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Gas-phase thermolysis of *N*-methyl-*N*-phenyl-*tert*-butylsulfenamide and morpholinyl-*tert*-butylsulfenamide

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ABSTRACT: *N*-Methyl-*N*-phenyl-tert-butylsulfenamide (MPSA) and morpholinyl-tert-butylsulfenamide (MOSA) were thermolyzed in a stirred-flow reactor at temperatures of 340–390 °C and pressures of 7–13 Torr, using toluene as carrier gas, at residence times of 0.3–1.3 s. Isobutene was formed in 99% yield through first-order reactions having the following Arrhenius parameters (A,s^{-1}, E_a, kJ mol^{-1}): MPSA, log $A = 12.41 \pm 0.02$, $E_a = 158.8 \pm 0.2$; MOSA, log $A = 12.91 \pm 0.22$, $E_a = 159 \pm 3$. It is proposed that the elimination of isobutene takes place by unimolecular reaction mechanisms involving polar, four-center cyclic transition states, forming *S*-unsubstituted thiohydroxylamines as co-products. Thermochemical parameters, estimated by semiempirical AM1 calculations, are reported for the latter and for the parent molecules. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: gas-phase thermolysis; *N*-methyl-*N*-phenyl-*tert*-butylsulfenamide; morpholinyl-*tert*-butylsulfenamide

INTRODUCTION

Recent studies[1,2] on the gas-phase thermolyses of various alkyl *tert*-butylsulfenamides suggested that these systems decompose unimolecularly by mechanisms involving four-center cyclic transition states, with the formation of isobutene plus a hydrosulfenamide. Although the magnitudes of the Arrhenius frequency factors obtained for these reactions are within the range expected for such mechanisms ($10^{13.5 \pm 1.0}$ s^{-1}), they result in entropies of activation of -20 to $+20$ J K^{-1} mol^{-1}, a range too wide if these systems have very similar transition states. To reassess these previous results with new data, and to investigate further the influence of the amine moiety of the molecule on the reactivity, the thermolyses of *N*-methyl-*N*-phenyl-tert-butylsulfenamide (MPSA) and morpholinyl-*tert*-butylsulfenamide (MOSA) were studied in the present work.

EXPERIMENTAL

The *tert*-butylsulfenamides were synthesized by reaction of a hexane solution of 2-methyl-2-propanesulfenyl chloride with *N*-methylaniline or morpholine.[3] MPSA was purified by eluting with hexane through a 50×2.5 cm o.d. activated alumina column (yield 40%, 99.5% purity). MOSA was obtained in 66% yield, 99.2% purity, after reduced pressure distillation (b.p. 76–78 °C, 0.5 Torr). The mass (70 eV) and ^{1}H NMR (300.133 MHz, $CDCl_3$, external TMS, room temperature) spectra were as follows: MPSA: [*m/z* (%)] 195 (M^+) (22), 139 (100), 106 (64), 77 (37), 57 (40), 41 (21); ^{1}H NMR δ 7.23 (m, 2H arom.) 6.80 (m, 1H arom.) 6.61 (m, 2H arom.) 3.44 (s, CH_3, 3H) 1.28 ($3CH_3$, 9H); MOSA [*m/z* (%)] 175 (M^+) (14), 119 (94), 91 (16), 75 (34), 57 (100), 41 (44); ^{1}H NMR δ 3.64 (t, $^3J_{HH}$ 4.62 Hz, $2CH_2$, 4H), 2.93 (t, $^3J_{HH}$ 4.65 Hz, $2CH_2$, 4H), 1.20(s, $3CH_3$, 9H). GLC, MS and NMR analyses of the reactants and products were carried out using the same instruments previously reported[4]. The thiol-type products were quantified using Volhard's method[5] by collecting the reactor effluent in excess 0.1 M silver nitrate solution. The kinetics were measured in a 265 ml capacity spherical quartz stirred-flow reactor[6] by injecting 0.05–0.1 M solutions of the reactants in toluene by means of a precision peristaltic pump. The reaction order was examined by logarithmic plots of the equation[4,7] f_o-$f_a = kV(f_aP/RT\Sigma f_i)^a$, where f_o and f_a are the inflow and outflow of reactant, Σf_i is the total outflow in mol s^{-1}, V, P and T are the volume, pressure and absolute temperature of the reactor, respectively, R is the universal gas constant and a gives the order of the reaction with respect to the concentration of the reactant. First-order rate coefficients were calculated using the expression[4,7] $k = F/\theta(1-F)$, where F is the fraction reacted and θ the residence time given by $\theta = PV/RT\Sigma f_i$.

