

GAS PHASE THERMOLYSIS OF *N*-(*tert*-BUTYLTHIO)ALLYLAMINE AND *N*-(*tert*-BUTYLTHIO)DIETHYLAMINE

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The title sulphenamides were pyrolysed in a stirred-flow reactor at temperatures of 310–410 °C, pressures of 8–15 Torr and residence times of 0.4–2 s using toluene as the carrier gas. *N*-(*tert*-Butylthio)allylamine formed 73 ± 4% isobutene, 23 ± 3% propene and *N*-allylthiohydroxylamine. The first-order rate coefficients for the formation of isobutene and propene, respectively, followed the Arrhenius equations $k_{C4}(s^{-1}) = 10^{12.52 \pm 0.36} \exp(-163 \pm 5 \text{ kJ mol}^{-1} RT)$ and $k_{C3}(s^{-1}) = 10^{10.99 \pm 0.29} \exp(-151 \pm 4 \text{ kJ mol}^{-1} RT)$. *N*-(*tert*-Butylthio)diethylamine gave 97 ± 1% isobutene, 1.9 ± 0.4% isobutane and *N,N*-diethylthiohydroxylamine. The first-order rate coefficients for isobutene elimination followed the Arrhenius equation $k(s^{-1}) = 10^{13.45 \pm 0.24} \exp(-164 \pm 3 \text{ kJ mol}^{-1} RT)$. The formation of the products is interpreted in terms of an elimination reaction with a unimolecular, four-centered, cyclic transition state. The reactivity of these sulphenamides was found to be much higher than that of previously studied alkyl or aryl *tert*-butyl sulphides and disulphides.

INTRODUCTION

Previous work^{1–6} reported on the pyrolysis of compounds with the structure Bu^t–X–R for X = O, S and NH and R = alkyl, aryl or substituted aryl groups. These reactions produce isobutene and the corresponding HXR moiety by a first-order process, with Arrhenius parameters suggesting that four center cyclic transition states are involved in the mechanisms. The most reactive system corresponded to X = S, with activation energies in the range 185–238 kJ mol^{–1} and frequency factors of 10^{13 ± 1} s^{–1}. The effects of electron-donating and electron-attracting substituents in the group R on the reactivity of these molecules^{1,4} support the quadrupolar transition-state model.⁷ In this respect, the X–C bond polarization in the sense $\delta^{-}X-C^{\delta+}(Me)_3$ should be aided by electron withdrawal from X by the group R, as has been observed by the increase in reactivity in all these systems when R is a group capable of stabilizing partial charges by conjugative interaction, an example of this being a benzene ring bearing a –M substituent group. In the present work, *N*-(*tert*-butylthio)allylamine (BTAA) and *N*-(*tert*-butylthio)diethylamine (BTEA) were chosen to examine the reactivity of systems with a nitrogen atom attached to the sulphur atom and the possible formation of *S*-unsubstituted thiohydroxylamines by elimination of isobutene.

EXPERIMENTAL

BTAA and BTEA were synthesized by a method similar to that reported for *N*-alkyl-*N*-alkylthioamines.⁸ They were purified by several trap-to-trap vacuum fractionations and collected at –30 °C. The purity of the synthesized compounds was confirmed to be 99% or better by GLC as reported.¹ The gas hydrocarbon products were analysed in two columns, one 2 m × 3.2 mm o.d. packed with 60–80-mesh activated alumina at 170 °C and the other 1 m × 3.2 mm o.d. packed with 150–200-mesh Porapak Q at 100 °C. Thiol products were quantified by adding an excess of 0.1 M silver nitrate solution, filtering the silver mercaptide precipitate and titrating the filtrate using Volhard's method.⁹ The experimental technique, reaction order measurement and rate coefficient calculation have been reported in detail.^{4,5,10} The structures of reactants and products were confirmed by 1H NMR and mass spectrometry using Bruker AM300 and Kratos RFA25 GLC–MS instruments, respectively. The AM1 computations were made in a RISK 6000 Model 530 workstation.

