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Contribution from the Institute for Physical Chemistry,
University of Frankfurt, 6000 Frankfurt/Main, FRG

Effect of Pressure on the Photochemical Formation and Thermal Back-Isomerization of a Sulfinato-*O* Complex of Cobalt(III)

W. Weber, H. Maecke,[1] and R. van Eldik*

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Adamson and co-workers[2,3] recently reported an unique photochemical preparation of an sulfinato-*O* complex of Co(III). This is the first example of an O-bonded sulfinato ligand, since most Co(III) complexes containing sulfito, sulfinato, or sulfenato ligands show only Co–S bonding, such that very few O-bonded species have been reported.[4-8] They[2,3] found that the S-bonded tris chelate complex $Co(en)_2(SO_2CH_2CH_2NH_2)^{2+}$, hereafter referred to as CoSOON, can be photolyzed to the thermodynamically unstable O-bonded isomer $Co(en)_2(OS(O)CH_2CH_2NH_2)^{2+}$, hereafter referred to as CoOSON. The quantum yield for this conversion was shown[2,3] to depend on the wavelength of the incident light, being low in the region of the LF band around 400 nm and reaching a maximum value of 0.1 mol einstein^{-1} at the onset of the CT band ($\lambda < 340$ nm). It was therefore concluded that the photoreactive state is a LMCT state, either the one reached by initial excitation or a nonspectroscopic one reached by deactivation mechanisms such as internal conversion/intersystem crossing and/or cage recombination.

We have now studied the pressure dependencies of the photochemical and thermal isomerization reactions of the CoSOON and CoOSON species, respectively, in an effort to contribute to a better understanding of the underlying reaction mechanisms. Such measurements have assisted the elucidation of the intimate mechanisms of the photoisomerization and photosolvolysis reactions of a series of Rh(III) amine complexes.[9-12]

Experimental Section

The complex $[Co(en)_2(SO_2CH_2CH_2NH_2)](ClO_4)_2$ was prepared according to a published procedure,[13] and UV-vis spectral data were in good agreement with those reported before.[2] The photochemical measurements were performed by employing a high-pressure photolysis unit described in detail elsewhere.[9,10] Complex solutions in 0.01 M $HClO_4$ were irradiated at 313 nm under pressures up to 200 MPa. The irradiated samples were stirred inside the "pill-box" cuvette under pressure by using a small Teflon-coated stirring bar and an external magnetic stirrer. Photochemical conversions up to 20% were determined from the decrease in absorbance at 288 nm ($\Delta\epsilon = 17\,800$ M^{-1} cm^{-1}) by using a Perkin-Elmer 555 spectrophotometer. The resulting quantum yields were corrected for inner filter effects by extrapolating to 0% conversion.

The O-bonded isomer (CoOSON) was prepared in solution by almost complete photolysis of an aqueous solution of CoSOON using visible light. Such solutions were used for partial molar volume measurements and to study the pressure dependence of the thermal back-reaction by employing a modified Zeiss PMQ II spectrophotometer equipped with a thermostated (±0.1 °C) high-pressure cell.[14] Partial molar volumes were determined from density measurements with an Anton Paar DMA 02 densimeter, thermostated at 298.2 ± 0.002 K. Doubly distilled water was used in the preparation of all test solutions.

Table I. Quantum Yield as a Function of Pressure for the Reaction[a]

$$\mathrm{CoSOON} \xrightarrow{h\nu} \mathrm{CoOSON}$$

pressure, MPa	10Φ,[b] mol einstein^{-1}	pressure, MPa	10Φ,[b] mol einstein^{-1}
1	1.19 ± 0.02 (11)	125	0.90 ± 0.02 (8)
25	1.14 ± 0.02 (4)	150	0.81 ± 0.01 (5)
50	1.12 ± 0.04 (5)	175	0.79 ± 0.01 (6)
75	1.08 ± 0.01 (3)	200	0.79 ± 0.02 (5)
100	1.01 ± 0.02 (4)		

$\Delta V^{\ddagger}_{app} = +5.8 \pm 0.5$ cm^3 mol^{-1}

[a] $T = 298$ K; 0.01 M $HClO_4$; irradiation at 313 nm. [b] Mean value and standard deviation for the extrapolated quantum yield at 0% conversion determined from a linear least-square fit of Φ vs. % conversion for the number of experimental points indicated in parentheses.

