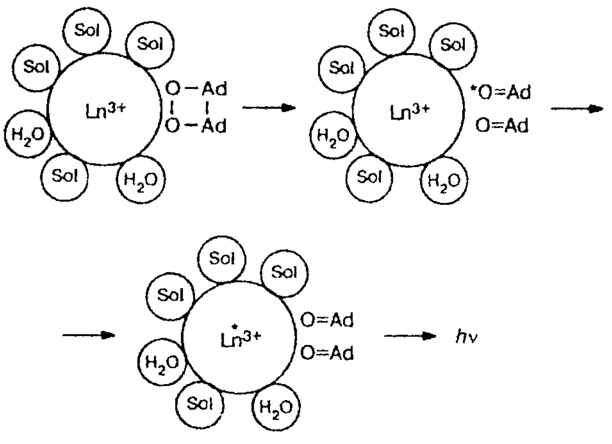
ment, have maxima at 980±10 nm (for the Yb^{III}—(—Ad—O)$_2$ system) and at 880±10 and 1060±10 nm (for the Nd^{III}—(—Ad—O)$_2$ system), which belong to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$, $^4F_{3/2} \rightarrow {}^4I_{9/2}$, and $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transitions, respectively, in Ln^{3+} ions (Fig. 1). Apparently, the major processes, which cause excitation of Ln^{3+} ions, are the decomposition of (—Ad—O)$_2$ in the coordination sphere of the lanthanide ion and the intracomplex energy transfer from $Ad{=}O_T{}^*$ to the excited levels of Ln^{3+}.



Sol are solvent molecules.

Excitation of Ln^{3+} according to the mechanism of intermolecular energy transfer $Ad{=}O_T{}^* + Ln^{3+} \rightarrow Ad{=}O + Ln^{*3+}$ ($k_{et} \approx 10^9$ L mol^{-1} s^{-1})[1] is also possible because the process of internal conversion $Ad{=}O_T{}^* \rightarrow Ad{=}O$ ($\tau(Ad{=}O_T{}^*) = 4 \cdot 10^{-9}$ s), which competes with energy transfer,[3] is not the major channel of deactivation of $Ad{=}O_T{}^*$ under conditions of thermolysis of the (—Ad—O)$_2$—Ln^{III} system.

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Selective oxidation of dialkyl sulfides into dialkyl sulfoxides by chlorine dioxide

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Selective oxidation of organic sulfides **1** to sulfoxides **2** and sulfones **3** is an important task for organic chemistry.[1] Several oxidants (peroxides, oxygen, ozone, and others)[1–3] make it possible to obtain sulfoxides under mild conditions. However, the majority of oxidants used in the present time has no sufficient selectivity, and sulfoxides that formed undergo easily subsequent oxidation to form sulfones.

For the purpose of development of a convenient and simple method for the synthesis of sulfoxides, we oxidized sulfides, dipropyl sulfide (**1a**), and dioctyl sulfide (**1b**) by a new reagent — chlorine dioxide (ClO_2). As has been shown previously,[4] ClO_2 is a selective oxidant of allylic alcohols to α,β-unsaturated carbonyl compounds.

The oxidation of sulfides **1a,b** at a substrate : reagent ratio of 1 : 0.5, without a solvent, using an aqueous solution of ClO_2 (concentration 4—5 g L^{-1}) occurs with almost complete conversion of **1a,b** and results in 95—97% yields of sulfoxides **2a** and dioctyl sulfoxide **2b**. Sulfoxide **2b** was obtained in 90% yield by passing ClO_2

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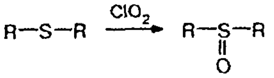
with air into a solution of sulfide **1b** in dichloromethane at 20 °C.



$$R{-}S{-}R \xrightarrow{ClO_2} R{-}\underset{\displaystyle O}{\underset{\|}{S}}{-}R$$

1a,b **2a,b** R = C_3H_7 (**a**), C_8H_{17} (**b**)

Oxidation of dipropyl sulfide. An aqueous solution of chlorine dioxide (48 mL, concentration of ClO_2 5 g L^{-1}) was added dropwise to sulfide **1a** (0.84 g) at 20 °C for 30 min. Then the reaction mixture was extracted with chloroform. Chloroform was distilled off, and the oxidized product (0.92 g, 97%) was obtained. According to the GLC chromatographic data with authentic samples, the product contained 95% sulfoxide **2a** and 2% dipropylsulfone. Compound **2a** was purified by vacuum distillation, it had b.p. 81 °C (2 Torr) (*cf.* Ref. 5: b.p. 80 °C (2 Torr)). IR (CCl_4), v/cm^{-1}: 1050 (S=O). ^1H NMR ($CDCl_3$), δ: 1.10 (t, 6 H, CH_3); 1.85 (m, 4 H, CH_2); 2.68 (m, 4 H, CH_2—S).

Oxidation of dioctyl sulfide. A mixture of air and chlorine dioxide (from 100 mL of an aqueous solution containing 4 g L^{-1} ClO_2) was passed through a solution of **1b** (4.25 g, 0.016 mol) in dichloromethane (25 mL). The reaction mixture was stirred at 20 °C for 2 h. The reaction course was monitored by TLC and GLC. Silufol plates used for TLC were developed by a 5% aqueous solution of $KMnO_4$ with several droplets of concentrated H_2SO_4. An ethanol—benzene (1 : 4) mixture was used as the eluent. After the end of the reaction, the solvent was distilled off. Sulfoxide **2b** (4.0 g) was obtained as white crystals with m.p. 68—69 °C (from EtOH). Found (%): C, 69.99; H, 12.46; S, 11.66. $C_{16}H_{34}OS$. Calculated (%): C, 70.01; H, 12.49; S, 11.68. IR (CCl_4), v/cm^{-1}: 1050 (S=O). ^1H NMR ($CDCl_3$), δ: 0.85 (t, 6 H, CH_3); 1.24 (m, 16 H, CH_2 in positions 4—7); 1.41 (m, 4 H, γ-CH_2), 1.73 (m, 4 H, β-CH_2); 2.61 (m, 4 H, CH_2—S).

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