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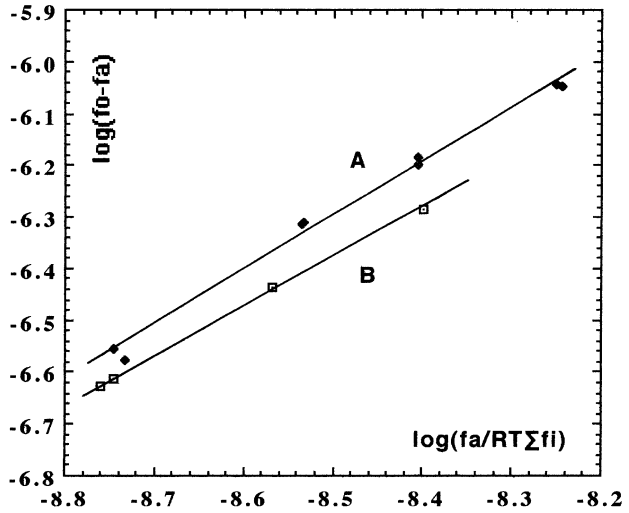


Figure 1. Reaction order plots: (A) MPSA; (B) MOSA

Table 1. MPSA and MOSA reaction product distributions (10^4 mol)

Reactant	Run No.	T (°C)	iC_4H_8	RNSH[a]
MPSA	10	351	2.22	1.83
	8	362	1.84	1.45
	3	370	2.01	2.72
	5	380	3.84	3.22
	1	391	3.19	2.22
MOSA	5	341	5.10	4.80
	10	350	6.07	5.52
	16	360	9.29	8.12
	23	371	7.90	7.29
	19	380	6.74	6.57

[a] RNSH means *N*-methyl-*N*-phenylhydrosulfenamide and morpholinylhydrosulfenamide for MPSA and MOSA, respectively.

RESULTS

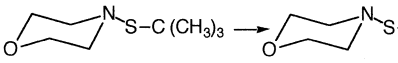
From the slopes of the plots shown in Fig. 1 the following initial orders for reactant consumption were obtained, at the indicated temperature, per cent reaction and variation of reactant inflow (Δf_o). MPSA, 0.95 ± 0.02 (380 °C, 25%, Δf_o = 2.2-fold); MOSA, 1.05 ± 0.05 (360 °C, 43%, Δf_o = 3.6-fold). Over the temperature range 340–390 °C MPSA formed a gaseous product mixture of $98.9 \pm 0.4\%$ isobutene, $0.8 \pm 0.3\%$ isobutane and $0.3 \pm 0.1\%$ C_2–C_3 hydrocarbons, while the MOSA gaseous product mixture was $99.2 \pm 0.7\%$ isobutene, 0.4% isobutane and 0.4% C_2–C_3 hydrocarbons. In the liquid product fractions from both MPSA and MOSA, collected at −78 °C, a thiol-type product was titrated in the amounts shown in Table 1. These products formed white precipitates with silver nitrate solution. These analyses (Table 1) indicated that, within experimental error, MPSA decomposed mainly into $53 \pm 6\%$ isobutene plus $47 \pm 6\%$ thiol whereas MOSA decomposed into $52 \pm 1\%$ isobutene plus $48 \pm 1\%$ thiol.

For both MPSA and MOSA, first-order rate coefficients were calculated assuming a stoichiometry of two product molecules formed from each decomposed reactant molecule. These are shown in Table 2 for representative runs. The Arrhenius parameters for MPSA and MOSA, derived from least-squares linear fits of the rate coefficients, are shown in Table 3, together with previously reported kinetic data for *tert*-butylsulfenamides. The error limits correspond to the standard error.[8]

DISCUSSION

The product analyses for MPSA and MOSA suggest the stoichiometries (1) and (2), respectively, for their thermolyses, which imply that the only sulfur-containing products are hydrosulfenamides.

$$C_6H_5N(CH_3)SC(CH_3)_3 \rightarrow C_6H_5N(CH_3)SH + i - C_4H_8 \quad (1)$$



(2)

The Arrhenius parameters for these first-order iso-

Table 2. Stirred flow pyrolysis results for MPSA and MOSA

Reactant	Run No.	T (°C)	k (10^4 s^{-1})[a]	Θ (s)[b]	%r (C_4H_8)[c]	P (Torr)	$f°_A \times 10^{8}$[d]	$f_c/f°_A$[e]
MPSA	10	351.1	1430	1.28	15.43	11.35	100.2	50
	8	361.8	2146	1.27	21.48	11.80	58.79	104
	3	369.8	3051	0.653	16.61	8.68	117.3	74
	5	380.2	5038	0.649	24.65	8.62	147.3	57
	1	391.3	9421	0.642	37.68	8.81	82.11	106
MOSA	5	340.8	2344	1.19	21.79	10.6	156.1	38
	10	349.6	3892	1.25	32.77	11.8	130.3	48
	16	359.5	5969	1.30	43.71	12.1	143.9	42
	23	370.8	9913	0.60	37.33	8.47	213.3	42
	19	379.6	15877	0.54	46.17	8.93	171.9	61

[a] Rate coefficient from isobutene measurement.
[b] Residence time.
[c] Percentage reaction from isobutene measurement.
[d] Reactant inflow (mol s^{-1}).
[e] Toluene to reactant flow ratio.