Table II. First-Order Rate Constant as a Function of Pressure for the Thermal Reaction[a]

$$\mathrm{CoOSON} \xrightarrow[\Delta]{} \mathrm{CoSOON}$$

pressure, MPa	10^5k_{obsd},[b] s^{-1}	pressure, MPa	10^5k_{obsd},[b] s^{-1}
1	1.53 ± 0.16	100	2.09 ± 0.22
50	1.87 ± 0.17	150	2.55 ± 0.23

$\Delta V^{\ddagger} = -9.0 \pm 0.7$ cm^3 mol^{-1}

[a] $T = 332.7$ K; 0.01 M $HClO_4$; [Co] = 10^{-3} M; reaction monitored spectrophotometrically at 335 nm. [b] Mean value of at least three kinetic runs.

Results and Discussion

Irradiation of the CoSOON complex under pressures up to 200 MPa resulted in spectral changes similar to those reported before[2] for irradiation at ambient pressure. Also the thermal back-reaction from CoOSON to CoSOON exhibited clean isosbestic points for pressures up to 150 MPa. These results indicate that neither the photochemical nor the thermal reverse processes are influenced by the application of pressure. However, the resulting quantum yields and rate constants do exhibit a meaningful pressure dependence, as summarized in Tables I and II, respectively. More than 50 photolysis experiments were performed at elevated pressure to enable a meaningful extrapolation to 0% conversion and to reduce the experimental error limits. The quantum yield and rate constant at 1 MPa are in close agreement with those reported at ambient pressure (0.1 MPa) before.[2,3,15] The thermal back-reaction is so slow that it does not interfere with the photochemical measurements at 298 K. Plots of ln Φ and ln k_{obsd} vs. pressure are linear within the error limits involved, and the corresponding volumes of activation are included in Tables I and II. The photochemical isomerization reaction is characterized by a slight decrease in Φ with increasing pressure, which corresponds to a positive volume of activation, whereas k_{obsd} for the thermal back-reaction increases with increasing pressure, resulting in a negative volume of activation.

The wavelength dependence of Φ for the isomerization of CoSOON was interpreted[2,3] as evidence for the isomerization taking place from a CT state via recombination of the redox products. It was argued[3] that the isomerization took place from a CT state that is not that of the $S(\sigma) \rightarrow Co(\sigma^*)$ transition at 288 nm, but rather of a lower lying $S(\pi) \rightarrow Co(\sigma^*)$ transition.

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(15) Rate constants for the thermal back-reaction[2,3] at ambient pressure are 3.23×10^{-7}, 1.64×10^{-6}, 5.47×10^{-6}, and 2.31×10^{-5} s^{-1} at 301, 315, 325, and 340 K, respectively. From these it follows that $\Delta H^{\ddagger} = 21.7 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -15.9 \pm 1.3$ cal K^{-1} mol^{-1}, which differ slightly from those reported before.[2] Extrapolation to 333 K results in a rate constant of 1.37×10^{-5} s^{-1}.

