The Unexpected Desulfurization of 4-Aminothiophenols

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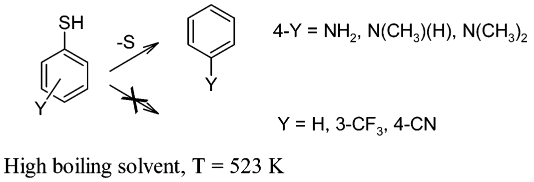

Thermolysis of 4-aminophenyl benzyl sulfide at 523 K in the hydrogen donor solvent (HDS), 9,10-dihydroanthracene (AnH_2), gave 4-aminothiophenol and toluene as the predominant products of the homolytic S−C bond cleavage. Under these conditions, a portion of the 4-aminothiophenol was desulfurized to aniline with first-order kinetics and with a rate constant estimated by kinetic modeling to be 7.0×10^{-6} s^{-1}. Starting with $4\text{-}NH_2C_6H_4SH$ at 523 K, it was found that sulfur loss was more efficient in the non-HDSs, anthracene and hexadecane, than in AnH_2. Under similar (competitive) reaction conditions, YC_6H_4SHs with Y = H, 4-CN, and 3-CF_3 were completely inert; with Y = 4-CH_3O, there was some very minor desulfurization, whereas with Y = 4-$N(CH_3)_2$ and 4-$N(CH_3)(H)$, the sulfur extrusions were as fast as that for Y = 4-NH_2. We tentatively suggest that this apparently novel reaction is a chain process initiated by the bimolecular formation of diatomic sulfur, S_2, followed by a reversible addition of ground state, triplet $^3S_2$ to the thiol sulfur atom, $4\text{-}NH_2C_6H_4S{\uparrow}(SS{\uparrow})H$, and insertion into the S−H bond, $4\text{-}NH_2C_6H_4SSSH$. In a cascade of reactions, aniline and S_8 are formed with the chains being terminated by reaction of $4\text{-}NH_2C_6H_4S{\uparrow}(SS{\uparrow})H$ with $4\text{-}NH_2C_6H_4SH$. Such a reaction mechanism is consistent with the first-order kinetics. That this reaction is primarily observed with $4\text{-}YC_6H_4SH$ having Y = $N(CH_3)_2$, $N(CH_3)(H)$, and NH_2 is attributed to the fact that these compounds can exist as zwitterions.

Introduction

Sulfur-containing organic compounds are among the many ingredients present in fossil fuels, particularly, coal.[1] The selective removal of sulfur from these fuels, desulfurization, has been, and still is, a challenge that must be met in order to comply with current and future emission standards for power plants, etc. To mimic the thermal processing of coal and gain insights into the mechanisms of desulfurization, the reactivities of sulfur-containing model compounds have been examined at high temperatures, frequently in the presence of hydrogen atom donor solvents (HDS). Phenyl benzyl sulfide, $C_6H_5SCH_2C_6H_5$, can be regarded as a prototypical sulfur compound with its S−aryl and S−benzyl bonds. The thermolysis of this compound has been investigated in a number of solvents and at various temperatures: cyclohexane (523 K),[2] water (523 K),[2] mesitylene (630 K),[3] tetrahydroquinoline/mesitylene (608−630 K),[3] Tetralin (661 K),[4] Tetralin (573−659 K),[5] water (573−659 K),[5] and methanol (573−659 K).[5] These studies have shown that in the presence of a HDS the main route for decomposition involves the cleavage of the S−benzylic bond with the resultant radicals then reacting with the HDS to form thiophenol and toluene (in a 1:1 ratio) as the main products (reaction 1):

$$C_6H_5SCH_2C_6H_5 \rightarrow C_6H_5S^\bullet + C_6H_5CH_2^\bullet \rightarrow C_6H_5SH + C_6H_5CH_3 \quad (1)$$

The major byproducts have been reported to be diphenyldisulfide and diphenylmethane.[4,5] The formation of diphenylmethane has

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† Leiden University.

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(1) Yan, J.; Yang, J.; Liu, Z. *Environ. Sci. Technol.* **2005**, *39*, 5043−5051 and references cited therein.

(2) Katritzky, A. R.; Lapucha, A. R.; Greenhill, J. V.; Siskin, M. *Energy Fuels* **1990**, *4*, 562−571.

(3) Panvelker, S. V.; Shah, Y. T.; Cronauer, D. C. *Ind. Eng. Chem. Fundam.* **1982**, *21*, 236−242.

(4) Ignasiak, T. M.; Strausz, O. P. *Fuel* **1978**, *57*, 617−621.

(5) Abraham, M. A.; Klein, M. T. *Fuel Sci. Technol. Int.* **1988**, *6*, 633−662.

10.1021/jo0624243 CCC: $37.00

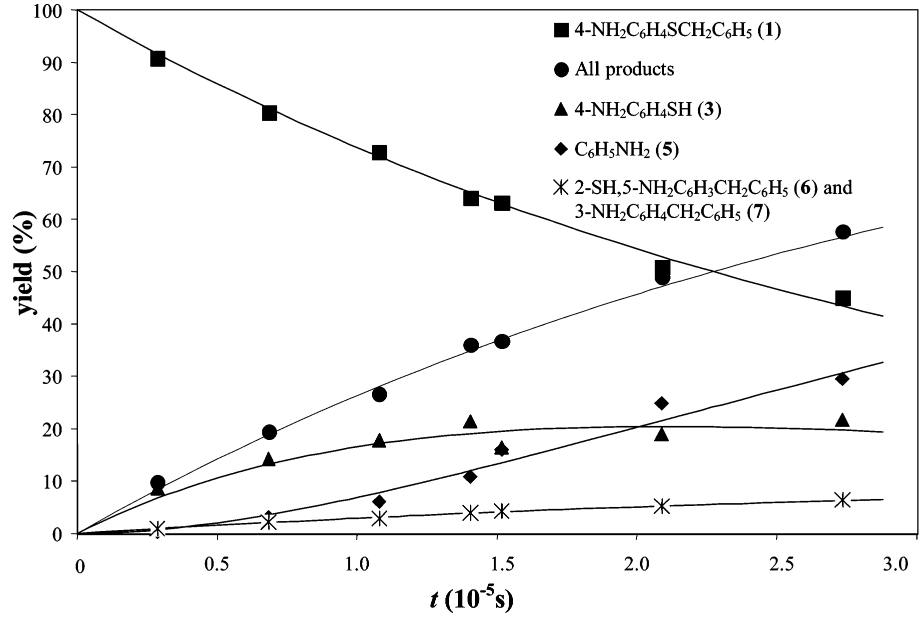

FIGURE 1. Product distributions obtained during thermolysis of 4-$NH_2C_6H_4SCH_2C_6H_5$, **1**, in AnH_2, **2**, at 523 K as a function of time. Yields defined as 100 × 0.5 × [**3**]/{0.5 × ([**3**] + [**4**] + [**5**] + [**8**]) + [**1**] + [**6**] + [**7**]}. All products are defined as, for example, 0.5 × ([**3**] + [**4**] + [**5**] + [**8**]) + [**6**] + [**7**]. Drawn lines are calculated yields based on kinetic modeling; see Scheme 1.

been rationalized as involving the abstraction of a benzylic hydrogen atom from $C_6H_5SCH_2C_6H_5$ with the resulting C_6H_5-$CH(^•)SC_6H_5$ radical then undergoing a neophyl-like rearrangement (1,2-migration of the phenyl group) to yield $C_6H_5CH(S^•)$-C_6H_5.[6] Hydrogen atom transfer then yields the thiol $C_6H_5CH(SH)$-C_6H_5, which has a weak S−C bond,[7] and is converted into C_6H_5-$CH_2C_6H_5$ and H_2S under high-temperature conditions. Alternatively, it has been suggested that the presumed spirocyclohexadienyl radical intermediate in the $C_6H_5CH(^•)SC_6H_5$ rearrangement may directly eliminate elemental sulfur.[2,10] Hence, diphenylmethane formation constitutes the only desulfurization pathway for $C_6H_5SCH_2C_6H_5$ because the main sulfur-containing product, thiophenol, appears to be thermally stable under the usual experimental conditions.[11]

