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Decomposition of Nitrosyldisulfonate Free-Radical Anion in Nonaqueous Solvents

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The moderately stable nitrosyldisulfonate free-radical anion, $ON(SO_3)_2^{2-}$, decomposed fairly rapidly in DMSO and some other solvents by a first-order process accompanied by a fast chain reaction. When the solvents were dried carefully or an inhibitor of sulfamic acid and potassium sulfamate was added, the chain process was suppressed leaving the reaction to proceed by the first-order process with a rate constant of about 10^{-5} s^{-1}. The products of the latter reaction were found to be hydroxylaminedisulfonate, hydroxylaminetrisulfonate, and a nitrogen(III) product (NO^+ or NO_2^-).

Introduction

The moderately stable nitrosyldisulfonate ion radical, $ON(SO_3)_2^{2-}$, has found diversified application including much use as an ESR standard, as a selective organic oxidizing agent, and in our laboratory in radical–radical kinetic reaction studies. In all of these applications the radical anion is decomposing and disproportionating slowly, a fact which has been ignored by most workers.

In the solid potassium salt the radical anion exists in one of two crystal modifications, a diamagnetic dimer and a paramagnetic monomer,[2] but in salts with larger cations and in solution the anion is always paramagnetic.[3] In acidic aqueous solutions the initial decomposition is first order at constant pH and is directly proportional to the hydronium ion concentration, but as the reaction proceeds, a chain reaction commences, propagated by nitrous acid, leading to rapid decomposition (about $^1/_2$ h at pH 3). The products of the rapid chain reaction were found to be sulfate ion, hydroxylaminedisulfonate ion, hydronium ion, and nitrous oxide. The stability of the radical is enhanced by the addition of sulfamic acid, which consumes nitrous acid, the chain propagator. The first-order rate constants so obtained were in the range 1.27 × 10^{-4}–2.5 × 10^{-4} s^{-1} for pH 1.84–4.95.[4]

In the pH region 6–11 the decomposition was found to be first order only and independent of pH. Rate constants at 25 °C were about 2.6 × 10^{-7} s^{-1}. The products of decomposition, complicated by several side reactions, included nitrite, sulfate, hydroxylaminedisulfonate, and hydroxylaminetrisulfonate ions with traces of nitrous oxide.[5]

It was the object of this study to ascertain the stability of the radical in various nonaqueous solvents and to determine the kinetics and products of decomposition so as to be able to select the solvents and conditions under which the radical is most stable. The mechanism for decomposition will also be of value in determining the initiating reaction for decomposition in aqueous solutions.

Experimental Section

Materials. Potassium nitrosyldisulfonate was prepared by the method of Raschig as modified by Murib and Ritter.[4] The salt was recrystallized every 5 days from 1 N potassium hydroxide at 50 °C, washed with cold water and absolute methanol, and stored in a vacuum desiccator. This salt is the most readily prepared and is the one used in most studies involving water, but of the organic solvents tried, only DMSO (dimethyl sulfoxide) dissolved it, so salts with tetraphenylarsonium and tetraphenylstibonium cations were used with the other nonaqueous solvents.

Tetraphenylarsonium nitrosyldisulfonate was prepared by addition of solid potassium nitrosyldisulfonate to a saturated aqueous solution of tetraphenylarsonium bromide or tetraphenylarsonium chloride hydrate. The tetraphenylarsonium bromide was prepared by the method of Chatt and Mann.[6] Tetraphenylarsonium chloride hydrate was obtained commercially. Tetraphenylstibonium nitrosyldisulfonate was prepared from tetraphenylstibonium bromide, which was prepared as was the tetraphenylarsonium bromide above.