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In this respect it was noted[3] that the S=O π system is a source of electron density that could cause a perturbation of the Co d(π) orbitals. However, the effect is expected to be small in the case of the CoSOON complex since the wider spatial distribution of π-electron density in sulfinate makes it a less anisotropic π donor than for instance sulfenate. It follows that this splitting is not observed in the UV–vis spectrum. Furthermore, the shorter S–O distance of 1.466 Å reported[16] for the CoSOON complex, compared to the average distance of 1.513 Å in free sodium hydroxymethanesulfinate, indicates that no significant interaction between the S=O π system and the metal center is present. We, therefore, prefer to associate the photoisomerization reaction with the CT state reached via the S(σ) → Co(σ^*) transition at 288 nm or from a higher energy state with unit efficiency. The following reaction sequence can be formulated on the basis of this concept.

$$\text{CoSOON} \xrightarrow[\text{CT}]{h\nu} [\text{CoSOON}]^* \quad (^1\text{CT or } ^3\text{CT}) \tag{1}$$

$$[\text{CoSOON}]^* \xrightarrow{k_1} \text{CoSOON} \tag{2}$$

$$[\text{CoSOON}]^* \xrightarrow{k_2} [\text{Co}^{\text{II}}\text{---SOON}]_{\text{cage}} \tag{3}$$

$$[\text{Co}^{\text{II}}\text{---SOON}]_{\text{cage}} \xrightarrow{k_3} \text{CoOSON} \tag{4}$$

$$[\text{Co}^{\text{II}}\text{---SOON}]_{\text{cage}} \xrightarrow{k_4} \text{CoSOON} \tag{5}$$

The CT excited state produced in (1) can either return to the ground state via nonradiative deactivation or produce a caged radical pair via reaction 3. This species can subsequently undergo cage recombination to produce the O-bonded (eq 4) or S-bonded (eq 5) isomer. Radiative deactivation is omitted from the scheme since no emission could be detected by using a Nd Yag laser. As a first approximation we assume that cage recombination mainly leads to the O-bonded isomer, such that reaction 5 does not contribute to the observed quantum yield. The cage recombination step can be rationalized by assuming a weak bond between the oxygen lone pair and Co^{2+}, since the sulfur atom has no basic properties in the radical pair configuration. In this case the quantum yield can be expressed as in (6), from which it follows

$$\Phi = \frac{k_2}{k_1 + k_2} \quad \text{or} \quad \frac{\Phi}{1 - \Phi} = \frac{k_2}{k_1} \tag{6}$$

that the pressure dependence of the photochemical reaction (eq 3) is given by the expression in (7) under the assumption that the

$$\frac{\partial}{\partial P}(\ln k_2) = \frac{\partial}{\partial P}\left(\ln \frac{\Phi}{1 - \Phi}\right) = -\frac{\Delta V^{\ddagger}{}_{\text{P}}}{RT} \tag{7}$$

rate constant for nonradiative deactivation is almost independent of pressure. This has been shown to be the case for the deactivation of LF excited states[10,11] of Rh(III) amine complexes. However, no information regarding the pressure dependence of k_1 could be obtained experimentally for the present system since this requires life time measurements as a function of pressure via the emission of the excited state, which could not be detected. The value of $\Delta V^{\ddagger}{}_{\text{p}}$, obtained from the slope of a plot of ln ($\Phi/(1 - \Phi)$) vs. pressure, is +6.5 ± 0.6 $\text{cm}^3\ \text{mol}^{-1}$ and almost is equal to the apparent volume of activation estimated from a plot of ln Φ vs. pressure, viz. $\Delta V^{\ddagger}{}_{\text{app}} = 5.8 \pm 0.5\ \text{cm}^3\ \text{mol}^{-1}$. The relatively small value of Φ brings about the result that $1 - \Phi \sim 1$ and $\Delta V^{\ddagger}{}_{\text{p}} \sim \Delta V^{\ddagger}{}_{\text{app}}$. This significantly positive volume of activation not only underlines the dissociative nature of photochemical reaction 3 but also proves the CT character of the reactive state. The equivalent reaction from a LF excited state would require a ring-opening step, during which significant charge creation (a 3+ metal center and 1− ligand moiety) occurs, accompanied by a large negative solvational contribution toward the observed $\Delta V^{\ddagger}$ (compare with the further discussion for the thermal process). Such effects have resulted in overall negative volumes of activation for the dissociative release of Cl^- and Br^- from the LF excited states of $\text{Rh(NH}_3)_5\text{Cl}^{2+}$ and $\text{Rh(NH}_3)_5\text{Br}^{2+}$, respectively.[10]