We have recently reported on the kinetics of the S−C bond homolysis in several 4-Y-substituted phenyl benzyl sulfides (Y = NH_2, CH_3O, H, CN, the first at 523 K, the remaining three at 548 K) using 9,10-dihydroanthracene as the HDS in order to establish the effect of substitution on the S−C bond dissociation enthalpies.[12] We noted that, for Y = NH_2 at 523 K, there was a unexpected desulfurization of the thiyl radical product, 4-$NH_2C_6H_4SH$, with the formation of $C_6H_5NH_2$. The other 4-Y-substituted thiophenols were inert under the same reaction conditions, and even at 548 K, only one of them, Y = CH_3O, underwent desulfurization, but to a very small extent. Herein, we report on the thermolysis of 4-$NH_2C_6H_4SCH_2C_6H_5$ and related compounds with the emphasis being on the products and possible mechanisms of desulfurization of 4-$NH_2C_6H_4SH$. We believe this work may improve understanding of the mechanisms by which sulfur could be extruded from other organic compounds.

Results

4-Aminophenyl Benzyl Sulfide. The product yields for the thermolysis of 4-$NH_2C_6H_4SCH_2C_6H_5$ (**1**), ca. 0.17 M, dissolved in 9,10-dihydroanthracene (AnH_2, **2**) at 523 K are presented in Figure 1. After homolytic S−C bond cleavage (reaction 2, see Scheme 1), the caged thiophenoxyl and benzyl radical pair either escape the solvent cage (reaction 2a) and are scavenged by **2** to form 4-$NH_2C_6H_4SH$ (**3**) and toluene (**4**), respectively, or they undergo an in-cage radical−radical combination to form the diphenylmethane derivative, 2-SH,5-$NH_2C_6H_3CH_2C_6H_5$ (**6**) (reaction 2b). The initial sulfur-containing products **3** and **6** undergo further reaction (desulfurization) during the course of the thermolysis. Thus, **3** is converted into aniline (**5**, reaction 3), and **6** is converted into 3-$NH_2C_6H_4CH_2C_6H_5$ (**7**, reaction 4). The ratio of [**5**]/[**3**] increases with the reaction time, but the fraction, 100 × ([**3**] + [**5**])/[**4**], remains close to 100%. The [**7**]/[**6**] ratio also increases with time, while the fraction, 100 × ([**6**] +[**7**])/([**4**] + [**6**] + [**7**]), remains constant at 10.8 ± 0.8%. A very minor product, $C_6H_5CH_2SH$ (**8**), is also formed (reaction 5), and the fraction, 100 × ([**8**]/([**4**] + [**8**]), remains constant at 1.7 ± 0.5% during the course of the thermolysis.

The in situ desulfurization of compounds **3** and **6** and the overall conversion of **1** are summarized in Table 1. These results show that the rates of reactions 3 and 4 (Scheme 1) are (almost) identical, as would be expected. An additional experiment was

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(6) (a) Alnajjar, M. S.; Franz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 1052−1058. (b) Ismall, K.; Mitchel, S. C.; Brown, S. D.; Snape, C. E.; Buchanan, A. C., III; Britt, P. F.; Franco, D. V.; Maes, I. I.; Yperman, J. *Energy Fuels* **1995**, *9*, 707−716.

(7) The S−C BDE in $C_6H_5CH(SH)C_6H_5$ can be estimated to be 57 kcal mol^{-1}.[8,9]

(8) Auxiliary thermodynamic data from http://webbook.nist.gov.

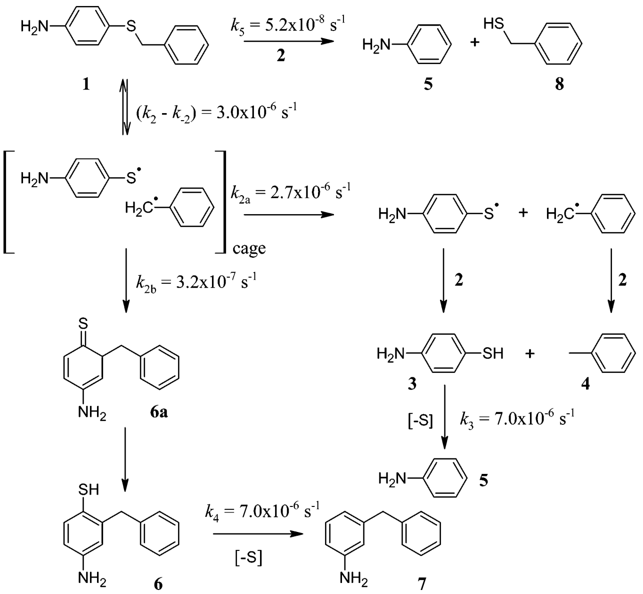
(9) Rossi, M. J.; McMillen, D. F.; Golden, D. M. *J. Phys. Chem.* **1984**, *88*, 5031−5039.

(10) The reaction enthalpy for sulfur elimination from the spirocyclohexadienyl radical intermediate → $C_6H_5CH(^•)C_6H_5$ + S can be estimated to be 35 kcal mol^{-1}.[6a,8,9]

(11) However, one study does claim that benzene and toluene were the products of $C_6H_5SCH_2C_6H_5$ thermolysis and that no thiophenol was detected.[3]

(12) Mulder, P.; Mozenson, O.; Lin, S.; Bernardes, C. E. S.; Minas da Piedade, M. E.; Santos, A. F. L. O. M.; Ribeiro da Silva, M. A. V.; DiLabio, G. A.; Korth, H.-G.; Ingold, K. U. *J. Phys. Chem. A* **2006**, *110*, 9949−9958.

SCHEME 1. Reaction Mechanism for the Thermolysis of $4\text{-}NH_2C_6H_4SCH_2C_6H_5$, 1, in AnH_2, 2, at 523 K (reaction numbers are indicated by the subscripts on the *k*s)



conducted with **1** ([**1**] = 0.17 M) in the presence of an excess of one of the products, $4\text{-}NH_2C_6H_4SH$ (**3**) ([**3**] = 0.3 M), in AnH_2 at 523 K. After 1.7×10^5 s, the overall conversion of **1** was 42.0% (based on the formation of **4**, **6**, **7**, and **8**), and the fractions, 100 × ([**6**] + [**7**])/([**4**] + [**6**] + [**7**]) and 100 × [**8**]/([**4**] + [**8**]), were 12.1 and 5.4%, respectively. The in situ desulfurization of **6** was 43.5% (see above). These results show that the decomposition of **1**, as presented in Scheme 1, is only marginally affected by the presence of a large excess of product **3**. However, **3** did accelerate the formation of benzyl sulfide (**8**), the yield of which increased from 1.7 to 5.4%. The formation of **8** will be acid-catalyzed (see below), and the excess of **3** may be the source of acid.

In our earlier study, we reported that the overall rate constant for disappearance of **1** was $3.05 \times 10^{-6}\ s^{-1}$ at 523 K.[12] With a parallel/consecutive kinetic model, as outlined in Scheme 1, the following additional rate constants have now been calculated on the basis of the product distribution: "effective" $(k_2 - k_{-2}) = 3.0 \times 10^{-6}\ s^{-1}$, $k_{2a} = 2.7 \times 10^{-6}\ s^{-1}$, $k_{2b} = 3.2 \times 10^{-7}\ s^{-1}$, $k_5 = 5.2 \times 10^{-8}\ s^{-1}$. By fitting the calculated yields from kinetic modeling with the experimental yields (Figure 1, drawn lines), the experimental first-order rate constants for desulfurization of **3** (k_3) and of **6** (k_4) at 523 K were both found to be $7.0 \times 10^{-6}\ s^{-1}$.