RESULTS

The reaction orders for BTEA and BTAA consumption were 1.0 ± 0.1 and 1.1 ± 0.2, measured at 350 and 390 °C, with a 2.3-fold increase of reactant inflow,

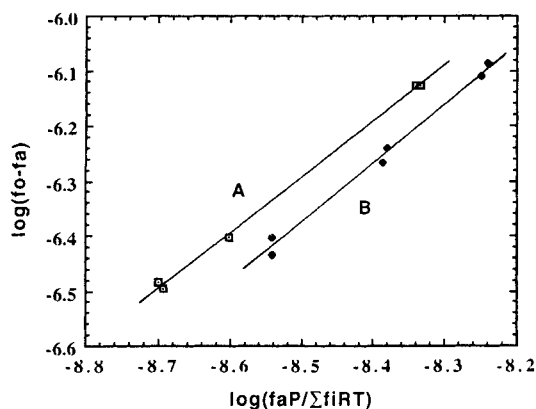


Figure 1. Reaction order plots. (A) BTEA; (B) BTAA. f_0 = reactant inflow; f_a = reactant outflow; Σf_i = total outflow; P = total pressure; R = gas constant; T = absolute temperature

respectively, for up to 30% reaction. The corresponding order plots are shown in Figure 1. Over the temperature range 311–350 °C, BTEA yielded a gas product mixture composed of $97 \pm 1\%$ isobutene plus $2.0 \pm 0.4\%$ isobutane. In the liquid production fraction, collected at -78°C , a product containing the SH moiety was quantitatively titrated. The ^1H NMR spectrum of this fraction distinctively showed the signals of a mixture of unreacted BTEA and another compound having only the signals of ethyl groups and a SH proton. The positions of all the signals of pure BTEA and those of the latter mixture were concentration dependent. [^1H NMR (300.133 MHz, CDCl_3 , TMS ext., room temperature), $5\ \mu\text{l}$ of BTEA in $0.4\ \text{ml}$ of CDCl_3 , δ 1.01 (t, $^3J_{\text{HH}} = 7.08\ \text{Hz}$, 2CH_3 , 6H), 1.14 (s, $3\ \text{CH}_3$, 9H), 2.90 (quad., $^4J_{\text{HH}} = 7.08$, 2CH_2 , 4H); run 80% conversion, $(\text{CH}_3\text{CH}_2)_2\text{NSH}$, δ 1.25 (t, $^3J_{\text{HH}} = 7.27$, 2CH_3 , 6H), 1.67 (bs, 1H), 2.88 (quad., $^4J_{\text{HH}} = 7.23$, 2CH_2 , 4H)]. The molar product distribution shown in Table 1 suggests that this thiol product and isobutene are formed in similar amounts. A small residue of involatile material remaining in the first cold trap gave a mass spectrum indicating the presence of free sulphur (S_8) plus complex sulphur-containing products (the signal of the largest m/z ratio was 429). The first-order rate coefficients were evaluated from the rate of production of isobutene. These coefficients are listed in Table 2 for a representative number of runs, together with the experimental conditions.

At temperatures of 368–410 °C, BTAA formed $73 \pm 4\%$ isobutene, $23 \pm 3\%$ propene plus less than 1% C_2 hydrocarbons. As in the above case of BTEA pyrolysis, a thiol compound was titrated in the liquid products fraction in the amounts shown in Table 3. Table 4 shows a sample of the first-order rate coeffi-

Table 1. *N*-(*tert*-Butylthio)diethylamine product distribution

mol $\times 10^4$			
<i>i</i> -C ₄ H ₁₀	<i>i</i> -C ₄ H ₈	DETH ^a	<i>T</i> (°C)
0.047	3.03	3.05	311.5
0.039	2.34	2.10	311.5
0.050	2.17	2.23	319.8
0.052	3.02	2.96	319.8
0.044	3.02	2.91	320.0
0.046	2.55	2.56	329.3
0.071	2.88	3.07	340.3
0.075	5.04	4.75	349.8
0.058	4.44	4.45	351.0

^a DETH = *N,N*-diethylthiohydroxylamine.