If we do not accept k_1 to be independent of pressure it follows that the pressure dependence of $\Phi/(1 - \Phi)$ results in $\Delta V^{\ddagger}{}_{\text{p}} = \Delta V^{\ddagger}(k_2) - \Delta V^{\ddagger}(k_1)$. Our earlier work[10] has clearly demonstrated that due to the strong-coupling effect $\Delta V^{\ddagger}(k_2)$ and $\Delta V^{\ddagger}(k_1)$ are of the same sign, from which it follows that $\Delta V^{\ddagger}(k_2) >> \Delta V^{\ddagger}(k_1)$ and the process must be dissociatively activated.

The volume of activation of ca. +6 $\text{cm}^3\ \text{mol}^{-1}$ for bond cleavage in the CT state during which no charge creation occurs (reaction 3), is in good agreement with other available data. The fairly low value of $\Delta V^{\ddagger}$ demonstrates that no Co(II) (low spin) → Co(II) (high spin) transition occurs, since high-spin Co(II) complexes have significantly larger Co–L bond lengths, which should lead to significantly larger $\Delta V^{\ddagger}$ values. The release of NH_3 in the LF state of $\text{Rh(NH}_3)_5\text{Cl}^{2+}$ and $\text{Rh(NH}_3)_5\text{Br}^{2+}$ is characterized by $\Delta V^{\ddagger}{}_{\text{p}}$ values of +9.3 ± 1.9 and +8.1 ± 1.2 $\text{cm}^3\ \text{mol}^{-1}$, respectively.[10] Similarly, bond cleavage in the CT states of *trans*-$\text{Pt(CN)}_4(\text{N}_3)_2{}^{2-}$ and $\text{Fe(CN)}_5\text{NO}^{2-}$ result in volumes of activation of +8.1 ± 0.4 and +6 ± 1 $\text{cm}^3\ \text{mol}^{-1}$, respectively.[17,18] Despite this good agreement, it is important for our further discussion to note that CT states are expected to be much less distorted from the ground-state configuration than LF states. This was recently demonstrated to be the case for the excited states of $\text{Ir(Me}_2\text{phen)}_2\text{Cl}_2{}^+$ in DMF solution.[19] It follows that, in contrast to the LF state, which could be as much as 10 $\text{cm}^3\ \text{mol}^{-1}$ larger than the ground-state species,[10] the CT state can be expected to have a volume slightly larger than or close to that of the ground state.

If the cage recombination step (eq 5) is included in the reaction scheme, eq 6 modifies to (8). The rate constants for the cage

$$\Phi = \left(\frac{k_2}{k_1 + k_2}\right)\left(\frac{k_3}{k_3 + k_4}\right) \tag{8}$$

recombination processes (k_3 and k_4) are expected to exhibit very similar pressure dependencies, since these reactions involve very similar ring closure of the ring-opened caged radical species Co^{II}---SOON to produce a Co–O or Co–S bond, respectively. Under such conditions the pressure dependence of Φ will once again depend on that of k_1 and k_2. It follows that inclusion of reaction 5 in the overall reaction scheme does not influence the interpretation of the observed pressure dependence of Φ.

The thermal back-reaction exhibits a fairly large negative volume of activation (Table II), which can be ascribed to either an associative attack of a water molecule or a ring-opening reaction of the sulfinate ligand accompanied by significant charge creation. The associative attack of a water molecule on a Co(III) center is rather unlikely in light of much evidence in favor of an I_d or D mechanism for closely related complexes.[20-22] However, ring opening of the sulfinate chelate will lead to a transition state of the type $[(\text{en})_2\text{Co}^{3+}\text{–NOSO}^-]^{\ddagger}$, which is expected to show large electrostriction due to the creation of charges. An increase in the volume due to an intrinsic contribution from bond breakage could be overruled by the negative solvational contribution, to result in an overall $\Delta V^{\ddagger}$ value of −9 $\text{cm}^3\ \text{mol}^{-1}$. The postulated transition state also nicely accounts for the formation of the thermodynamically more stable five-membered ring species, since the lone pair of electrons is now on the sulfur atom. A very similar result was reported[23-25] for the trans to cis isomerization reaction of

