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Reversible N–N Bond Homolysis in $(CF_3S)_2N–N(SCF_3)_2$ at Room Temperature. Electron Spin Resonance, Thermodynamic, and Kinetic Results

K. Schlosser*[1] and S. Steenken[2]

Contribution from Lehrstuhl für Anorganische Chemie, Ruhr Universität Bochum, D-4630 Bochum, West Germany, and Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim, West Germany. *Received July 20, 1982*

Abstract: In perhaloalkane solvents at 250–315 K $(CF_3S)_2N–N(SCF_3)_2$ undergoes a reversible homolytic N–N cleavage reaction to yield $(CF_3S)_2\dot{N}$ radicals which were identified by ESR. From the dependence of the stationary concentration of $(CF_3S)_2\dot{N}$ on temperature the N–N bond dissociation energy is determined to be 32 ± 2 kJ/mol (7.7 kcal/mol). At 298 K the equilibrium constant for N–N homolysis is $(4 \pm 2) \times 10^{-6}$ M. The change in entropy occurring on N–N homolysis corresponds to 3 J/K mol (0.7 eu). The activation enthalpy and entropy for N–N bond cleavage are 77 kJ/mol (18.4 kcal/mol) and 5 J/K mol (1 eu), respectively. The experimental results concerning the facile N–N homolysis are interpreted in terms of sterically and electronically induced destabilization of the N–N bond in $(CF_3S)_2N–N(SCF_3)_2$.

Introduction

In comparison with the well-known[3-5] aminyl radicals $R_2\dot{N}$, thiylaminyl radicals of the types $(RS)_2\dot{N}$ (R = phenyl and substituted phenyl,[6-8] R = CF_3[9]) and $R(R'S)\dot{N}$[10] have been much less thoroughly studied. Unless sterically hindered, the alkyl- and aryl-substituted aminyl radicals tend to undergo rapid dimerization reactions to yield the corresponding hydrazines, which can be isolated and which generally show only a very weak tendency for homolytic dissociation.[5] In contrast, thiylaminyl radicals $(RS)_2\dot{N}$ seem to be extraordinarily persistent,[8,9] and their dimerization has so far not been observed.[6-9]

In this paper the first example for a dimerization/homolysis equilibrium at room temperature between thiylaminyl radicals and the corresponding hydrazine is described. As with the C–C bond in the system[11] $(CF_3S)_3C–C(SCF_3)_3 \rightleftarrows 2(CF_3S)_3\dot{C}$, substitution by CF_3S groups of the N–N bond in hydrazine leads to an extreme reduction in the N–N bond energy.

Experimental Section

A. Preparation of Tetrakis(trifluoromethylthiyl)hydrazine. Eight grams of $(CF_3S)_3N$,[12] dissolved in 300 mL of CCl_3F, were irradiated under N_2 at 200 K in a quartz Rayonet photoreactor equipped with a stirrer, condenser, gas inlet, and sample removal tube. The photolysis was controlled by monitoring the increase in the ^{19}F NMR signal of $(CF_3S)_2NN(SCF_3)_2$ at 49.7 ppm. The irradiation was stopped when the amplitude of this signal reached a plateau (at ~6 h after starting the photolysis). The solution was then concentrated to 10% of its original volume by removing the solvent and $CF_3S_2CF_3$ at 220 K. The resulting solution, which contains CCl_3F, $(CF_3S)_3N$, and 40–50% $(CF_3S)_2N–N(SCF_3)_2$ (**1**), is essentially inert with respect to decomposition of **1** only at ≤220 K. If solutions are needed for experiments at higher temperatures, dilution is necessary; 10^{-3} to 10^{-2} M solutions of **1** are essentially stable at room temperature. Physical properties of **1**: ^{19}F NMR: δ (12 F) = 49.7 (s), rel. to CCl_3F; ^{13}C NMR: δ (4 C) = 129.4 (qu), rel. to C_6D_6, ^1J (^{19}F - ^{13}C) = 316.5 Hz.

B. The methods used for purification of solvents and the other materials and for measurements and double integration of the ESR spectra were as described.[11] The reaction between $(CF_3S)_2\dot{N}$ and galvinoxyl[13] or bis(biphenylene)allyl[14] was studied by monitoring the decrease in the concentrations of the latter two radicals[11] at 444 and 490 nm, respectively, using a Durrum stopped-flow apparatus connected with a transient digitizer and a minicomputer.