Table 2. Stirred-flow pyrolysis of *N*-(*tert*-butylthio)diethylamine

<i>T</i> (°C)	$k \times 10^4$ (s ⁻¹) ^a	Θ (s) ^b	% <i>r</i> (C ₄ H ₈) ^c	<i>P</i> (Torr)	$f_{0A} \times 10^8$ (mol s ⁻¹) ^d	f_c/f_{0A} ^e
311.4	710	1.94	12.12	15.0	148.5	37
311.4	689	1.95	12.16	15.3	119.4	46
319.8	1146	1.30	13.01	14.0	140.2	54
320.0	1136	1.26	12.55	13.6	201.6	37
330.4	1828	1.32	19.41	14.5	104.5	73
330.7	1943	0.80	13.48	9.5	219.2	37
340.5	3219	0.84	21.23	9.7	152.3	51
340.3	3052	0.91	21.70	9.5	106.2	67
351.0	5960	0.81	32.46	9.6	121.5	65
350.8	5932	0.78	31.74	9.6	100.6	82
350.5	6001	0.78	31.85	9.9	243.5	36

^a Rate coefficient from isobutene measurement.

^b Residence time.

^c Percentage reaction from isobutene measurement.

^d Reactant inflow.

^e Toluene to reactant flow ratio.

Table 3. *N*-(*tert*-Butylthio)allylamine product distribution

mol $\times 10^4$				
C ₃ H ₆	<i>i</i> -C ₄ H ₁₀	<i>i</i> -C ₄ H ₈	ATH ^a	<i>T</i> (°C)
1.22	0.067	4.02	3.95	379.8
1.13	0.110	4.30	4.65	380.0
0.98	0.079	3.24	3.35	380.7
1.18	0.128	3.79	3.65	390.2
1.07	0.064	3.83	3.65	389.6
0.78	0.051	2.71	2.65	389.7
0.79	0.079	2.54	2.35	389.4
1.56	0.093	5.10	4.85	390.8
1.56	0.133	5.00	5.15	399.9
1.59	0.081	4.99	5.10	399.2
1.09	0.041	3.61	3.25	399.6
1.50	0.035	4.93	4.75	410.9
1.48	0.069	5.19	5.25	409.0

^a ATH = *N*-allylthiohydroxylamine.

Table 4. Stirred-flow pyrolysis of *N*-(*tert*-butylthio)allylamine

<i>T</i> (°C)	<i>k</i> × 10 ⁴ (s ⁻¹) ^a	<i>k</i> × 10 ⁴ (s ⁻¹) ^f	Θ (s) ^b	% <i>r</i> (C ₄ H ₈) ^c	% <i>r</i> (C ₃ H ₆) ^g	<i>P</i> (Torr)	<i>f</i> _{0A} × 10 ⁸ (mol s ⁻¹) ^d	<i>f</i> _c / <i>f</i> _{0A} ^e
368·6	1725	429	0·73	11·16	3·03	9·81	235·0	37
368·9	2084	536	0·67	12·20	3·45	9·63	280·0	33
380·0	2969	783	0·76	18·47	5·64	11·76	253·2	38
380·7	2967	773	0·77	18·69	5·65	12·41	197·1	51
390·2	4961	1304	0·53	20·80	6·46	10·83	260·7	49
389·4	4786	1276	0·53	20·09	6·28	10·76	182·4	70
390·3	5165	1359	0·46	19·36	5·94	10·54	400·8	35
399·9	7521	1825	0·55	29·11	9·06	10·76	233·4	52
399·6	7318	1723	0·56	29·09	8·81	11·12	170·9	72
409·0	11955	2420	0·47	36·17	10·29	8·60	177·6	62
409·8	11449	2719	0·43	33·04	10·45	7·80	322·7	34

^{a-c} See Table 2.^f Rate coefficient from propene measurement.^g Percentage reaction from propene measurement.