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$$\mathrm{Co(SOON)^{2+}} \underset{\Delta}{\overset{h\nu,\ \mathrm{CT}}{\rightleftharpoons}} \mathrm{Co(OSON)^{2+}}$$

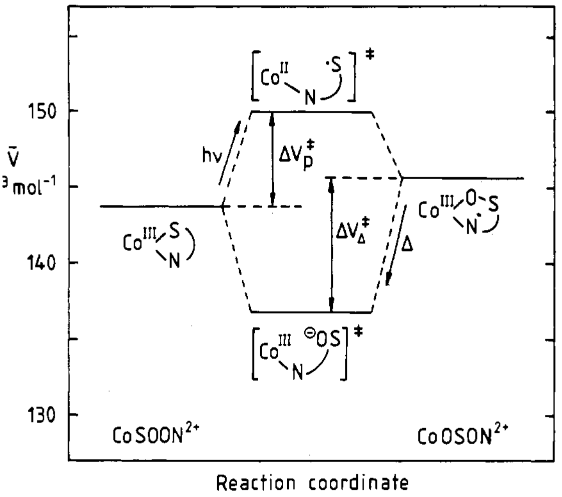

Figure 1. Reaction volume profile for the photochemical and reverse thermal isomerization of CoSOON. In this scheme it is assumed that $\bar{V}(\mathrm{CoSOON^{*CT}}) \sim \bar{V}(\mathrm{CoSOON})$ (see Discussion).

trans-$\mathrm{Cr(C_2O_4)_2(H_2O)_2^-}$, for which a volume of activation of −16 ± 1 cm^3 mol^{-1} was found. In this case all the available evidence is consistent with a rate-determining opening of the oxalate ring,[23-25] and the large negative ΔV^* was ascribed to the increase in electrostriction around the negatively charged free end of the oxalate ligand.

We conclude that both the photochemical and thermal isomerization back-reactions occur via ring opening of the sulfinate ligand. No charge creation occurs in the case of the photochemical reaction such that the increase in volume of 6 cm^3 mol^{-1} should represent the pure intrinsic component. For the thermal reaction, ring opening accompanied by charge creation results in a volume decrease ca. 15 cm^3 mol^{-1} more negative, such that this quantity must present the change in volume due to electrostriction. In order to combine these data in an overall volume profile, the partial molar volume of $\mathrm{[Co(en)_2(SO_2CH_2CH_2NH_2)](ClO_4)_2}$ was measured at 244.8 ± 1.8 cm^3 mol^{-1} from the apparent molar volume, which was independent of concentration over the range investigated. Taking into account that $\bar{V}(\mathrm{ClO_4^-}) = 50.7$ cm^3 mol^{-1},[10,11] it follows that $\bar{V}(\mathrm{CoSOON}) = 143.8 \pm 1.8$ cm^3 mol^{-1}. Density measurements on a sample of CoSOON irradiated almost to completion resulted in $\bar{V}(\mathrm{CoOSON}) = 145.7 \pm 1.6$ cm^3 mol^{-1}. The trend in the $\bar{V}$ data is in agreement with a slight increase in volume due to the formation of a six- instead of a five-membered ring complex. A combination of these $\bar{V}$ data and the reported volumes of activation enable the construction of the reaction volume profile given in Figure 1. It was assumed that the CT state has a partial molar volume close to that of the ground-state species as discussed above. If this is not the case, the transition state for the photochemical path will have an even higher partial molar volume, since the CT state can be up to 10 cm^3 mol^{-1} larger than the ground state (see earlier discussion). The profile clearly demonstrates the difference of at least 13 cm^3 mol^{-1} between the two transition states and the effect of electrostriction during the thermal back-reaction. To our knowledge this is the first example of a volume profile for a combined photochemical forward reaction and thermal back-reaction.