Table I. Comparison of Rate Constants for the First-Order Decomposition of Nitrosyldisulfonate Ion

Solvent	Cation	Initial [nitrosyldisulfonate ion] × 10^{+2}, M	First-order rate const × 10^{+5}, s^{-1}	Temp, °C	Notes
DMSO	K^+	1.00	0.55 ± 0.08	25.0	*a*
		0.10	0.89	≃26.0	*a*
		1.00	0.80	25.0	*b*
		1.80	1.1	25.0	*b*
		2.22	2.2 ± 0.4	35.0	*a*
		2.08	1.85	25.0	*a*
		2.08	2.1	25.0	*c*
	$(C_6H_5)_4Sb^+$	2.58	3.2	≃28	*a*
	$(C_6H_5)_4As^+$	3.24	1.3	25.0	*a*
		2.32	1.3	25.0	*a*
		2.01	1.7	25.0	*a*
		2.06	0.36 ± 0.07	25.0	*b*
		0.30	0.45	25.0	*b*
		2.13	2.2 ± 0.5	35.0	*a*
		2.09	3.4	45.0	*a*
Pyridine	$(C_6H_5)_4Sb^+$	3.36	2.8	25.0	*a*
Nitromethane	$(C_6H_5)_4Sb^+$	3.47	3.4	25.0	*a*
Acetonitrile	$(C_6H_5)_4As^+$	2.1	1.6	25.0	*d*
		2.7	1.2 ± 0.4	25.0	*e*
		2.83	3.5 ± 0.2	35.0	*e*
		2.91	5.33	45.0	*e*
	$(C_6H_5)_4Sb^+$	5.43	3.4	25.0	*a*
Dichloromethane	$(C_6H_5)_4As^+$	0.10	1.6	25.0	*d*
		0.014	1.7	26	*f*

[a] Reaction initially first order, followed by rapid chain reaction. Rate constant calculation influenced by the latter. [b] First-order reaction only; chain inhibitor added. [c] 10% water in DMSO solvent. [d] First-order reaction only; solvent very dry. [e] Fast initial reaction, then slow first order; no chain reaction. [f] ESR study; first-order reaction only.

Reagent grade DMSO was dried by passing it through a silica gel column and was stored over molecular sieves. Reagent grade dichloromethane was shaken and stored with Linde type "4A" molecular sieves to dry the solvent. The other solvents were dried and stored over Drierite.

Hexaamminecobalt(III) chloride was prepared using the method of Bjerrum and McReynolds.[7] Potassium sulfamate was prepared from reagent grade sulfamic acid by neutralization with potassium hydroxide. All other chemicals were reagent grade and used as obtained from the supplier.

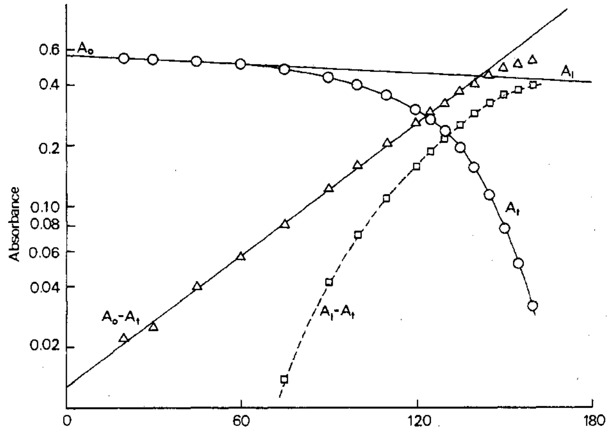

Figure 1. Decomposition of 0.023 M $ON(SO_3K)_2$ in DMSO at 25.0 °C.

Kinetic Studies. Kinetic data were obtained spectrophotometrically with Beckman DK-2 and Beckman DU spectrophotometers. Between readings the samples were placed in a constant-temperature bath maintained to within 0.03 °C of the desired temperature by a Bronwill constant-temperature circulator. Readings on the DU spectrophotometer were made at constant wavelength. In most cases the monochromator was set at the nitrosyldisulfonate ion absorption maximum, 550 nm. The absorptivity of nitrosyldisulfonate ion at 550 nm was determined to be 24.5 M^{-1} cm^{-1} in DMSO and acetonitrile and 20.2 M^{-1} cm^{-1} in dichloromethane.