Results

1. ESR Studies. Figure 1 shows an ESR spectrum typical for a carefully deoxygenated 10^{-3} M solution of $(CF_3S)_2NN(SCF_3)_2$ (**1**) in CCl_4, CCl_3F, or C_6F_6. The spectrum of the radical (g = 2.00652, line width 0.8 G), which does not change in kind or amplitude within ≤4 h, consists of a 1:1:1 triplet ($a(^{14}N)$ = 13.20 G) of septets with a line intensity ratio of 1:6:15:20:15:6:1, indicating 6 equivalent ^{19}F nuclei ($a(^{19}F)$ = 1.95 G). The spectrum is obviously due to $(CF_3S)_2\dot{N}$. The same spectrum is observed on dissolving **1** in, e.g., alkanes or benzene; however, in contrast to the fully halogenated solvents, the stationary concentration of $(CF_3S)_2\dot{N}$ decreases with time. This is suggested to result from reaction of $(CF_3S)_2\dot{N}$ with the solvent. $(CF_3S)_2\dot{N}$ can also be produced by reaction of $(CF_3S)_2NH$ with photochemically generated $(CH_3)_3C\dot{O}$ radicals or by oxidation with PbO_2.

Lines due to $^{13}C_\gamma$ or $^{33}S_\beta$ were not observed in the ESR spectrum, although the intensity of the signal was sufficient to detect lines from these nuclei present in natural abundance. It is therefore concluded that $a(^{13}C_\gamma)$ and $a(^{33}S_\beta)$ ≤ line width = 0.8 G.

If molecular oxygen is allowed to enter solutions of $(CF_3S)_2\dot{N}$ in, e.g. CCl_4, reversible line-broadening is observed. If the solutions are saturated with O_2, the fine structure due to ^{19}F is completely lost. The resulting spectrum consists of a 1:1:1 triplet with identical $a(^{14}N)$ and g-factor as in the absence of O_2. Removal of O_2 results in the quantitative regeneration of the original spectrum. These results show that the line broadening is due to magnetic dipole interaction of the radicals with the paramagnetic O_2 and that $(CF_3S)_2\dot{N}$ does not chemically react with oxygen. This lack of reactivity probably results from the pronounced electron deficiency of $(CF_3S)_2\dot{N}$.

The concentration of $(CF_3S)_2\dot{N}$ in ≤ 10^{-3} M solutions of **1** in perhaloalkane solvents reversibly increases with increasing temperature in the range 250–315 K. Below 250 K the concentration

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(2) Max-Planck-Institut für Strahlenchemie.

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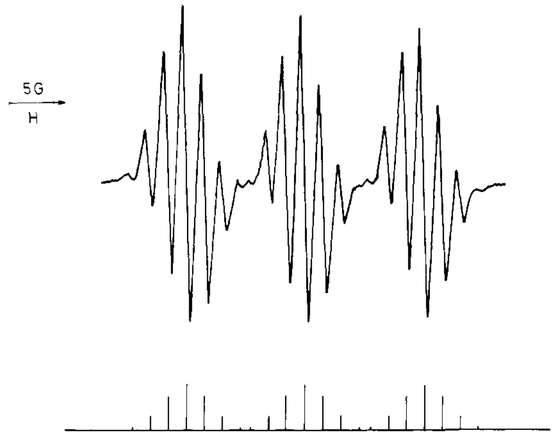

Figure 1. ESR spectrum of a solution containing 1 mM $(CF_3S)_4N_2$ in CCl_3F at 298 K: $a(^{14}N) = 13.20$ G, $a(^{19}F) = 1.95$ G.

drops below the detection limit; above 320 K the concentration decreases with time and the system loses its reversibility. At ≥320 K the solutions slowly evolve N_2, and CF_3SSCF_3 is produced, as shown by ^{19}F NMR. Obviously, under these conditions, reaction 1 becomes important

$$\underset{\mathbf{1}}{(CF_3S)_2NN(SCF_3)_2} \rightarrow N_2 + 2CF_3SSCF_3 \qquad (1)$$

Reaction 1 is also observed at much lower temperatures if the concentration of **1** is $>10^{-3}$ M.