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Registry No. $\mathrm{Co(en)_2(SO_2CH_2CH_2NH_2)^{2+}}$, 75249-42-2; $\mathrm{Co(en)_2(OS(O)CH_2CH_2NH_2)^{2+}}$, 75235-15-3.

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Contribution from the Institut für Anorganische Chemie
und Strukturchemie, Universität Düsseldorf,
D-4000 Düsseldorf, Federal Republic of Germany

Fluorides and Fluoro Acids. 10.[1] Crystal Structures of Acid Hydrates and Oxonium Salts. 23.[2] Crystal Structure of the Low-Temperature Form of Oxonium Hexafluoroarsenate(V)

Dietrich Mootz* and Michael Wiebcke

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Oxonium hexafluoroarsenate(V), $\mathrm{H_3OAsF_6}$, is reported[3,4] to be cubic at room temperature, with disordered ions centered on the atomic positions of the NaCl structure, and to exist in a second, less symmetrical form below a transition point of 271 ± 5 K. The present paper deals with a complete X-ray single-crystal structure analysis of the low-temperature form.

Experimental Section

Preparation and Phase Analysis. $\mathrm{H_3OAsF_6}$ was prepared as described[3] by reacting $\mathrm{AsF_5}$ with HF and $\mathrm{H_2O}$ in a PTFE vacuum system. The $\mathrm{AsF_5}$ was prepared by D. Naumann by reacting arsenic with a fluorine–nitrogen stream. The anhydrous HF was obtained by rectifying technical grade hydrofluoric acid (Riedel-de Häen, 71–75%) in a PTFE apparatus.

DTA and X-ray powder analysis between 103 and 303 K were applied to check the phase transition and high-temperature unit cell. The apparatus and techniques used are described and referred to elsewhere.[5]

Crystal Growth. A single crystal of the low-temperature form of $\mathrm{H_3OAsF_6}$ was grown on a Syntex $P2_1$ four-circle diffractometer equipped with a modified low-temperature device. The starting material, a solution of $\mathrm{H_3OAsF_6}$ in anhydrous HF, was sealed in polyethylene tubing (diameter 0.4 mm inside, 0.8 mm outside), which in turn for mechanical fixation was enclosed in a thin-walled glass capillary. A miniature zone-melting technique using focused heat radiation[6] was applied with the temperature of the cold gas stream at 243 K.

Structure Determination. The X-ray measurements for the structure determination were done on the diffractometer with the temperature of the crystal lowered to 208 K. The reflection intensities were not corrected for absorption because of an uncertain shape and size of the crystal within the tubing and angular restrictions for a ψ-scan with the low-temperature device used. The structure was solved from the Patterson function and refined in the space group $P\bar{1}$ by the method of full-matrix least squares minimizing the function $\sum w(|F_o| - |F_c|)^2$ with the weights $w = 1/(\sigma_F{}^2 + 0.0004F_o{}^2)$. The hydrogen atoms were located in a difference Fourier map of the electron density and included in the refinement. An isotropic extinction correction $F' = F_c/(1 + 0.002gF_c{}^2/\sin 2\theta)^{1/4}$ was applied and refined to $g = 0.144$ (6). More experimental and computational figures of the structure determination are assembled in Table I. Scattering factors of the neutral atoms with anomalous dispersion coefficients[7] were used in the SHELXTL[8] program system on a Data General Eclipse S/200 computer.

Since a statistical analysis of the normalized structure factor amplitudes had given some evidence for an acentric structure, in accordance with the IR and Raman spectra,[3,4] refinement in the space group $P1$ was also tried but not found preferable.

Results

Phase Transition. From the DTA and X-ray powder measurements the (reversible) phase transition to the high-temperature

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