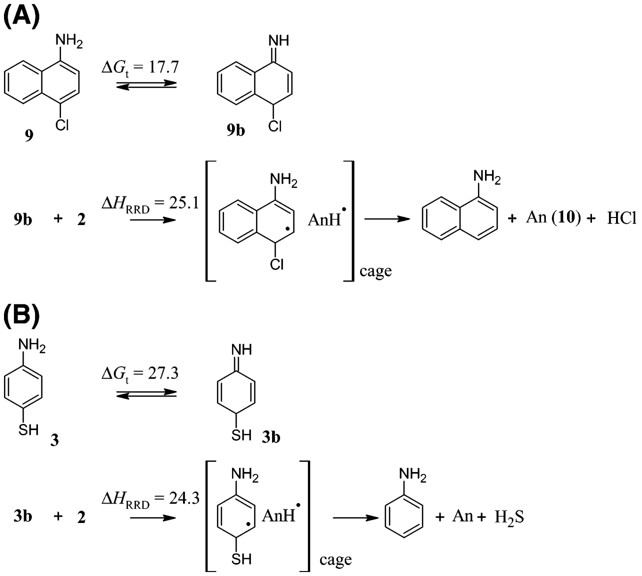
The thermolysis of **1** yields a very different product distribution from the product distributions obtained with the other $4\text{-}YC_6H_4SCH_2C_6H_5$ (Y = OCH_3, H, CN) under the same reaction conditions. A careful re-examination of the products obtained from the 548 K thermolyses of $C_6H_5SCH_2C_6H_5$ and $4\text{-}CNC_6H_4SCH_2C_6H_5$ showed absolutely no traces of C_6H_6 and C_6H_5CN, respectively, for conversions (within brackets are the corresponding reaction times) of the starting material of 69% (1.3×10^6 s) and 46.6% (1.1×10^6 s), respectively. Because $C_6H_5OCH_3$ had been used as an external standard for the GC analyses, the 548 K thermolysis of $4\text{-}CH_3OC_6H_4SCH_2C_6H_5$ (about 0.17 M in 9,10-dihydroanthracene) was repeated without adding anisole. By using an internal mass balance, an overall conversion of 56.3% was calculated after 1.7×10^5 s. This yields an overall first-order rate constant for S−C homolysis of $4.8 \times 10^{-6}\ s^{-1}$, in full agreement with our earlier reported value of $5.1 \times 10^{-6}\ s^{-1}$ (obtained from a series of experiments).[12] The in situ 548 K desulfurization for $4\text{-}CH_3OC_6H_4SH$ to $C_6H_5OCH_3$ in the above experiment was found to be 2.2%, indicating that this is only a minor reaction pathway in comparison with the desulfurization of $4\text{-}NH_2C_6H_4SH$ during the 523 K thermolysis of $4\text{-}NH_2C_6H_4SCH_2C_6H_5$ (see Table 1). The formation of $C_6H_5CH_2SH$, **8**, during the thermolyses of $4\text{-}YC_6H_4SCH_2C_6H_5$ was observed only for Y = NH_2, not for Y = CH_3O, H, and CN.

TABLE 1. In situ Desulfurization (in %, 100 × [Product]/{[Product] + [Reactant]}) of $4\text{-}NH_2C_6H_4SH$ (3), to Give $C_6H_5NH_2$ (5), and of $2\text{-}SH,5\text{-}NH_2C_6H_3CH_2C_6H_5$ (6) to Give $3\text{-}NH_2C_6H_4CH_2C_6H_5$ (7), Together With the Overall Conversion (in %) of $4\text{-}NH_2C_6H_4SCH_2C_6H_5$ (1) Into Products at 523 K[a]

$\tau/10^{-5}$ s	3	6	1
0.29	3.0	8.5	9.4
0.68	17.9	17.7	19.8
1.08	25.4	22.4	27.3
1.41	33.6	37.0	36.2
1.52	49.4	43.3	37.0
2.09	56.7	59.0	49.3
2.74	57.6	64.7	55.2

[a] In situ desulfurization defined as 100 × [**5**]/([**3**] + [**5**]) and as 100 × [**7**]/([**6**] + [**7**]). The overall conversion of **1** was defined as 100 × {0.5 × ([**3**] + [**4**] + [**5**] +[**8**]) + [**6**] +[**7**]}/{0.5 × ([**3**] +[**4**] +[**5**] +[**8**]) +[**1**] +[**6**] +[**7**]}. τ = reaction time.

SCHEME 2[a]



[a] (A) Dechlorination of 4-chloro-1-naphthylamine, **9**, according to a tautomerization/RRD mechanism in AnH_2, **2**. The thermodynamic data (in kcal mol^{-1} and at 298 K) are obtained by computational chemistry: B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p).[13a] (B) Desulfurization in AnH_2, **2**, of 4-aminothiophenol, **3**, according to a potential tautomerization/RRD mechanism. The thermodynamic data (in kcal mol^{-1} and at 298 K) are obtained by computational chemistry: B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p).[13b]

The facile desulfurization of the thiophenol, $4\text{-}NH_2C_6H_4SH$, has not, apparently, been previously reported. The mechanism of this desulfurization was, at first, thought to be similar to that suggested for the dechlorination of phenols and anilines under the same reaction conditions.[13a] A key observation for the

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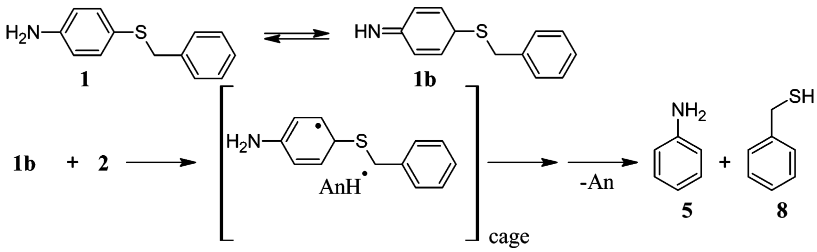
(13) (a) Mulder, P.; Arends, I. W. C. E.; Santoro, D.; Korth, H.-G. *J. Org. Chem.* **2003**, *68*, 4247−4257. (b) Korth, H.-G. Private communication.

SCHEME 3. Formation of Benzyl Sulfide, 8



proposed dechlorination mechanism was that phenols with a chlorine atom at C-3 were thermally stable, whereas those with a chlorine atom at C-2 or C-4 lost their chlorine at appreciable rates. The mechanism of the 523 K dechlorination of 4-chloro-1-naphthylamine, **9**, into 1-naphthylamine and hydrochloric acid in AnH_2 was investigated in detail.[13a] The rate of dechlorination increased with the initial concentration of **9**, eventually reaching a constant (plateau) value. At high concentrations of **9**, 1,1′-dinaphthylamine emerged as a product with a concomitant increase in the overall conversion of **9**, whereas at low [**9**], the dechlorination reaction was catalyzed by an added organic acid. These features led to the mechanistic rationale presented in Scheme 2A. The first step is the establishment of an equilibrium between **9** and its tautomeric imine. Subsequently, a hydrogen atom is transferred from AnH_2 to the imine by a reverse radical disproportionation (RRD) reaction, and this ultimately leads to 1-naphthylamine, hydrochloric acid, and anthracene, **10**. Tautomerization is an acid/base-catalyzed reaction, and at low [**9**], the rate of equilibration becomes rate limiting. At high concentrations of **9**, this compound combines with its tautomer to form an intermediate that is more reactive in the RRD reaction and yields the observed 1,1′-dinaphthylamine. In biphenyl, a non-hydrogen donor solvent, **9**, was thermally stable.[13a] A similar mechanism for desulfurization of $4\text{-}NH_2C_6H_4SH$ is shown in Scheme 2B.

At 523 K, the bimolecular rate constant for dechlorination of **9** was calculated from the pseudo-first-order rate constants using an average AnH_2 concentration of 4 M and gave $k_{Cl} = 5.11 \times 10^{-5}\ M^{-1}\ s^{-1}$.[13a] A similar calculation of the bimolecular rate constant for desulfurization of **3** at 523 K gave $k_S = (k_3/[AnH_2]) = 1.75 \times 10^{-6}\ M^{-1}\ s^{-1}$.