In the temperature range 250–315 K and at concentrations of $\mathbf{1} \leq 10^{-3}$ M, the reversible formation of $(CF_3S)_2\dot{N}$ is explained by homolytic cleavage of the N–N bond in **1**

$$(CF_3S)_2N\text{-}N(SCF_3)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2(CF_3S)_2\dot{N} \qquad (2)$$

$$K_c = [(CF_3S)_2\dot{N}]^2/[(CF_3S)_2NN(SCF_3)_2] = k_1/k_{-1}$$

In order to determine the equilibrium constant K_c, the ESR spectra of $(CF_3S)_2\dot{N}$ were doubly integrated[11] and compared with corresponding data for 10^{-5} M solutions of diphenylpicrylhydrazyl. The concentration of **1** was determined by comparing its ^{19}F NMR signal with those of known concentrations of $(CF_3S)_4C$. At 298 K, the equilibrium constant $K_c = (4 \pm 2) \times 10^{-6}$ M, from which ΔG, the free-energy change accompanying the N–N homolysis of **1**, is calculated as 31 ± 2 kJ/mol. ΔH, the enthalpy of homolysis of **1** (the N–N bond enthalpy), was determined (by measuring the concentration of $(CF_3S)_2\dot{N}$ as a function of temperature) to be 32 ± 2 kJ/mol. The entropy change is therefore $\Delta S = (\Delta H - \Delta G)/T = 3$ JK^{-1}/mol.

2. Kinetic Studies. The rate of homolysis of **1** was determined by scavenging $(CF_3S)_2\dot{N}$ by reaction with the stable radicals galvinoxyl and bis(biphenylene)allyl. This method is analogous to that[14] described by Bartlett and Funahashi. The reactions can be represented as follows, where S symbolizes the scavenger molecule

$$>N\text{-}N< \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2>\dot{N} \xrightarrow[k_2]{+S} \text{product} \qquad (3)$$

In this system, the rate of formation of $>\dot{N}$

$$d[>\dot{N}]/dt = 2k_1[>N\text{-}N<] - 2k_{-1}[>\dot{N}]^2 - k_2[>\dot{N}][S] \qquad (4)$$

Assuming a stationary state for $[>\dot{N}]$, $[>N\text{-}N<] \approx$ constant, and $k_2[S] >> 2k_{-1}[>\dot{N}]$, $d[S]/dt = -2k_1[>N\text{-}N<]_0$, which represents a pseudo-zero-order rate law. When a 20 to 100-fold excess of $(CF_3S)_2NN(SCF_3)_2$ over galvinoxyl (2.5×10^{-5} to 10^{-4} M) was used, a zero-order depletion of galvinoxyl was in fact observed experimentally in the range of 20–70% conversion. The rate constants k_1 obtained from these experiments in the temperature range 294 to 308 K are between 1 and 5 s^{-1} (Table I). An Arrhenius plot for k_1 yields the activation parameters for N–N homolysis $E_a = (81 \pm 5)$ kJ/mol and $\Delta S^{\ddagger} = 5 \pm 12$ J K^{-1}/mol, corresponding to a preexponential factor of 2×10^{14} s^{-1}, and an activation enthalpy of (77 ± 5) kJ/mol, i.e., $k_1/\text{s}^{-1} = 2 \times 10^{14} \exp(-81/RT)$.

Table I. Rate Constants and Activation Parameters for Dissociation of $(CF_3S)_2N\text{-}N(SCF_3)_2$

scavenger	t/°C	k_1/s^{-1}	ΔH^*/ kJ mol^{-1}	ΔS^*/ J mol^{-1} K^{-1}
galvinoxyl	20.5	1.1	77 ± 5	5 ± 12
	25.0	1.9		
	26.0	2.0		
	28.1	2.6		
	30.5	3.1		
	35.1	5.1		
bis(phenylene)-allyl	25.0	1.9		

Table II. ESR Parameters for Aminyl Radicals

radical	$a(^{14}N)$/G	g	ref
$(CF_3S)_2\dot{N}$	13.20	2.00652	this work
$(C_6H_5S)_2\dot{N}$	11.41	2.0082	8
$(C_6H_5)(C_6H_5S)\dot{N}$	9.59	2.0059	10
$(C_6H_5)_2\dot{N}$	8.80	2.0032	23

Since K_c is known from the ESR measurements, k_{-1}, the rate constant for dimerization of $(CF_3S)_2\dot{N}$, can be calculated. At 298 K and with CCl_4 as a solvent, $k_{-1} = (5 \pm 2) \times 10^5$ M^{-1} s^{-1}, which is ~4 orders of magnitude below the diffusion-controlled limit.

