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Photoreactivity of Fremy's salt in aqueous solution

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Abstract

The absorption spectrum of Fremy's salt, $K_2[ON(SO_3)_2]$, in water shows two bands at $\lambda_{max} = 545$ and 248 nm which are assigned to $\sigma^b \rightarrow \pi^n$ and $\pi^n \rightarrow \sigma^*$ transitions, respectively. The photolysis of Fremy's salt leads to a decomposition. It is assumed that a homolytic cleavage of a N–S bond is the primary photochemical step.

Keywords: Fremy's salt; Absorption spectra

1. Introduction

Since its first preparation 150 years [1] ago, Fremy's salt ($K_2[ON(SO_3)_2]$), has attracted much attention. For many years this commercially available reagent has been used as ESR standard [2,3] and selective oxidant in organic chemistry [4]. The anion $[ON(SO_3)_2]^{2-}$ is one of the few stable small inorganic radicals such as NO, NO_2, O_2^- and ClO_2 [2]. In solution, Fremy's salt exhibits a striking violet color of unknown origin. In aqueous [5–9] and non-aqueous [10] solution, the salt undergoes a thermal decomposition which has been studied in quite some detail. A degradation is also induced by radiolysis [11]. Surprisingly, the photochemistry of Fremy's salt has apparently not yet been investigated. Accordingly, the present work was undertaken to characterize the excited states of $[ON(SO_3)_2]^{2-}$ and their reactivity. At this point, it should be emphasized that other nitrogen-based radicals such as NO, NO_2, and NO_3 are well known to participate in important photoreactions which take place in the atmosphere and contribute to air pollution. In this context the photoproperties of Fremy's salt may be quite interesting despite the fact that it is not volatile and can be studied only in the condensed phase.

2. Experimental

2.1. Materials

The compound $K_2[ON(SO_3)_2]$ was available commercially (Aldrich) and used as received. The purity of the complex was confirmed by UV–vis spectroscopy. The water used was triply distilled.

2.2. Photolyses

The light source was an Osram HBO 200 W/2 lamp for white light or a Hanovia Xe/Hg 977 B-1 (1 kW) lamp for irradiation at selected wavelengths. Monochromatic light was obtained by means of a Schoeffel GM 250/1 high-intensity monochromator (band width 23 nm). The photolyses were carried out in aqueous, freshly prepared solutions in 1 cm spectrophotometer cells at room temperature. All solutions were air saturated since deaeration did not affect the results. Progress of the photolyses was monitored by UV–vis spectrophotometry. The photoproducts were identified by their absorption spectra. For quantum yield determinations, the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer which was calibrated by actinometry and equipped with a RkP-345 detector.

2.3. Instrumentation

Absorption spectra were measured with a Hewlett Packard 8452A diode array or a Shi-madzu UV-2100 absorption spectrometer.

3. Results

The absorption spectrum of aqueous $K_2[ON(SO_3)_2]$ (Fig. 1) agrees with previous results [5,12,13]. Band max-

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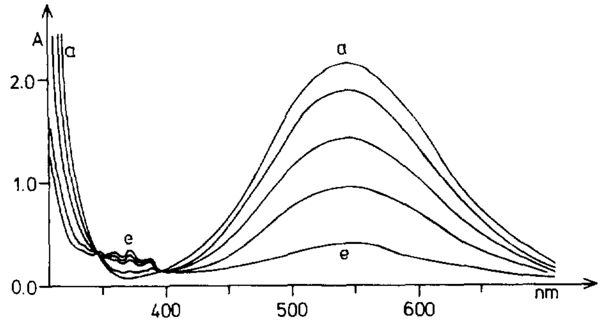
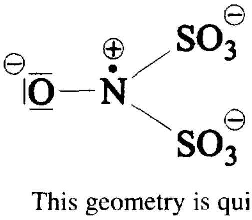


Fig. 1. Spectral changes during the photolysis of 1.04×10^{-2} M $K_2[ON(SO_3)_2]$ in water at r.t. after 0 (a), 2, 4, 7 and 10 (e) min irradiation time with white light, 1 cm cell.