In Scheme 2, the DFT-calculated free energy changes for tautomerization, ΔG_t, and the RRD reaction enthalpies, ΔH_{RRD}, are presented for **9**[13a] and **3**[13b]. The rather small difference (0.8 kcal mol^{-1}) in the ΔH_{RRD} values for these two reactions implies that their RRD rate constants will not be dramatically different. However, the large difference in their ΔG_t values (9.4 kcal mol^{-1}), which determine the amine/imine equilibrium ratios for **3** and **9**, would lead to the expectation that k_S would be smaller than k_{Cl} by about a factor of about 8.5×10^3; that is, the "expected" $k_S = 5.1 \times 10^{-5}/8.5 \times 10^3 = 6.0 \times 10^{-9}\ M^{-1}\ s^{-1}$, a value very much lower than the experimental, $k_S = 1.75 \times 10^{-6}\ M^{-1}\ s^{-1}$. This suggests that tautomerization followed by RRD cannot be the dominant mechanism for desulfurization of **3**. On the other hand, the formation of minor amounts of benzyl sulfide (**8**)[14] during the thermolysis of **1** indicates that a tautomerization/RDD mechanism does occur to a small extent (Scheme 3) and as outlined above is acid catalyzed.[15] The ΔG_t values for tautomerization of **1** and **3** are probably almost identical. With [AnH_2] equal to 4 M, the bimolecular rate constant for the conversion of **1** into **8** can be calculated from the experimental first-order rate constant to be $5.2 \times 10^{-8}/4 = 1.3 \times 10^{-8}\ M^{-1}\ s^{-1}$, which is reasonably close to the predicted value of $6.0 \times 10^{-9}\ M^{-1}\ s^{-1}$ based on the analogy with **9** (see above).

4-Aminothiophenol. The reactivity (desulfurization) of $4\text{-}NH_2C_6H_4SH$, **3** (ca. 0.3 M), at 523 K was investigated in more detail using various high-boiling HDSs and non-HDSs: hexadecane, 9,10-dihydroanthracene, 9,10-dihydroanthracene mixed with anthracene (w/w = 1:1), and anthracene. The results are summarized in Table 2.

In hexadecane, the desulfurization of **3** was about 66%, and two additional products were found: $(2\text{-}NH_2C_6H_4)(4\text{-}NH_2C_6H_4)S$ and $(4\text{-}NH_2C_6H_4)_2S$ (mass spectra are presented in the Supporting Information). These two byproducts are probably formed by radical−radical combination reactions between the 4-aminothiophenoxyl radical and the anilinyl radical. The equilibrium shown in eq 6 is estimated to have $\Delta H_6 = 14.5$ kcal mol^{-1}.[16]

$$4\text{-}NH_2C_6H_4S^\bullet + C_6H_5NH_2 \rightleftharpoons 4\text{-}NH_2C_6H_4SH + C_6H_5NH^\bullet \quad (6)$$

This means that the concentration $4\text{-}NH_2C_6H_4S^\bullet$ will be much higher than the concentration of $C_6H_5NH^\bullet$ even when [$4\text{-}NH_2C_6H_4SH$] << [$C_6H_5NH_2$]. Consequently, the coupling of two $C_6H_5NH^\bullet$ radicals will be very unlikely, a conclusion that is consistent with the fact that $(C_6H_5NH)_2$ products were not observed. The coupling between two $4\text{-}NH_2C_6H_4S^\bullet$ radicals would presumably yield the disulfide, $(4\text{-}NH_2C_6H_4S-)_2$, but the estimated S−S BDE in this compound is only 44.3 kcal mol^{-1}; hence, there would be no build up of this product during the thermolysis of $4\text{-}NH_2C_6H_4SH$.[18]

In AnH_2, the conversion of **3** into **5** (ca. 33%) is a clean reaction, with no detectable byproducts. The (pseudo-)first-order rate constant for desulfurization of **3**, k_3, was calculated to be $2.4 \times 10^{-6}\ s^{-1}$ (using an internal mass balance), a value that is

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(14) The S−C BDE in $C_6H_5CH_2SH$, **8**, can be estimated to be 61.2 kcal mol^{-1},[8] which means that the thermolysis of **8** according to $C_6H_5CH_2SH \rightarrow C_6H_5CH_2^\bullet + {}^\bullet SH$ does not take place under the reaction conditions.

(15) An induced decomposition of **1** by means of a hydrogen atom addition to sulfur followed by elimination of **8** can be ruled out (see Supporting Information).

(16) The S−H BDE in $4\text{-}NH_2C_6H_4SH$ is 76.5 kcal mol^{-1}; that is, it is 3.6 kcal mol^{-1} weaker than the S−H BDE in C_6H_5SH (80.1 kcal mol^{-1});[12] the N−H BDE in $C_6H_5NH_2$ is 91.0 kcal mol^{-1}.[17]

(17) Colussi, A. J.; Benson, S. W. *Int. J. Chem. Kinet.* **1978**, *10*, 1139−1149.

(18) The S−S BDE in $(C_6H_5S-)_2$ is 51.5 kcal mol^{-1} (based on a heat of formation for the phenylthiyl radical of 54.9 kcal mol^{-1}).[8,12] With twice the bond weakening effect by the 4-NH_2 substitutent (−3.6[12]), the S−S BDE in $(4\text{-}NH_2C_6H_4S-)_2$ is calculated to be $51.5 - 2 \times 3.6 = 44.3$ kcal mol^{-1}. This implies that the rate constant for S−S homolysis of $(4\text{-}NH_2C_6H_4S-)_2$ would be $7 \times 10^{-4}\ s^{-1}$ at 523 K ($\log A/s^{-1} = 15.2$[12]), which is about 240 times higher than the rate constant for S−C cleavage in **1**.

TABLE 2. Desulfurization of 4-$NH_2C_6H_4SH$ in Various Solvents at 523 K[a]

solvent	hexadecane	AnH_2	AnH_2/An (1:1)	An
4-$NH_2C_6H_4SH$ (initial)	156	177	162	158
4-$NH_2C_6H_4SH$ (remaining)	22.9	124.3	14.7	8.4
$C_6H_5NH_2$	66.6	61.7	169.0	94.3
others	24.0[b]		3.7[c]	37.4[d]
mass balance (%)[e]	88	105	113	78
desulfurization (%)[f]	66	33	90	97

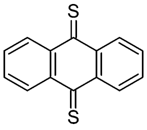
[a] In μmol, the reaction time, τ, was 48 h ($\sim 1.7 \times 10^5$ s), and with ca. 500 mg of solvent, the initial [4-$NH_2C_6H_4SH$] was ca. 0.3 M. Mass spectra of tentatively identified products are presented in the Supporting Information. [b] Additional products: 3.4 μmol (2-$NH_2C_6H_4$)(4-$NH_2C_6H_4$)S and 20.6 μmol (4-$NH_2C_6H_4$)$_2$S. [c] Additional product: 3.7 μmol dibenzothiophene. [d] Additional products: three isomers of $NH_2C_6H_4$-An (4.2, 8.8, and 0.4 μmol); 4.9 μmol $C_{14}H_8S_2$; 14.6 μmol $C_{14}H_9SH$ (two isomers, ratio 6/1); 3.1 μmol dibenzothiophene; 1.9 μmol (2-$NH_2C_6H_4$)(4-$NH_2C_6H_4$)S; 1.6 μmol (4-$NH_2C_6H_4$)$_2$S. [e] Nitrogen mass balance, defined as $100 \times \sum$[N-containing compounds]$_{t=\tau}$/[4-$NH_2C_6H_4SH$]$_{t=0}$, the [N-containing compounds]$_{t=\tau}$ includes a stoichiometric factor of 2 for (2-$NH_2C_6H_4$)(4-$NH_2C_6H_4$)S and (4-$NH_2C_6H_4$)$_2$S. [f] Desulfurization is defined as $100 \times (1 - \sum$[S-containing compounds]$_{t=\tau}$/($\sum$ [N-containing compounds]$_{t=\tau}$); see also footnote *e*; the [S-containing compounds] do not include $C_{14}H_9SH$ and $C_{14}H_8S_2$.