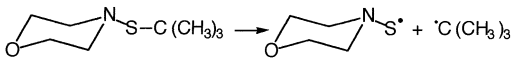
Table 3. Kinetic parameters for sulfenamides *t*-C_4H_9SR

R	Experimental				Corrected			Ref.
	E_a (kJ mol^{-1})	Log A	T_m[a]	k_{T_m} (s^{-1})[b]	E_a/kJ mol^{-1}	Log A	$\Delta S^{\ddagger}$[c]	
$N(CH_3)_2$	175 ± 5	14.45 ± 0.46	350	0.58 ± 0.02	164 ± 6	13.5 ± 0.5	-1.5 ± 9	2
$N(C_2H_5)_2$	164 ± 3	13.45 ± 0.24	330	0.19 ± 0.01			-2.5	1
$N(H)(C_4H_9$-*t*)	184 ± 7	14.75 ± 0.37	370	0.59 ± 0.01	169 ± 6	13.5 ± 0.5	-1.5 ± 9	2
NC_7H_{14}[d]	161 ± 3	14.38 ± 0.26	290	0.31 ± 0.01	151 ± 6	13.5 ± 0.5	-1.5 ± 9	2
NC_4H_8O[e]	159 ± 3	12.91 ± 0.22	360	0.58 ± 0.03			-13	This work
$N(C_6H_5)(CH_3)$	158.8 ± 0.2	12.41 ± 0.02	370	0.31 ± 0.01			-22	This work
$N(H)(CH_2CHC$-$H_2)$	163 ± 5	12.52 ± 0.36	390	0.52 ± 0.02			-20	1

[a] T_m = middle of the range temperature (°C).
[b] Measured rate coefficient at T_m with standard deviation.
[c] J mol^{-1} K^{-1} at 400 °C.
[d] C_7H_{14} = 2,6-dimethylpiperidinyl.

butene eliminations probably correspond to mechanisms involving polar, four-center cyclic transition states, similar to those proposed for other *tert*-butylsulfenamides.[1,2] Their frequency factors, within the range $10^{12.7 \pm 0.3}$ s^{-1}, suggest such a mechanism.[9,10] An alternative path for isobutene formation which has to be evaluated, however, would be via *tert*-butyl radicals generated from the parent molecules by S—C bond cleavage, according to steps (3) and (4), together with step (5).

$$C_6H_5N(CH_3)SC(CH_3)_3 \rightarrow C_6H_5N(CH_3)S^{\bullet} + {}^{\bullet}C(CH_3)_3 \quad (3)$$



(4)

$$(CH_3)_3C^{\bullet} \rightarrow i-C_4H_8 + i-C_4H_{10} \quad (5)$$

By using the data shown in Table 4 (maximum error limit about ± 25 kJ mol^{-1}), the reaction enthalpies (ΔH°_{298}) for reactions (3) and (4) can be estimated to be 169 and 250 kJ mol^{-1}, respectively. Since the experimental E_a for both MPSA and MOSA is 159 kJ mol^{-1}, the value for reaction (3), unless affected by a considerable error, appears to be close enough to this E_a to make this step competitive with reaction (1), whereas that for reaction (4) makes it a very unlikely competitor with reaction (2). If *tert*-butyl radicals had been present in significant steady-state concentrations, however, the observed yields of isobutane would be expected to be higher. For example, in the case of MPSA, if one assumes $k_3 = 10^{15}\exp[-169$ kJ mol$^{-1}(RT)^{-1}]$, then at 370 °C $k_3 = 19$ s^{-1} and the yield of isobutane would have been about 50 times the yield actually observed for isobutene. Previously studied[2] 2,6-dimethylpiperidinyl-*tert*-butylsulfenamide (PISA) produced the highest yield of isobutane observed, about 3%, while its estimated *tert*-butyl C—S bond dissociation energy is 191 kJ mol^{-1} and $E_a = 161 \pm 3$ kJ mol^{-1}. The unimolecular, polar four-center complex fission process then appears to fit better to reactions (1) and (2), with reactions (3) and (4) taking place to a negligible extent. In view of the present results, it seems appropriate to reconsider the magnitudes of the Arrhenius parameters for *N*-dimethyl-*tert*-butylsulfenamide (DMSA), *N*-*tert*-butyl-*tert*-butylsulfenamide (TBSA) and 2,6-dimethylpiperidinyl-*tert*-butylsulfenamide (PISA) (Table 3).