Table 5. Kinetic parameters

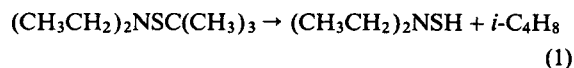
Substrate	<i>E</i> _a (kJ mol ⁻¹)	Log <i>A</i>	Δ <i>S</i> ⁺ ^a	<i>k</i> × 10 ² ^b	<i>k</i> ^c	Ref.
<i>t</i> -C ₄ H ₉ SNHCH ₂ CH=CH ₂ ^d	163 ± 5	12·52 ± 0·36	-26	74·8	32·3	This work
<i>t</i> -C ₄ H ₉ SNHCH ₂ CH=CH ₂ ^e	151 ± 4	10·99 ± 0·29	-50	18·8	6·20	This work
<i>t</i> -C ₄ H ₉ SN(C ₂ H ₅) ₂	164 ± 3	13·45 ± 0·24	-2·5	532	235	This work
<i>t</i> -C ₄ H ₉ SCH ₃	238 ± 4	14·49 ± 0·28	17	0·01	0·03	3
<i>t</i> -C ₄ H ₉ SCH ₂ C≡CH	203 ± 3	13·79 ± 0·24	4	1·10	1·20	4
<i>t</i> -C ₄ H ₉ SCH ₂ CN	202 ± 4	12·63 ± 0·23	-18	0·09	0·10	6
<i>t</i> -C ₄ H ₉ SC ₆ H ₅	188 ± 6	12·03 ± 0·39	-30	0·28	0·21	5
<i>t</i> -C ₄ H ₉ SCH ₂ C ₆ H ₅	214 ± 6	13·82 ± 0·41	5	0·16	0·23	5
<i>t</i> -C ₄ H ₉ SSC ₆ H ₅	182 ± 4	13·49 ± 0·31	-2	0·16	0·23	2
CH ₂ =CH(CH ₂) ₂ OH	170	11·64	-37	2·82	1·43	12
CH≡C(CH ₂) ₂ OH	167	11·2	-45	1·75	0·83	12

^a J mol⁻¹ K⁻¹ at 400 °C.^b Calculated rate coefficient (s⁻¹) at 400 °C.^c Calculated rate coefficient (s⁻¹) at 500 °C.^d From isobutene measurement.^e From propene measurement.

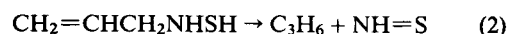
cients obtained from isobutene and propene formation, respectively, and the experimental conditions. The Arrhenius parameters derived from the respective least-squares fits of the rate coefficients for BTEA and BTAA are given in Table 5 together with other relevant data from the literature. The error limits correspond to the standard error.¹¹

DISCUSSION

The molar product distribution for BTEA (Table 1) suggests the stoichiometry represented by equation (1) for the first-order consumption of this reactant:



The Arrhenius parameters for this process (Table 5) are consistent with a four-centre cyclic transition-state unimolecular elimination mechanism. Two processes, however, seem to be involved in the pyrolysis of BTAA. The primary one would involve the elimination of isobutene by a reaction similar to reaction (1). The measured Arrhenius parameters (Table 5) again agree with a four-centre cyclic transition-state mechanism. A consecutive reaction, involving the decomposition of the *N*-allylthiohydroxylamine product, according to equation (2), could explain the formation of propene.