TABLE 3. Thermolysis of 4-$N(CH_3)_2C_6H_4SCH(CH_3)C_6H_5$, 11, in 9,10-Dihydroanthracene at 523 K: Product Distribution (in %) after 1 and 48 h[a]

	1 h	48 h
$C_6H_5C_2H_5$[b]	20.6[b]	48.9[b]
$C_6H_5C_2H_3$	0.4	nd
$C_6H_5N(CH_3)(H)$	nd	3.2
$C_6H_5N(CH_3)_2$	tr	14.1
4-$N(CH_3)(H)C_6H_4SH$[c]	0.8	4.3
4-$N(CH_3)_2C_6H_4SH$[c]	17.1	20.1
4-$N(CH_3)(H)C_6H_4SCH_3$	nd	1.9
4-$N(CH_3)_2C_6H_4SCH_3$	1.2	7.5
11	60.0	0.02

[a] tr = trace, identified but less than 0.1%, nd = not detected less than 0.01%. Compound **11** contained 10% of 4-$N(CH_3)_2C_6H_4SCH(C_4H_9)C_6H_5$ as an impurity (see Experimental Section). The product distributions presented in this table have been corrected for the thermolysis products arising from this impurity by utilizing the quantities of $C_6H_5C_5H_{11}$ that were formed. Product distributions have been calculated using the internal mass balance: [**11**]$_{t=0}$ = [**11**]$_{t=\tau}$ + 0.5$\sum$[products]. [b] Including 2.2% (1 h) and 8.0% (48 h) of 9,10-dihydro-9-(1-phenylethyl)-anthracene. [c] The desulfurizations of 4-YC_6H_4SH with Y = $N(CH_3)_2$ and $N(CH_3)(H)$, defined as $100 \times [C_6H_5Y]/([4\text{-}YC_6H_4SH] + [C_6H_5Y] + [4\text{-}YC_6H_4SCH_3])$, are 33.8% (Y = $N(CH_3)_2$) and 34.0% (Y = $N(CH_3)(H)$).

about one-third of the k_3 value of 7.0×10^{-6} s^{-1} obtained from the kinetic modeling of the decomposition of **1** (see above). In the AnH_2/An solvent mixture, the conversion of **3** into **5** increased to ca. 90%, with only dibenzothiophene as a minor byproduct. Finally, in anthracene, the overall conversion of **3** increased even further, but in addition to **5**, there was also an array of byproducts. The main fraction consisted of condensation products between aniline and anthracene (three isomers, mass spectra are presented in the Supporting Information). Interestingly, three sulfur-derived compounds were also formed which are identified, on the basis of their recorded mass spectra (Supporting Information), as condensation products between sulfur species and anthracene: $C_{14}H_{10}S$ (two isomers, ratio 6/1, with identical mass spectra) with $M = 210$ (100), $M - 32$ (73), $M - 45$ (40), and $C_{14}H_8S_2$ (dithioanthraquinone)[19] with $M = 240$ (100), $M - 45$ (11), $M - 77$ (11):



The Anthracene + Sulfur Reaction. Thermolysis of 8 μmol S_8 in 500 mg of anthracene under standard conditions (523 K and 48 h reaction time) gave the same three sulfur/anthracene condensation products mentioned above in yields of 2.9 μmol $C_{14}H_{10}S$ (two isomers, ratio 2.5/1) and 9.3 μmol $C_{14}H_8S_2$. We prefer not to speculate about the mechanism(s) by which these compounds are formed because cyclic S_8 has an S−S bond dissociation enthalpy of only 32.8 kcal mol^{-1},[20] and, at the reaction temperature, not only will various S_8 isomers be present, but also there will be linear species including the linear S_8 biradical, its polymers (e.g., $S_8 + S_8 \rightarrow S_{16}$...etc.) and dissociation products (e.g., $S_8 \rightleftharpoons 4S_2$), an altogether incredible mixture of reactive species that has been aptly referred to as "the sulfur zoo".[21]

4-Dimethylaminophenyl-1-phenylethyl Sulfide and 4-Dimethylaminothiophenol. The thermolysis of 4-$N(CH_3)_2C_6H_4SCH(CH_3)C_6H_5$ (**11**) in 9,10-dihydroanthracene was employed for the in situ generation of 4-$N(CH_3)_2C_6H_4SH$ at 523 K. After reaction times of 1 and 48 h, the overall conversion of **11** (using an internal mass balance) reached 40.0 and 99.98%, respectively,[22] which indicates that reaction is essentially complete in 3−4 h. The product distribution (Table 3) was markedly different from that obtained during the thermolysis of **1**. Isomerization did not occur, and the analogue of **8**, $C_6H_5CH(CH_3)SH$, was not formed. After 48 h, the desulfurization of the 4-$N(CH_3)_2C_6H_4SH$ formed in the reaction to $C_6H_5N(CH_3)_2$ was about 34% (=$100 \times [C_6H_5N(CH_3)_2]/([4\text{-}N(CH_3)_2C_6H_4SH] + [C_6H_5N(CH_3)_2] + [4\text{-}N(CH_3)_2C_6H_4SCH_3])$). That is, the rate (and extent) of desulfurization of 4-$N(CH_3)_2C_6H_4SH$ and 4-$NH_2C_6H_4SH$ (see Table 2) were equal under identical reaction conditions. When calculated in the same way, the in situ desulfurization of 4-$N(CH_3)(H)C_6H_4SH$ under these conditions is also 34%.

The desulfurization of 4-$N(CH_3)_2C_6H_4SCH(CH_3)C_6H_5$ was accompanied by the formation of methylation/demethylation products. Interestingly, the ratios $C_6H_5N(CH_3)(H)/C_6H_5N(CH_3)_2$, 4-$N(CH_3)(H)C_6H_4SH$/4-$N(CH_3)_2C_6H_4SH$, and 4-$N(CH_3)(H)C_6H_4SCH_3$/4-$N(CH_3)_2C_6H_4SCH_3$ were almost identical: 0.23, 0.21, and 0.25, respectively; see Table 3. Because the sum of all the nitrogen-containing products was almost equal to the yield of ethylbenzene, there was no loss of methyl groups. This means that methylation/demethylation did not involve free methyl radicals because most of the methyl radicals would have been scavenged by the HDS to produce methane.

The methylating agent is presumably 4-$N(CH_3)_2C_6H_4SH$ since this compound is highest in concentration and methylation/

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(19) (a) Heilbron, I. M.; Heaton, J. S. *J. Chem. Soc. Trans.* **1923**, *123*, 173−185. (b) Yousif, N. M.; Shabana, R.; Lawesson, S. O. *Bull. Soc. Chim. Fr.* **1986**, 283−287. (c) Lakshmikantham, M. V.; Levinson, M.; Menachery, M.; Cava, M. P. *J. Org. Chem.* **1986**, *51*, 411−412.

(20) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23−35.

(21) Wong, M. W.; Steudel, Y.; Steudel, R. *Chem. Phys. Lett.* **2002**, *364*, 387−392.

(22) For the S−C bond cleavage, 4-$N(CH_3)_2C_6H_4SCH(CH_3)C_6H_5$ (**11**) → 4-$N(CH_3)_2C_6H_4S^\bullet$ + $C_6H_5C(^\bullet)(H)(CH_3)$, these results lead to an average first-order rate constant of 9.3×10^{-5} s^{-1} at 523 K, indicating that this reaction is some 30 times faster than the S−C bond cleavage in 4-$NH_2C_6H_4SCH_2C_6H_5$ (**1**).