The data were treated by a least-squares regression analysis using programs written for a Hewlett-Packard Model 9100B calculator to which an XY plotter was interfaced.

Product Analysis. Procedures for the product analysis were based on the spectral and chemical properties of the expected products. The presence of nitrite ion and nitrous acid was confirmed spectrally. Hydroxylaminetrisulfonate was determined gravimetrically as the highly insoluble hexaamminecobalt(III) salt.

The purple solution resulting from the oxidation of hydroxylaminedisulfonate ion to nitrosyldisulfonate ion by lead dioxide was used as a qualitative test for the presence of hydroxylaminedisulfonate ion. After removal of hydroxylaminetrisulfonate ion with hexaamminecobalt(III) ion, oxidation with ferric ion was used as a quantitative measure of hydroxylaminedisulfonate ion.[8] Any hydroxylamine or hydroxylaminemonosulfonate ion formed by decomposition of hydroxylaminedisulfonate ion before the oxidation with ferric ion was conducted would be accounted for in the iron salt determination.

An aqueous barium chloride solution was added to decomposed nitrosyldisulfonate ion in DMSO. A white precipitate of barium sulfate formed immediately. The precipitate was filtered, washed with cold water, dried at 800 °C, and weighed. Although barium sulfate is moderately soluble in DMSO, the sulfate determination using barium ion was quantitative when tested on a standard sulfate sample, if aqueous barium chloride was added to give a 1:1 volume ratio of water to DMSO.

ESR measurements were made on a dichloromethane solution of tetraphenylarsonium nitrosyldisulfonate as it decomposed. A Varian 4500-10A ESR control unit with a Spectromagnetic Industries Model L 12-A 12-in. magnet was used, along with a Varian V-FR 2100 field-regulated magnet power supply. A g value of 2.0057 ± 0.0002 was calculated for tetraphenylarsonium nitrosyldisulfonate in dichloromethane. This was comparable to a reported value of 2.0056 ± 0.0001 for a solid sample of tetraphenylarsonium nitrosyldisulfonate.[3]

Results

Order and Rate Constants for the Reaction. Potassium and tetraphenylarsonium salts were used for the decomposition studies in DMSO by following the loss of color at 550 nm. In all cases the reaction started with what appeared to be a first-order process accompanied by a rapidly forming chain process, as shown in Figure 1, where A_t represents the absorbance measured. This decomposition is similar to that observed in acidic aqueous solution by Murib and Ritter and was handled by the same technique they described for a first-order process accompanied by a chain-propagated reaction.[4] A_1 represents the first-order process. If the reaction proceeds by a chain process only, the line $A_0 - A_t$ should be linear and start at the origin (with the observed absorbance related to time by $A_0 - A_t = A_0e^{\phi t}$, where A_0 is the initial absorbance and ϕ is the chain rate constant.) If both first-order and chain processes occur, the plot of log $(A_0 - A_t)$ vs. t is curved, but the plot of log $(A_1 - A_t)$ vs. time would be linear. In this study the line $A_0 - A_t$ is fairly linear but does not pass through the origin, which suggests that the reaction is predominantly chain and that the first-order rate constant obtained from the graphs is probably too large, being influenced by the chain process. There appears to be no ionic strength effect on the first-order process.

On the addition of a suitable chain inhibitor, a mixture of sulfamic acid and potassium sulfamate, the chain process was prevented and the decomposition proceeded by the first-order process only, with rate constants as shown in Table I.

Decomposition in acetonitrile and dichloromethane occurred in a similar manner, but if these solvents were carefully dried, the chain process was completely suppressed. However, in a few runs with these solvents an unusual behavior was noted, in that rapid reaction occurred, followed by a much slower first-order reaction with rate constants about the same as noted in the normal first-order decomposition. This was not further studied as it only occurred in a few runs.