Process (2) would involve a retro-ene reaction with a 1,5 H-atom transfer similar to that reported for β-hydroxyolefins.¹² The Arrhenius parameters (Table 5)

Table 6. Mass spectral data

BTAA		BTEA	
<i>m/z</i>	Relative intensity (%)	<i>m/z</i>	Relative intensity (%)
57	100	90	100
41	58.3	105	70.7
89	55.1	57	44.0
43	23.5	41	21.3
56	19.1	161 (M ⁺)	8.0
145 (M ⁺)	16.9		
39	14.4		

obtained from the rate coefficients for the production of propene have the expected values for a six-centre cyclic transition-state mechanism, such as those shown in Table 5 for the pyrolyses of but-3-en-1-ol and but-3-yn-1-ol. The HNS moiety can be expected to form complex, non-volatile oligomeric products.

The above reaction scheme for BTAA implies a material balance in which the moles of isobutene formed should be equal to the moles of propene plus *N*-allylthiohydroxylamine. However, the product distribution shown in Table 3, indicates an excess of the latter product. The titration of *N*-allylthio-

hydroxylamine may not be quantitative owing to complexation of the Ag⁺ cation with the allyl-NH moiety.¹³ It was noticed that the initially white precipitate of silver mercaptide turns dark very quickly, indicating a high instability.

In relation to the isobutene elimination mechanism proposed above, it is interesting to consider the most relevant peaks in the mass spectra of BTEA and BTAA, shown in Table 6. The peaks of *m/z* ratio which can be assigned to *N,N*-diethyl- and *N*-allylthiohydroxylamines, 105 and 89, respectively, are prominent, suggesting as in the case of other *tert*-butyl sulphides and disulphides^{2,14,15} that the same 1,3 H-atom transfer from the *tert*-butyl group to the S atom occurs under electron impact conditions. It was not possible to obtain the mass spectra of the pure thiohydroxylamines because they seemed to decompose during the elution through the capillary column of the GLC-MS instrument.

In Figure 2 are shown the net atomic charges in the optimized ground-state configuration of BTEA, obtained by the AM1 calculation procedure.^{16,17} A similar charge distribution was obtained for BTAA. Table 7 shows selected parameters obtained from these calculations for BTEA and BTAA, and also for thiohydroxylamine, diethylthiohydroxylamine and allylthiohydroxylamine. The values in Figure 2 indicate that the bonding of the more electronegative N atom to

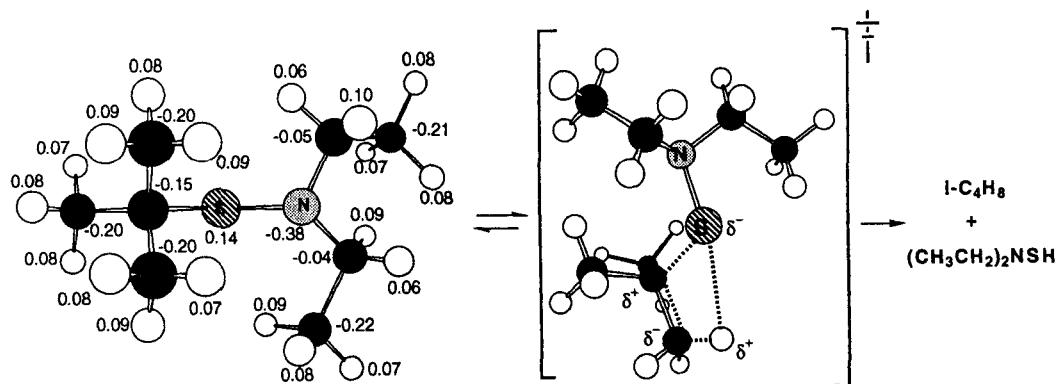


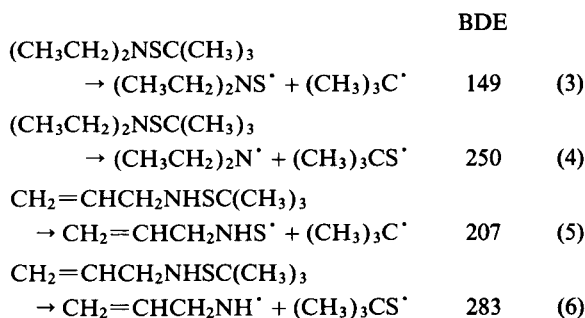
Figure 2. Net atomic charges in BTEA (atomic units) and transition-state configuration