When bis(biphenylene)allyl was used as a scavenger using the same concentration ratios as with galvinoxyl, a zero-order decay of the scavenger was not observed. However, when the concentration of **1** was increased to 10^{-2} M, a *first*-order depletion was found. This indicates that under these conditions $2k_{-1}[>N\text{-}N<] > k_2[S]$. From a stationary-state treatment, the rate of decay of S is then given by

$$d[S]/dt = -k_2K_c[>N\text{-}N<]_0[S] \qquad (5)$$

From the experimental decay rates of bis(biphenylene)allyl at different $[>N\text{-}N<]$ at 298 K and inserting the value of K_c into the integrated form of eq 5, k_2 is obtained as $(1.5 \pm 0.2) \times 10^6$ M^{-1} s^{-1}. This value is three times larger than k_{-1}. If, instead, conditions are chosen such that $[>N\text{-}N<]$ and [S] are equal and large as compared to $[>\dot{N}]$, eq 4 reduces to

$$d[S]/dt = 2k_1(\tfrac{1}{2}[S]_0 - [>N\text{-}N<]_0) - k_1[S] \qquad (6)$$

i.e., a first-order rate law from which k_1 can be determined. From the experimental data at 298 K for bis(biphenylene)allyl k_1 is obtained as 1.9 ± 0.3 s^{-1}, in very good agreement with the value found using galvinoxyl as a scavenger for $(CF_3S)_2\dot{N}$.

Discussion

1. The Structure of the Radical. The hyperfine splitting constant $a(^{14}N)$ of 13.20 G is typical for aminyl radicals with a π configuration.[5] E.g., $a(^{14}N)$ is 10.33 G for $H_2\dot{N}$,[15] 16 G for $F_2\dot{N}$,[16] and 14.78 G for $(CH_3)_2\dot{N}$.[17] For σ radicals (with the unpaired electron in a sp^3 orbital) $a(^{14}N)$ is expected to be ~80 G.[18,19]

Compared to alkylaminyl[17] and alkoxyaminyl radicals (e.g., $(CH_3)(CH_3O)\dot{N}$, $a(^{14}N) = 14.30$ G[20]), the alkylthiyl- and arylthiylaminyls have lower ^{14}N splittings; e.g., for $(C_6H_5S)_2\dot{N}$, $a(^{14}N) = 11.41$ G.[8] This may be evidence for some spin delocalization to the sulfur $\text{-}\dot{N}\text{-}S\text{-} \leftrightarrow \text{-}N^{-}\text{-}\dot{S}^{+}\text{-}$. However, it may also be due to an increase in the $\dot{N}<$ bond angle ∠. E.g., $a(^{14}N)$ increases from 10.33 G[15] for $H_2\dot{N}$, where ∠ is 103.3°,[21] to 14.78

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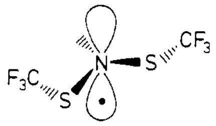
G[17] for $(CH_3)_2\dot{N}$, where ∠ = 117°.[22]

Another aspect is the decrease in $a(^{14}N)$ that occurs on replacing CF_3 or CF_3S groups in $(CF_3S)_2\dot{N}$ by phenyl groups (Table II).[23] The decrease reflects delocalization of the unpaired spin into the phenyl system. The increase in g factor in going from $(C_6H_5)_2\dot{N}$ to $(C_6H_5S)_2\dot{N}$ probably results from the larger spin-orbit coupling due to the S atoms.[24,25]

From molecular models the following W-shaped structure is suggested for $\dot{N}(SCF_3)_2$. For $(CH_3)(CH_3O)\dot{N}$ this type of



structure has also been suggested, based on INDO calculations.[20]

The C-S-N-S-C skeleton together with the lone electron pair are assumed to be approximately in the nodal plane of the p-orbital occupied by the unpaired electron. This is supported by the low coupling constants for $^{33}S_\beta$ and $^{13}C_\gamma$. The S-N-S angle is assumed to be <119 °C based on analogy with $(CF_3S)_3N$, where the S-N-S angle is 118.8°[26] together with theoretical calculations,[27] which indicate that this angle decreases on elimination of a $CF_3S\cdot$ group to form $(CF_3S)_2\dot{N}$.