In one study a solution of tetraphenylarsonium nitrosyldisulfonate in very dry dichloromethane was placed in an ESR cavity at about 26 °C and the spectra were obtained periodically. A slow decrease in peak heights was noted. A plot of the log of the peak heights vs. time yielded a straight line, indicating a first-order decomposition with a rate constant of 1.7×10^{-5} s^{-1}. This compares very favorably with a rate constant of 1.6×10^{-5} s^{-1} obtained spectrophotometrically at 25 °C.

Reaction Products. As was expected, the reaction products of the two routes are different. The products from the first-order-only process in DMSO and acetonitrile were found to be hydroxylaminedisulfonate ion, hydroxylaminetrisulfonate ion, and nitrosyl cation or nitrite ion. No sulfate ion or gaseous products were detected. Gravimetric analysis with hexaamminecobalt(III) ion established that 1.9 hydroxylaminetrisulfonate ions were produced from each 4 nitrosyldisulfonate ions decomposed. Analysis by the ferric ion oxidation of the hydroxylamine produced by hydrolysis indicated that 0.99 hydroxylaminedisulfonate ion was produced from each 4 nitrosyldisulfonate ions decomposed. Spectroscopic analysis for nitrous acid after an acid was added suggested that at least 0.56 molecule was present, although this test was not very quantitative. These values suggest the stoichiometry

$$4ON(SO_3)_2^{2-} \rightarrow 2ON(SO_3)_3^{3-} + {}^{-}ON(SO_3)_2^{2-} + NO^+$$

with side reactions modifying the quantities slightly.

The ESR spectra, obtained at intervals during an 8-h period, of a 10^{-4} M solution of tetraphenylarsonium nitrosyldisulfonate in dichloromethane gave no indication of any other free radicals, at least in detectable quantities.

Decomposition by the rapid chain process produced hydroxylaminedisulfonate and sulfate ions. There was no evidence for hydroxylaminetrisulfonate. During the decomposition four distinct peaks were noted in the near-ultraviolet region, but these disappeared as the reaction ended. A solution of nitrite ions in DMSO did not exhibit this spectrum, but an identical spectrum with four distinct peaks appeared when any acid was added. This absorption pattern was interpreted as being that of nitrous acid which does exhibit four peaks located between 340 and 380 nm.[9] Nitrous acid, produced from the N(III) product of the first-order reaction and trace water, appears to be the chain propagator, as was noted[4] in decomposition in acidic, aqueous solutions, where the overall stoichiometry was represented as

$$\mathrm{4ON(SO_3)_2{}^{2-} + 3H_2O \rightarrow 2HON(SO_3)_2{}^{2-} + N_2O + 4SO_4{}^{2-} + 4H^+}$$

In this study, at the low concentrations of nitrosyldisulfonate used, no gas bubbles were observed so this stoichiometry was not confirmed for the rapid decomposition products.

Conclusions

Care must be used in selecting and purifying the solvents to be used in studies involving the nitrosyldisulfonate free-radical anion. The only nonaqueous solvent found for potassium nitrosyldisulfonate (the most readily prepared salt) was DMSO; however, it could never be dried well enough to prevent the chain decomposition process. If an inhibitor of potassium sulfamate and sulfamic acid were added to consume nitrous acid, the chain process was stopped, which otherwise would lead to complete decomposition in about $2^1/_2$ h, and the reaction proceeded by a slow first-order process with a rate constant of about 10^{-5} s^{-1} at 25 °C.

The other solvents used required the tetraphenylarsonium salt and exhibited the rather rapid chain reaction also, unless dried very carefully. This salt decomposed more slowly than did the tetraphenylstibonium salt under the same conditions.

Water seemed to have little effect on the slow first-order decomposition, but its presence promoted the chain process which rapidly leads to complete loss of the radical.

For those uses of nitrosyldisulfonate ion radical that involve a period of time the reaction products must be considered also. The products of the slow first-order decomposition were found to be nitrite, hydroxylaminedisulfonate, and hydroxylaminetrisulfonate ions. The much more rapid chain process was found to produce hydroxylaminedisulfonate and sulfate ions. Other products remain unidentified.

