of rate constant, k_2 has been evaluated (Table 1).

The activation parameters are calculated using Eyring equation and the data (Table 2) indicate that irradiation decelerates the rate of reaction and lowers marginally the enthalpy and entropy of activation which may arise due to decrease in the nucleophilic attack of sulphide ion on the oxidant¹¹⁻¹³, resulting in a less stable complex, giving rise to sulphone in subsequent stages. The other contributing factors are formation of sulphide radical ion ($\text{R}_2\text{S}^+\cdot$) and cleavage of 'C-C' bonds by irradiation.

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