As a conclusion, from the above discussion it appears that $(CF_3S)_2\dot{N}$ is not stabilized significantly by spin delocalization. In support of this are the very small (<0.8 G) coupling constants for $^{13}C_\gamma$ and $^{33}S_\beta$. For this reason, the extremely small N-N bond energy in **1** cannot be related to the stability of the resulting radicals. It must therefore be due to destabilization of **1**. This is clearly shown by the extremely low value for the N-N bond dissociation energy in **1** (32 kJ/mol) which may be compared with 296 kJ/mol[28] for N-N bond dissociation in hydrazine. The low value (5 J K^{-1}/mol) found for the activation entropy for N-N bond homolysis in **1** demonstrates that the transition state for bond homolysis strongly resembles the ground state.

2. Nature of the N-N bond. The principal reason for the extremely low N-N bond energy in **1** is suggested to be a combination of steric and electronic factors. As a result of the strong electron withdrawing properties of SCF_3 (Hammett $\sigma(SCF_3)$ = 0.64), SCF_3 groups are expected to reduce the N-N bond distance. This type of effect is seen with F_2NNF_2 (N-N bond distance 1.25 Å) as compared to H_2NNH_2 (bond distance 1.45 Å). A decrease of the N-N bond distance will, however, be prevented by strong steric interaction between the bulky SCF_3 groups. The lone electron pairs on the nitrogens also contribute to steric repulsion.[27] In the analogous case $(CF_3S)_3CC(SCF_3)_3$, the C-C bond distance is 1.7 Å,[11] to be compared with a C-C bond distance of 1.54 Å for ethane. This shows that the steric effect, which tends to widen the bond length, predominates over the electronic effect, which tends to decrease the bond distance. In the case of F_2NNF_2 the N-N bond strength (88 kJ/mol)[29] is strongly reduced as compared to that in H_2NNH_2, *although* the N-N bond length of 1.25 Å in F_2NNF_2 is considerably smaller than the 1.45 Å for H_2NNH_2. The combination of small bond length and low bond energy in F_2NNF_2 may be explained by assuming that the bond length results as a compromise between bond shortening effects due to the electronegative fluorines and steric effects that prevent the further approach of the two NF_2 moieties. With this bond length, the bond energy is only 88 kJ/mol. If analogous arguments are applied to $(CF_3S)_2NN(SCF_3)_2$, it is clear that steric effects prevent the N-N bond from reaching the low distance required by the electron-withdrawing effect of the SCF_3 groups. As a result, the N-N bond is very weak, as shown by the extremely low bond energy of 32 kJ/mol.

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Registry No. 1, 80653-51-6; $(CF_3S)_3N$, 4317-00-4; $(CF_3S)_2N\cdot$, 80653-52-7; galvinoxyl, 2370-18-5; Koelsch radical, 2152-02-5.

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Laser Photodissociation of Nitrogenous Bases from Pentacoordinated Cobalt(II) Porphyrins

Catherine Tetreau,* Daniel Lavalette,[†] and Michel Momenteau[†]

Contribution from the Institut Curie, Section de Biologie, Batiment 112, Centre Universitaire, 91405 Orsay, France.

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Abstract: Pentacoordinated complexes of cobalt(II)-deuteroporphyrin IX dimethyl ester with nitrogenous bases ((L)Co^{II}DPDME) can be photodissociated by a laser pulse. The rate constants for ligand binding and dissociation are found to decrease upon increasing the pK_a of the external base. The kinetic results are compared to those previously found for the binding of the same ligands to pentacoordinated iron(II)-5,10,15,20-tetraphenylporphyrin-base$_2$ complexes (Fe^{II}TPP-B). The compared pK_a dependence of the "on" rates in both systems confirms the role of an electrostatic repulsion barrier between ligand and Fe^{II}TPP-B dipole moments, and its absence in the cobalt(II)-porphyrin case. Except for this term, the association rates are not very different in both systems. On the contrary, the dissociation rates are about two orders of magnitude larger for (L)Co^{II}DPDME complexes than for the hexacoordinated iron(II) porphyrins (hemochromes). The results are discussed in terms of the relative metal orbital occupancies. The comparison also suggests that the contribution of π bonding in pentacoordinated Co(II) complexes is smaller than in hemochromes.

Introduction

Ligand photodissociation from low-spin hexacoordinated iron(II) porphyrins is well documented. Extensive studies have been devoted to natural complexes of biological importance and to synthetic heme models. Among the compounds which have been reported to be photosensitive are oxy- and carboxyhemoproteins,[1,2] carboxyhemochromes,[3] and hemochromes.[4,5] Pho-

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