ima appear at $\lambda_{max}=545$ ($\varepsilon=21$ dm^3 M^{-1} cm^{-1}) and 248 nm (1690). Solutions of Fremy's salt in water are light sensitive. Upon irradiation $[ON(SO_3)_2]^{2-}$ undergoes a decomposition as indicated by the concomitant spectral changes (Fig. 1). While the original spectrum disappears a new absorption shows up which consists of four peaks at 387, 372, 360 and 346 nm (Fig. 1). This spectrum is diagnostic for the presence of HNO_2 [10,14,15]. The photolyzed solution contains also $[ON(SO_3)_2]^{3-}$ (or $[HON(SO_3)_2]^{2-}$). Upon oxidation of this anion with PbO_2, $[ON(SO_3)_2]^{2-}$ is regenerated. In the early stages of the photolysis at about 20% disappearance of Fremy's salt, 35% of this loss is recovered by oxidation as indicated by the accompanying spectral changes. The anion $[ON(SO_3)_2]^{3-}$ is a further photolysis product which is precipitated with $[Co(NH_3)_6]^{3+}$ [9,10]. Small amounts of SO_4^{2-} are also formed, in particular at later stages of the photolysis. The disappearance of Fremy's salt is determined by the decrease of the optical density at 545 nm. The quantum yields of disappearance are $\phi=0.005$ at $\lambda_{irr}=546$ nm and $\phi=0.26$ at $\lambda_{irr}=254$ nm.

4. Discussion

In the anion of Fremy's salt, the central nitrogen atom is bonded to oxygen and two sulfur atoms of the sulfonate groups in a pseudo-trigonal planar structure [16,17].



This geometry is quite analogous to that of simple seven-electron AH_3 radicals with a first-row atom A (e.g., CH_3, NH_3^+) [18,19]. The bonding interaction in the NOS_2 moiety is described by a simplified MO scheme assuming a D_{3h} symmetry with three equivalent substituents S at nitrogen (Fig. 2). Finally, it will be shown that reducing the symmetry from D_{3h} of the NS_3 chromophore to C_{2v} of the NOS_2 fragment does not affect the general conclusions. The σ overlap between nitrogen and sulfur is certainly not very strong. The π interaction in the NS_3 moeity is neglected since sulfonate groups do not provide low-energy π orbitals at the sulfur atoms. While the a_2'' is then a non-bonding π orbital, e' and a_1' are σ bonding and antibonding MOs, respectively. The two lowest-energy transitions e' (σ^b) $\rightarrow a_2''$ (π^n) and a_2'' (π^n) $\rightarrow a_1'$ (σ^*) are forbidden and allowed, respectively [20,21].

The anion of Fremy's salt is obtained by replacing one of the sulfonate substituents of the hypothetical ion $N(SO_3)_3^{2-}$ by an oxygen atom. This involves a symmetry change from D_{3h} to C_{2v}. The a_1' and a_2' orbitals (Fig. 2) are then transformed to a_1 and b_1 (C_{2v}), respectively [18,22]. The degeneracy of the e' orbitals is lifted and two orbitals, a_1 and b_2, are generated. This is important with regard to the σ-bonding MOs. The b_2 component of these e' orbitals represents mainly the N–S σ bonds while the a_1 component is more localized in the N–O σ bond. Since the valence orbitals of oxygen are very stable, the σ-bonding a_1 orbital should be placed at rather low energies and should thus not participate in low-energy transitions. On the other side, the b_2 orbital is not expected to shift much from the position of σ-bonding e' orbitals (Fig. 2). The non-bonding π orbital a_2'' (Fig. 2) may be somewhat destabilized by N–O.π interaction in the NOS_2 moiety (b_1 in C_{2v} symmetry). According to these considerations, the two lowest-energy transitions $e'\rightarrow a_2''$ and $a_2''\rightarrow a_1'$ (D_{3h}, Fig. 2) are now replaced by $b_2\rightarrow b_1$ and $b_1\rightarrow a_1$ (C_{2v}). While the $b_2\rightarrow b_1$ transition is forbidden, the $b_1\rightarrow a_1$ transition is allowed [22,23]. This situation is quite equivalent to that derived for D_{3h} (see above).