Table 7. Selected parameters from AM1-optimized molecular geometries^a

Parameter	BTEA	BTAA	DETH	DETS	ANSH	ANS	H ₂ NSH	H ₃ NS
ΔH_{f298}° (kJ mol ⁻¹)	-91.79	4.618	-4.465	92.16	93.88	197.97	6.94	111.4
Total energy (eV)	-1688.14	-1504.29	-1065.08	-1064.08	-881.20	-880.13	-442.81	-441.73
Ionization potential (eV)	8.339	8.401	8.673	7.794	8.830	8.013	8.763	8.169

^a DETH = (C₂H₅)₂NSH; DETS = (C₂H₅)₂NHS; ANSH = CH₂=CHCH₂NSH; ANS = CH₂=CHCH₂NHS.

the S atom causes the atomic charges in the *t*-C₄H₉S moiety of these molecules to be different from those previously reported^{1,2} for *tert*-butylarylamines, ethers, sulphides and disulphides. If the ground and transition states in BTEA and BTAA have similar charge distributions, the polarities of the latter would be different to those proposed⁷ for the quadrupolar transition-state model. However, in the case of BTEA and BTAA, a charge redistribution may take place during the C—S bond-breaking step, so that the S atom, being electronegative, receives electronic density from the *tert*-butyl C atom. The transition state would then be as represented in Figure 2. BTEA and BTAA are much more reactive than the Bu^t-X-R systems mentioned earlier, as can be seen in Table 5 for the sulphides and disulphides. This higher reactivity suggests that the Bu^t-S bond-breaking step in BTEA and BTAA should be more facile than in those other systems. An estimation of the homolytic bond dissociation energy (BDE) for reactions (3)–(6) by using the ΔH_{f298}° values given in Tables 7 and 8 yield the values (kJ mol⁻¹) shown at the right-hand side of the equations.



The C—S BDE for PhS—Bu^t and MeS—Bu^t have been estimated^{3,5} as 247 and 290 kJ mol⁻¹, respectively. The BDE values for reactions (4) and (6) suggest that the N—S bond fission should be less facile; however, the presence of about 2% isobutane as pyrolysis product of BTEA implies the formation of *tert*-butyl radicals, so reaction (3) occurs to a small extent.

The literature on the synthesis and properties of S-

unsubstituted thiohydroxylamines is very scarce.^{20–23} It has been reported^{21,22} that the most stable isomer of thiohydroxylamine is possibly H₃NS. However, the microwave spectrum of H₂NSH has been studied.²³ The AM1 calculations in the present work (Table 7) yield total energy values and enthalpies of formation for these thiohydroxylamines which suggest that the thiol isomer should be the more stable one. For the compound H₃NS, a $\Delta H_{f298}^\circ \leq 109$ kJ mol⁻¹ has been reported,²⁴ in fair agreement with the value calculated in this work.

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Table 8. Enthalpies of formation (kJ mol⁻¹)

Species	ΔH_{f298}°	Ref.
(CH ₃ CH ₂) ₂ NS [•]	8 ^a	18
<i>t</i> -C ₄ H ₉ [•]	49 ± 2	19
(CH ₃ CH ₂) ₂ N [•]	129 ^a	18
<i>t</i> -C ₄ H ₉ S [•]	29	2
CH ₂ =CHCH ₂ NHS [•]	163 ^a	18
CH ₂ =CHCH ₂ NH [•]	258 ^a	18

^a Estimated by using the group additivity method of Ref. 18.

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