TABLE 4. Desulfurization (in %) after 48 h of Mixtures of 4-YC$_6$H$_4$SH in 9,10-Dihydroanthracene at 523 K[a]

	4-CH$_3$OC$_6$H$_4$SH	3-CF$_3$C$_6$H$_4$SH	4-NH$_2$C$_6$H$_4$SH
mix 1[b]	0.92	nd	
mix 2[c]	0.13	nd	32.8

[a] Results are the average of two runs using toluene as an external standard for the GC analyses; nd = not detected (less than 0.01%). Desulfurization defined as 100 × $[C_6H_5Y]_{t=\tau}/\{[YC_6H_4SH]_{t=\tau} + [C_6H_5Y]_{t=\tau}\}$. [b] Mix 1: 4-CH$_3OC_6H_4$SH (146 μmol) and 3-CF$_3C_6H_4$SH (29 μmol) dissolved in ca. 500 mg of 9,10-dihydroanthracene. [c] Mix 2: 4-CH$_3$OC$_6$H$_4$SH (149 μmol), 3-CF$_3$C$_6$H$_4$SH (30 μmol), and 4-NH$_2$C$_6$H$_4$SH (162 μmol) dissolved in ca. 500 mg of 9,10-dihydroanthracene.

demethylation can be represented by eqs 7 and 8. If, as would be expected, the rate constants for methylation of the two

$$4\text{-N(CH}_3)_2C_6H_4SH + 4\text{-N(CH}_3)_2C_6H_4SH \rightarrow 4\text{-N(CH}_3)(H)C_6H_4SH + 4\text{-N(CH}_3)_2C_6H_4SCH_3 \quad (7)$$

$$4\text{-N(CH}_3)_2C_6H_4SH + 4\text{-N(CH}_3)(H)C_6H_4SH \rightarrow 4\text{-N(CH}_3)(H)C_6H_4SH + 4\text{-N(CH}_3)(H)C_6H_4SCH_3 \quad (8)$$

thiols are approximately equal (i.e., $k_7 \approx k_8$), the ratio [4-N(CH$_3$)(H)C$_6$H$_4$SCH$_3$]/[4-N(CH$_3$)$_2$C$_6$H$_4$SCH$_3$] should be similar to the product ratio {([C$_6$H$_5$N(CH$_3$)(H)] + [4-N(CH$_3$)(H)C$_6$H$_4$SH])/([C$_6$H$_5$N(CH$_3$)$_2$] + [4-N(CH$_3$)$_2$C$_6$H$_4$SH])}, and this is indeed the case (0.25 versus 0.22).

Mixtures of 4-YC$_6$H$_4$SH. Because desulfurization might be due to the formation of some specific reactive species from the 4-aminothiophenols that would desulfurize other thiophenols, two experiments were conducted using mixtures of thiophenols in 9,10-dihydroanthracene at 523 K. The results are compiled in Table 4.

In both mixtures, there was no desulfurization of 3-CF$_3$C$_6$H$_4$SH (just as there was no desulfurization of 4-CNC$_6$H$_4$SH and C$_6$H$_5$SH used alone under these conditions). The conversion of 4-CH$_3$OC$_6$H$_4$SH to C$_6$H$_4$OCH$_3$ was very slow, but it could be detected in both mixtures. The desulfurization of 4-NH$_2$C$_6$H$_4$SH in the presence of 4-CH$_3$OC$_6$H$_4$SH and 3-CF$_3$C$_6$H$_4$SH (32.8%) occurred to the same extent as in the absence of these two thiophenols (33%, see Table 2). From Table 4, it can be estimated that the rate of desulfurization of 4-NH$_2$C$_6$H$_4$SH is at least 300 times greater than the rate for 4-CH$_3$OC$_6$H$_4$SH, while the rate for 3-CF$_3$C$_6$H$_4$SH must be at least 3 orders of magnitude smaller.

Discussion

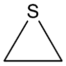
There is a remarkable difference in the thermal stability of ring-substituted thiophenols, YC$_6$H$_4$SH. For Y = 4-H, 4-CN, and 3-CF$_3$, the thiophenols are inert under the standard conditions of 523 K in 9,10-dihydroanthracene and a reaction time of 48 h. In contrast, for Y = 4-NH$_2$, 4-N(CH$_3$)(H), and 4-N(CH$_3$)$_2$, desulfurization to the responding anilines takes place at appreciable *and identical* rates. Desulfurization also occurs with 4-CH$_3$OC$_6$H$_4$SH, albeit at a rate which is at least 300 times slower than the rate for 4-NH$_2$C$_6$H$_4$SH. The possibility that the desulfurization of 4-NH$_2$C$_6$H$_4$SH follows a tautomerization/RRD mechanism (Scheme 2B) can be excluded for two simple reasons: (i) The thermolysis of 4-NH$_2$C$_6$H$_4$SCH$_2$C$_6$H$_5$ (**1**) actually does yield the product of a tautomerization/RRD mechanism, benzyl sulfide, **8** (Scheme 3), but only in a very low yield. (ii) Sulfur is extruded from 4-N(CH$_3$)$_2$C$_6$H$_4$SH, although tautomerization cannot occur.

Surprisingly, desulfurization does not require an external source of hydrogen (atoms) because the reaction decreased in efficiency along the solvent series: anthracene, hexadecane, 9,10-dihydroanthracene (see Table 2). Since the loss of sulfur from 4-NH$_2$C$_6$H$_4$SH follows first-order kinetics, the desulfurization of this compound could, most simply, be represented by reaction 9. However, a unimolecular elimination of atomic sulfur *cannot*

$$4\text{-NH}_2C_6H_4SH \rightarrow C_6H_5NH_2 + S \quad (9)$$

be the mechanism of desulfurization because reaction 9 has an enthalpy, ΔH_9, of about 60 kcal mol^{-1}.[8,23] If the activation enthalpy is assumed to have its minimum value of 60 kcal mol^{-1} and A_9 is assumed to have the very high value of 10^{15} s^{-1}, then k_9 will be 10^{-10} s^{-1} at 523 K, a value that is 5 orders of magnitude smaller than the experimental rate constant for this desulfurization at this temperature (i.e., $k_3 = 7.0 \times 10^{-6}$ s^{-1}; see Scheme 1). To fit the experimental rate constant using the same *A* factor would require an activation enthalpy of about 48 kcal mol^{-1}, which is at least 12 kcal mol^{-1} lower than the minimum value of E_9.

A similar problem exists for the thermal elimination of sulfur from thiirane, reaction 10.



$$\rightarrow C_2H_4 + S(^3P) \quad (10)$$

That is, $\Delta H_{10} = 59.1$ kcal mol^{-1},[8,20] but if the sulfur atom was formed in its excited singlet state for reasons of spin conservation, the required enthalpy would be even higher. However, the measured activation enthalpy in the gas phase is 40−42 kcal mol^{-1},[24] ruling out desulfurization by a simple unimolecular extrusion of atomic sulfur, despite the fact that the reaction is first order in thiirane.[24−27] Attempts to explain this anomaly have been inconsistent with experimental data. For example, Benson[20] suggested a complex chain reaction initiated by reaction 10, the atomic sulfur produced then attacks the thiirane to form S$_2$ which is the chain carrier and reacts with thiirane in the rate-determining step (rds), eq 11. The S$_2$ is

$$S + C_2H_4S \rightarrow C_2H_4 + S_2 \xrightarrow[\text{rds}]{C_2H_4S} C_2H_4 + S_3 \rightarrow\rightarrow S_8 \rightleftharpoons 4\,S_2 \quad (11)$$

in equilibrium with S$_8$. Such a mechanism can be ruled out on several grounds, most tellingly by the fact that Gunning and

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[23] The heat of formation, ΔH_f, of 4-NH$_2$C$_6$H$_4$SH can be calculated to be 26.95 kcal mol^{-1} using the isodesmic reaction: C$_6$H$_5$NH$_2$ + C$_6$H$_5$SH → 4-NH$_2$C$_6$H$_4$SH + C$_6$H$_6$ (computed reaction enthalpy, −0.91 kcal mol^{-1})[12] in conjunction with auxiliary thermodynamic data, cf. ΔH_f(C$_6$H$_5$SH) = 26.9 kcal mol^{-1}.[8] With a 4-NH$_2$C$_6$H$_4$S−H BDE of 76.5 kcal mol^{-1}, the ΔH_f(4-NH$_2$C$_6$H$_4$S$^\bullet$) = 51.4 kcal mol^{-1}.