The products of the first-order process are about the same as those obtained by decomposition in mildly alkaline aqueous solutions and probably are formed by the mechanism

$$\mathrm{O\dot{N}(SO_3)_2{}^{2-}} \xrightarrow{k_1} \mathrm{O\dot{N}SO_3 + SO_3{}^{2-}} \tag{1}$$

$$\mathrm{O\dot{N}SO_3} \xrightarrow{k_2} \mathrm{NO^+ + \cdot SO_3{}^-} \tag{2}$$

$$\mathrm{O\dot{N}(SO_3)_2{}^{2-} + SO_3{}^{2-}} \xrightarrow{k_3} \mathrm{{}^-ON(SO_3)_2{}^{2-} + \cdot SO_3{}^-} \tag{3}$$

$$\mathrm{2[O\dot{N}(SO_3)_2{}^{2-} + \cdot SO_3{}^-} \xrightarrow{k_4} \mathrm{ON(SO_3)_3{}^{3-}]} \tag{4}$$

$$\mathrm{4O\dot{N}(SO_3)_2{}^{2-} \rightarrow NO^+ + {}^-ON(SO_3)_2{}^{2-} + 2ON(SO_3)_3{}^{3-}}$$

The initial breaking of an N–S bond is proposed as the rate-determining step of the overall reaction. Reaction 2 is fast relative to reaction 1 as no detectable amounts of any other radicals were observed. Reactions 3 and 4 are known[10] to be much faster than the observed rate of color loss in this study. Applying steady-state assumptions and assuming that k_2, k_3, and k_4 are large in comparison to k_1 the observed first-order rate constant for color loss is equal to $4k_1$.

The NO^+ formed could react with traces of water to form nitrous acid which was found to be the chain propagation for rapid decomposition in acidic solutions; hence use of an inhibitor or very dry solvent prevents this fast reaction and permits the radical to decompose by the slow first-order process.

Registry No. $ON(SO_3)_2{}^{2-}$, 15177-44-3; $ON(SO_3)_2{}^{2-}$-$((C_6H_5)_4Sb^+)_2$, 20475-16-5; $ON(SO_3)_2{}^{2-}$-$((C_6H_5)_4As^+)_2$, 20582-58-5.

References and Notes

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Molecular Structure and Absolute Configuration of $(-)_{280}$-*cis*-Dichloro(1-methylamino-2(*S*)-aminopropane)platinum(II)

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The molecular structure and absolute configuration of $(-)_{280}$-*cis*-dichloro(1-methylamino)-2(*S*)-aminopropane)platinum(II), $Cl_2Pt(CH_3NHCH_2CHCH_3NH_2)$, have been determined from three-dimensional x-ray data collected by counter methods. The molecule crystallizes in the orthorhombic space group $P2_12_12_1$ with four formula units per cell. The unit cell dimensions are a = 10.488 (3), b = 11.034 (4), and c = 7.432 (2) Å. The structure has been refined by full-matrix least-squares techniques on F, using 3297 unique reflections for which $F^2 > 3\sigma(F^2)$, to a final agreement factor of 0.035. The complex is square planar with an average Pt–Cl distance of 2.303 (3) Å and an average Pt–N distance of 2.021 (8) Å. The absolute configuration of the chelate ring as determined by the Bijvoet absorption-edge technique is δ, and the N-methyl substituent is in the axial position.

Introduction

The conformation adopted by the five-membered chelate ring formed upon coordination of a substituted ethylenediamine ligand to a metal atom is generally dictated by the nonbonding interactions associated with the puckered ring.[1] Thus most C-substituted ethylenediamine ligands in octahedral complexes adopt a gauche conformation, with the substituent in the equatorial position. In the case of N-substituted ethylenediamine ligands in monodiamine and *trans*-bis(diamine) complexes of Co(III), the substituent was also shown by ^1H NMR and circular dichroism studies[2] to adopt preferentially the equatorial position. More recently, a conformational