The well-known absorption spectrum of Fremy's salt in solution [5,12,13] shows a weak but very broad band at $\lambda_{max}=545$ nm and an intense absorption at 248 nm. We suggest that the low-energy band which causes the violet color of $[ON(SO_3)_2]^{2-}$ is assigned to the forbidden $b_2\rightarrow b_1$ (or $e'\rightarrow a_2''$ in D_{3h}) transition while the high-energy absorption belongs to the allowed $a_2''\rightarrow a_1'$ transition.

The photoactivity of Fremy's salt is apparently based on $\sigma^b\rightarrow\pi^n$ and $\pi^n\rightarrow\sigma^*$ transitions with the larger quantum yield

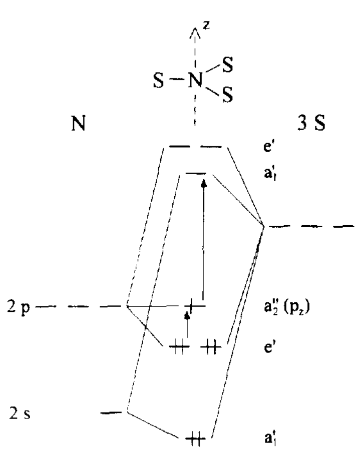


Fig. 2. MO scheme of σ interaction and lowest-energy transitions in a trigonal-planar (D_{3h}) NS_3 moiety with seven valence electrons (adopted from Ref. [18], p. 56) as a simplified model for $[ON(SO_3)_2]^{2-}$.

associated with the higher-energy excitation. Both transitions should lead to a weakening of the N–S bonds. Ultimately, a cleavage of a N–S bond should yield $ONSO_3^-$ and a SO_3^- radical. The product formation can be described by the following scheme:

$$\begin{array}{rcl}
\dot{\mathrm{O}\mathrm{N}}(\mathrm{SO_3})_2^{2-} & \xrightarrow{h\nu} & \mathrm{ONSO_3^-} + {}^\bullet\mathrm{SO_3^-} \\
\mathrm{ONSO_3^-} + \mathrm{H_2O} & \rightarrow & \mathrm{HNO_2} + \mathrm{HSO_3^-} \\
\mathrm{O\dot{N}(SO_3)_2^{2-}} + \mathrm{HSO_3^-} & \rightarrow & \mathrm{HON(SO_3)_2^{2-}} + {}^\bullet\mathrm{SO_3^-} \\
\mathrm{O\dot{N}(SO_3)_2^{2-}} + {}^\bullet\mathrm{SO_3^-} & \rightarrow & \mathrm{ON(SO_3)_3^{3-}} /2\mathrm{x} \\
\hline
\text{sum } 4\,\mathrm{O\dot{N}(SO_3)_2^{2-}} + \mathrm{H_2O} & \rightarrow & \mathrm{HNO_2} + \mathrm{HON(SO_3)_2^{2-}} + 2\mathrm{ON(SO_3)_3^{3-}}
\end{array}$$

Similar schemes have been derived for the thermal decomposition of Fremy's salt in aqueous [5–9] and non-aqueous [10] solution. However, these reactions are complicated by a competing chain reaction which is catalyzed by nitrous acid. Since HNO_2 is already formed during the first stages of the photolysis, the stoichiometry given above cannot be reproduced by the product analysis. For example, 35% instead of 25% of $HON(SO_3)_2^{2-}$ were formed in the photolysis of Fremy's salt. This excess could result from the partial hydrolysis of $ON(SO_3)_3^{3-}$ which would afford $HON(SO_3)_2^{2-}$ and SO_4^{2-}. The formation of some sulfate was confirmed by its precipitation as $BaSO_4$.

Acknowledgements

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