[24] There have been three reports on the thermolysis of thiirane in the gas phase.[26−28] All are agreed that this reaction follows first-order kinetics, and the following Arrhenius parameters have been reported: log *A*/s^{-1}, E_a/kcal mol^{-1}; 13.2, 40.2;[25] 15.8, 42.4;[26] and 13.2, 40.9.[27]

[25] Lown, E. M.; Sandhu, H. S.; Gunning, H. E.; Strausz, O. P. *J. Am. Chem. Soc.* **1968**, *90*, 7164−7165. The reported activation entropy of −2.5 eu is in error. Recalculation using the rate constant of 3.70 × 10^{-5} s^{-1} at 498 K and E_a = 40.2 leads to a reaction entropy of −1.1 eu. In subsequent studies[26−28] on the thermolysis of thiirane, the erroneous value (−2.5 eu) has been quoted without comment.

[26] Amano, A.; Yamada, M.; Mizuuchi, K.; Kamo, T. *Kenkyu Hokoku: Asahi Garasu Kogyo Gijutsu Shoreikai* **1982**, *41*, 151−157.

[27] Yamada, M.; Kamo, T.; Tang, J.; Amano, A. *Nippon Kagaku Kaishi* **1987**, *60*, 1377−1384.

co-workers[25] demonstrated experimentally that atomic sulfur was not produced during the desulfurization of thiirane. Most recently, Steudel and co-workers[28] carried out a very thorough theoretical study of this reaction and concluded that the thermochemical requirements could be met by a bimolecular elimination of S_2 in its excited singlet state, reaction 12 (and even more favorably if the S_2 were eliminated from the

$$2\,C_2H_4S \xrightarrow{\text{rds}} \rightarrow C_2H_4 + C_2H_4S{=}S \rightarrow C_2H_4 + {}^1S_2 \quad (12)$$

intermediate thiirane-1-sulfide, $C_2H_4S{=}S$, in its triplet ground state, ${}^3S_2$). Of course, this would mean that the reaction would be second order in thiirane, a fact that forced these authors[28] to conclude that "the reported first-order rate law[25] is unlikely" to be correct. However, Gunning and co-workers[25] were highly experienced gas kineticists, and they would have been very unlikely to make an error of this magnitude. Moreover, later work (not cited by Steudel and co-workers[28]) has confirmed that the desulfurization of thiirane in the gas phase follows first-order kinetics.[26,27] Fortunately, as we show below in dealing with a possible mechanism of desulfurization of 4-aminothiophenols, a bimolecular formation of S_2 can still lead to overall first-order kinetics.

The bimolecular formation of S_2 (reaction 13) has ΔH_{13} =

$$2\ 4\text{-}NH_2C_6H_4SH \rightarrow 2\ C_6H_5NH_2 + S_2 \quad (13)$$

32.7 kcal mol^{-1}, if the S_2 is eliminated in its excited singlet state (18.4 kcal mol^{-1} if spin conservation is not obeyed and elimination yields S_2 in its triplet ground state).[8,23,29] We now assume that the ground state ${}^3S_2$ initiates a chain reaction with chain termination being proportional to [thiophenol]^2 because this leads to overall first-order kinetics. There are many possibilities.[31] One of the simplest is presented below, solely for illustrative purposes (reactions 14−19):

Chain Propagation:

$$ {}^3S_2 + 4\text{-}NH_2C_6H_4SH \underset{k_b}{\overset{k_f}{\rightleftharpoons}} 4\text{-}NH_2C_6H_4S{\uparrow}(SS{\uparrow})H \xrightarrow[\text{rds}]{k_p} 4\text{-}NH_2C_6H_4SSSH \quad (14)$$

$$4\text{-}NH_2C_6H_4S_xH \rightarrow C_6H_5NH_2 + S_x \qquad x = 3{-}6 \quad (15)$$

$$S_y + 4\text{-}NH_2C_6H_4SH \rightarrow 4\text{-}NH_2C_6H_4S_xH \qquad y = 3{-}5;\ x = y + 1 \quad (16)$$

$$S_6 \rightarrow S_4 + S_2 \quad (17)$$

$$S_4 + S_4 \rightarrow S_8 \text{ (and all the species } S_8 \text{ gives rise to at these temperatures)} \quad (18)$$

Chain Termination:

$$4\text{-}NH_2C_6H_4S{\uparrow}(SS{\uparrow})H + 4\text{-}NH_2C_6H_4SH \xrightarrow{k_t} 2\ C_6H_5NH_2 + S_4 \quad (19)$$

Analysis of this reaction scheme yields the overall first-order kinetic rate law, eq 20:

$$-\mathrm{d}[4\text{-}NH_2C_6H_4SH]/\mathrm{d}t = k_{13}k_p[4\text{-}NH_2C_6H_4SH]/k_t \quad (20)$$

Zwitterionic structures are a characteristic, and probably unique, feature of 4-aminothiophenols.[32,33] It therefore appears logical to attribute the extremely facile desulfurization of 4-aminothiophenols (relative to other thiophenols) to reactions involving their zwitterions. For example, the formal initiation reaction (13) could be presented as the reaction sequence 13a to 13d. In favor of such a mechanism is the well-known fact

$$4\text{-}NH_2C_6H_4SH \rightleftharpoons 4\text{-}N^+H_3C_6H_4S^- \quad (13a)$$

$$4\text{-}N^+H_3C_6H_4S^- + 4\text{-}NH_2C_6H_4SH \rightleftharpoons 4\text{-}N^+H_3C_6H_4SS^-(H)C_6H_4(4\text{-})NH_2 \quad (13b)$$

$$4\text{-}N^+H_3C_6H_4SS^-(H)C_6H_4(4\text{-})NH_2 \rightarrow 4\text{-}N^+H_3C_6H_4SS^- + C_6H_5NH_2 \quad (13c)$$

$$4\text{-}N^+H_3C_6H_4SS^- \rightarrow C_6H_5NH_2 + S_2 \quad (13d)$$

that thiolates are good nucleophiles and readily substitute divalent sulfur[34] (i.e., reaction 21).

$$RS^- + R'SX \rightarrow RSSR' + X^- \quad (21)$$

The rate-determining step in the above initiation sequence would probably be the (formal) proton shift from sulfur to the aromatic carbon in reaction 13c with $4\text{-}N^+H_3C_6H_4SS^-$ being the leaving group, X^-. For the first step in the chain propagation, reaction 14, the presence of zwitterions may again provide a rationale for the unexpectedly facile desulfurization of 4-aminothiophenols. This is because the intermediate obtained after the addition of ${}^3S_2$ will be in equilibrium with its zwitterionic counterpart (reaction 14a) which will provide additional stabilization to

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[28] Steudel, Y.; Steudel, R.; Wong, M. W. *Chem.—Eur. J.* **2002**, *8*, 217−228.

[29] From experimental studies, the energy difference between ${}^1S_2$ and ${}^3S_2$ has been estimated as 13 ± 2 kcal mol^{-1};[30] according to G3(MP2) level computations the energy difference is 15.5 kcal mol^{-1}.[28] We use $\Delta H_f({}^1S_2) = \Delta H_f({}^3S_2) + 14.3$ (average value) $= 30.7^{20} + 14.3 = 45.0$ kcal mol^{-1}.

[30] Carleer, M.; Colin, R. *J. Phys. B* **1970**, *3*, 1715−1723.