Table 4. Thermochemical parameters

Species	$\Delta H_f^{\circ}{}_{298}$ (kJ mol^{-1})	IP[a] (eV)	Total energy (eV)	$S^{\circ}{}_{298}$ (J K^{-1} mol^{-1})	$C_p{}^{\circ}{}_{298}$ (J K^{-1} mol^{-1})	Enthalpy (kJ mol^{-1})
$C_6H_5N(CH_3)SH$	168.0	8.60	-1420.7	396.5	143.2	25.93
$C_6H_5(H)(CH_3)N{=}S$	293.0	7.92	-1419.4	256.1	133.8	24.05
OC_4H_8NSH[b]	-142.5	9.05	-1357.9	354.5	115.6	21.52
$OC_4H_8(H)N{=}S$[b]	-34.2	8.02	-1356.8	337.9	106.8	19.34
$C_6H_5N(CH_3)SC_4H_9$-*t*	79.6	8.41	-2043.7	536.9	233.8	42.43
$OC_4H_8NSC_4H_9$-*t*[b]	-232.0	8.43	-1980.9	490.3	205.9	37.64
$C_6H_5N(CH_3)S^{\bullet}$	(200)[d]					
$OC_4H_8NS^{\bullet}$[b]	(-31)[d]					
t-$C_4H_9^{\bullet}$[c]	48.6					

[a] Ionization potential.
[b] OC_4H_8N = morpholinyl.
[c] Ref. 11.
[d] Values in parentheses estimated by group additivity method, Refs 9 and 12. All other values this work, estimated by AM1 method, Refs 13 and 14.

A method[10] for carrying out activation parameter reassessments consists in assigning a higher reliability to the experimental values of the rate coefficients measured at a temperature in the middle of the range used for each reactant. By using the average value of these rate coefficients, and the most likely value for the *A* factor, one can calculate the corresponding E_a. In applying this method, *A* factors in the range $10^{13.5 \pm 0.5}$ s^{-1}, corresponding to values of $\Delta S^{\ddagger}$ of -1.5 ± 9 J K^{-1} mol^{-1}, are the most likely for DMSA, TBSA and PISA, so the calculated activation energies remain within 10% of the experimental values. In Table 3 are shown the figures pertaining to these calculations. The likely explanation for the high experimental values of *A* for DMSA, TBSA and PISA is some systematic error in the measurements of the rate coefficient at the upper end of the temperature ranges. The reactivity sequence for the *tert*-butylsulfenamides studied so far is $C_7H_{14} > (CH_3)_2 \approx (C_2H_5)_2 > C_4H_8O >$ (H)(*tert*-C_4H_9) > $(CH_3)(C_6H_5)$ > (H)(CH_2-$CH{=}CH_2$).

As was discussed in previous work,[1] the presence of the more electronegative N atom bonded to the S atom causes the net atomic charges in the $(CH_3)_3CS$ moiety of the sulfenamides to be different from those in disulfides.[15] In the latter, the S atom has a net negative charge and the *tert*-butyl C atom a positive charge, so the ground state of the disulfide molecule has a charge distribution already resembling that of the quadrupolar, four-center cyclic transition state.[16] In the case of the *tert*-butylsulfenamides, the net ground state charge on the S atom (atomic units), estimated in this work by the AM1 method, is 0.164 in PISA, 0.271 in MPSA and 0.286 in MOSA. The charge on the *tert*-butyl C atom is -0.164, -0.214 and -0.236, respectively. The charge on the N atom is -0.42 ± 0.03 and those on the H atoms of the methyl groups are 0.075 ± 0.007. A charge redistribution must then take place in the transition state of the *tert*-butylsulfenamides during the C—S bond-breaking step, so that the S atom receives electron density for the transfer of a partially positive H atom from one of the CH_3 groups. The S atom in PISA appears to be at least less positive than that in MPSA and MOSA, so the necessary shift of electron density and the transfer of a partially positive H atom towards this S atom in the transition state would be more easily achieved. The fact that PISA is almost 20 times more reactive than MOSA and 50 times more reactive than MPSA supports this argument.

In connection with the stability of the hydrosulfenamides, the present (Table 4), like the previously computed,[1,2] total energies and $\Delta H_{f^\circ 298}$ suggest that the thiol isomer should be more stable than the thione isomer. Since C_7H_{14}NSH, *tert*-C_4H_9NSH and $(CH_3)_2$NSH decomposed rapidly,[2] whereas $(C_2H_5)_2$NSH, allyl-NSH, $(C_6H_5)(CH_3)$NSH and OC_4H_8NSH could be titrated, the latter appear to be more stable.

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