[31] Calculated reaction enthalpies for some of the possible reactions follow. The S−C BDE in $C_6H_5SS^\bullet$ is given as 60 kcal mol^{-1},[20] which, combined with a S−H BDE in C_6H_5SSH of 70 kcal mol^{-1},[20] leads to $\Delta H_f(C_6H_5SSH) \approx \Delta H_f(4\text{-}NH_2C_6H_4SSH) = 32.5$ kcal mol^{-1}.[8,23] Insertion of S in $H_2S_2 \rightarrow H_2S_3$ or $H_2S_3 \rightarrow H_2S_4$ increases the $\Delta H_f(H_2S_3)$ by 3.6 and $\Delta H_f(H_2S_4)$ by 3.2 kcal mol^{-1}, respectively. With this increment for S insertion, the $\Delta H_f(4\text{-}NH_2C_6H_4SSSH)$ is estimated as 32.5 + 3.4 (average) = 35.9 kcal mol^{-1}. The overall enthalpy change for ${}^3S_2 + 4\text{-}NH_2C_6H_4SH \rightarrow 4\text{-}NH_2C_6H_4SSSH$ (reaction 14) is calculated to be $35.9 - 30.7^{20} - 26.95^{23} = -21.8$ kcal mol^{-1}. The reaction enthalpy for S−S cleavage, $4\text{-}NH_2C_6H_4SSSH \rightarrow 4\text{-}NH_2C_6H_4S^\bullet + HS_2^\bullet$, is $51.4^{23} + 22.1^{20} - 35.9 = 37.6$ kcal mol^{-1}; this means that under our thermal conditions the homolysis reaction is fast. However, the reaction enthalpy for the S_3 extrusion, $4\text{-}NH_2C_6H_4SSSH \rightarrow C_6H_5NH_2 + S_3$, reaction 15, $x = 3$, is only $20.8^8 + 32.5^{20} - 35.9 = 17.4$ kcal mol^{-1}. In view of the large difference in the reaction enthalpies for S−S cleavage in and for S_3 extrusion from $4\text{-}NH_2C_6H_4SSSH$, ca. 20 kcal mol^{-1}, it seems most likely that the S_3 extrusion reaction prevails.

[32] We thank an anonymous reviewer for pointing out the presence of zwitterions.

[33] 4-Aminothiophenol exists in the solid state and in the liquid state as the zwitterion: Jetti, R. K. R.; Boese, R.; Thakur, T. S.; Vangala, V. R.; Desiraju, G. R. *Chem. Commun.* **2004**, 2526−2527.

[34] (a) Pryor, W. A. *Mechanisms of Sulfur Reactions*; McGraw-Hill: New York, **1962**. (b) Peach, M. E. In *The Chemistry of the Thiol Group*; Patai, S., Ed.; Wiley: New York, 1974; Chapter 16.

$4\text{-}NH_2C_6H_4S^{\uparrow}(SS^{\uparrow})H$ (and its singlet) and make the addition of $^3S_2$ less reversible. It is also possible that the 4-aminothiophenols

$$4\text{-}NH_2C_6H_4S{\uparrow}(SS{\uparrow})H \rightleftharpoons 4\text{-}N^+H_3C_6H_4S^-{\uparrow}(SS{\uparrow}) \quad (14a)$$

show unique desulfurizartion properties because the zwitterions both eliminate polysulfur (reaction 15a) and add polysulfur (reaction 16a) more readily than non-zwitterionic thiophenols.[35]

$$4\text{-}N^+H_3C_6H_4S_x^- \rightarrow C_6H_5NH_2 + S_x \quad (15a)$$

$$S_y + 4\text{-}N^+H_3C_6H_4S^- \rightarrow 4\text{-}N^+H_3C_6H_4S_x^- \quad (16a)$$

This could explain why, in a reaction mixture containing $4\text{-}NH_2C_6H_4SH$ and two other thiophenols, only the aminothiophenol underwent desulfurization (see Table 4).

The foregoing "illustrative" desulfurization of 4-aminothiophenol by a chain reaction would be subject to autocatalysis by the generated elemental sulfur (see the equilibrium in eq 11, i.e., $S_8 \rightleftharpoons 4\ S_2$). However, Benson[20] has pointed out in his discussion of the mechanism of desulfurization of thiirane that such a rate acceleration would be proportional to $[S_8]^{1/4}$ so that a 4-fold change in $[S_8]$ would produce only a 40% change in $[S_2]$. If such autocatalysis occurs during the thermal desulfurization of 4-aminothiophenols, it was not detected possibly because sulfur quickly reaches its solubility limit.

Experimental Section

Materials. The synthesis of $4\text{-}NH_2C_6H_4SCH_2C_6H_5$, **1**, has been reported.[12]

Synthesis of 4-Dimethylaminophenyl-1-Phenylethyl Sulfide, 11: Originally we tried to synthesize $4\text{-}N(CH_3)_2C_6H_4SCH_2C_6H_5$ from $NH_2C_6H_4SCH_2C_6H_5$. Two attempts were made, but the final product contained an additional methyl group at the benzylic carbon. The first followed a literature procedure[37] and used $(CH_3O)_3PO$ as the methylating reagent. It gave a complex mixture containing (according to GC/MS) $4\text{-}N(CH_3)_2C_6H_4SCH_3$, $4\text{-}N(CH_3)_2C_6H_4SC_6H_4\text{-}CH_3$, $4\text{-}N(C_6H_5CH_2)(CH_3)C_6H_4SCH_2C_6H_5$, and $4\text{-}N(C_6H_5CH_2)_2C_6H_4\text{-}SCH_2C_6H_5$, with only minor amounts of $4\text{-}N(CH_3)_2C_6H_4SCH_2C_6H_5$ and $4\text{-}N(CH_3)_2C_6H_4SCH(CH_3)C_6H_5$. It appeared impossible to isolate a sufficient quantity of the desired compound from this mixture by standard preparative chromatographic methods.

The second attempt involved the addition of *n*-butyllithium (2.0 M in hexanes, 5.2 mL, 10.32 mmol) dropwise via syringe to a colorless solution of 4-aminophenyl benzyl sulfide (1.11 g, 5.16 mmol) in anhydrous THF (20 mL) at 0 °C. The reaction mixture, which turned dark green when the addition was complete, was stirred at 0 °C for 2 h. Methyl iodide (0.64 mL, 10.32 mmol) was then added dropwise via syringe, and the resulting dark-brown solution was stirred at 0 °C for 2 h then at room temperature overnight. The reaction mixture was poured onto ice water and extracted with ethyl acetate (3 × 30 mL), and the combined organics were washed with brine, dried with anhydrous magnesium sulfate, and concentrated by rotary evaporation to give 1.30 g of crude product as a liquid. GC/MS showed that the crude product consisted mainly of $4\text{-}N(CH_3)_2C_6H_4SCH(CH_3)C_6H_5$ (60%) and that the desired $4\text{-}N(CH_3)_2C_6H_4SCH_2C_6H_5$ was not present. Further purification by preparative TLC (hexanes/EtOAc = 3:1) afforded a mixture of $4\text{-}N(CH_3)_2C_6H_4SCH(CH_3)C_6H_5$ (90%) and $4\text{-}N(CH_3)_2C_6H_4SCH\text{-}(C_4H_9)C_6H_5$ (10%) according to ^1H and ^{13}C NMR and GC/MS analysis (see Supporting Information).

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Supporting Information Available: General experimental and analytical methods; possible routes for the non-observed induced decomposition of $4\text{-}NH_2C_6H_4SCH_2C_6H_5$; ^1H and ^{13}C spectra of $4\text{-}N(CH_3)_2C_6H_4SCH(CH_3)C_6H_5$ containing 10% $4\text{-}N(CH_3)_2C_6H_4\text{-}SCH(C_4H_9)C_6H_5$ as the impurity, including their mass spectra; mass spectra of some products listed in Table 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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[35] In previous work, we have demonstrated that the reduction of a carbonyl group to a CH_2 group at high temperatures in nonpolar hydrogen atom donor solvents follows an ionic mechanism.[36]

(36) Mulder, P.; Hemmink, S.; De Heer, M. I.; Lupo, M.; Santoro, D.; Korth, H.-G. *J. Org. Chem.* **2001**, *66*, 6611−6619.

(37) Vogel, A. I.; Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*; Longman: New York, 1989.