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Kinetics and Mechanism of Pyrolysis of Sulphonyl Hydrazones and Oximes. Part 1. Contribution to Reactivity From Hydrazone HN–N and Oxime O–N Bond Polarity

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ABSTRACT: Rates were obtained for the pyrolysis of tosyl arenecarboxaldehyde hydrazones (**1-5**), and mesyl benzaldoxime (**6**). The substituted tosyl sulphonamides (*Ts*HNN=CHAr: **1-5**) and the mesylate (**6**) gave in a novel pyrolytic reaction the following Arrhenius log A/s^{-1} and E_a/kJ mol^{-1} values, respectively: 12.70 and 157.7 (**1**, Ar = C_6H_5), 12.29 and 152.6 (**2**, p-$NO_2C_6H_4$), 11.85 and 148.2 (**3**, m-$NO_2C_6H_4$), 12.17 and 152.0 (**4**, p-ClC_6H_4), 11.01 and 140.8 (**5**, p-$CH_3OC_6H_4$), and 12.96 and 109.9 for (**6**). Tosyl benzaldoxime (**7**) was also studied. The reactions yielded cyanoarenes together with sulphonic acids from **6** and **7**, and p-methylbenzenesulphonamide from compounds **1-5**.

INTRODUCTION

Chuchani and co-workers have investigated the kinetics of the homogeneous and unimolecular first-order gas-phase pyrolysis of a number of alkyl methanesulphonates, and have suggested a mechanism for the reaction involving an intimate ion pair.[1] They also noted that only one study on the thermal gas-phase 1,3-elimination of 2-adamantyl methanesulphonate predates their investigation.[2] In the present work we report what is believed to be the first study on the kinetics and mechanism of the gas-phase pyrolysis of sulphonyl hydrazones and their oxime analogues. However, investigations on the irradiation and pyrolysis of arenesulphonylhydrazine and hydrazone derivatives in the liquid phase and under an inert atmosphere or in acid/base media have been described,

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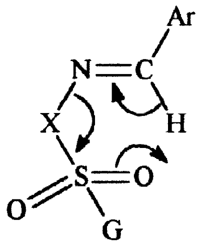
and the reaction has been used in synthesis.[3-5] Besides, part of our recent work involved kinetic and mechanistic studies on cyanoacetylhydrazones, aryl- and heteroarylcyanoacetylhydrazones and related compounds.[6,7] The molecularity, order and homogeneous nature of reaction, stereochemistry, Arrhenius parameters, Hammett correlations, and analysis of products of reaction combine to suggest a concerted six-membered transition state (Scheme) for the thermal gas-phase elimination reactions of the sulphonyl compounds under study.[8]



X = NH; O
G = CH_3; p-$CH_3C_6H_4$

Scheme. Concerted Transition State.

RESULTS AND DISCUSSION

The rate coefficients (k/s^{-1}) of Table 1 are used to determine the Arrhenius log A/s^{-1} and E_a/kJ mol^{-1} values of compounds **1-6** which are given in Table 2. Each rate coefficient represents the mean from three kinetic runs in agreement to within ±2% and for compounds **1-5**, the rates were measured over a temperature range exceeding 50 K. The reactions were ascertained to be homogeneous, unimolecular, and free of reactor surface effects. The Arrhenius plots were strictly linear up to ≥ 95% reaction. The reported log A/s^{-1} and E_a/kJ mol^{-1} values are correct to within ± 0.10 and ± 1.50, respectively. The rates of reaction at 540 K of these substrates are also recorded in Table 2 alongside relative rates and relevant Hammett substituent constants.[9] The homogeneous nature of the reaction was tested by comparing rates using a normal reactor with those obtained when the reactor vessel is packed with helices. Absence of a free radical pathway in the elimination reaction is confirmed using established procedures.[1,10]

The products of reaction have been identified using on-line GC-MS and FT-IR pyroprobe techniques. The hydrazone fragments yielded cyanoarene compounds, and the sulphonyl residues gave the corresponding sulphonamides and sulphonic acids.

Table 1. Rate Coefficients (10^4 k/s^{-1}) for Pyrolysis of GN=CHAr.

Compound (1): G = *Ts*NH ; Ar = C_6H_5

T/K :	493.8	510.7	518.9	530.1	532.2	539.1	546.3	
10^4 k/s^{-1} :	1.02	3.65	6.87	14.60	17.40	26.00	40.30	

Compound (2): G = *Ts*NH ; Ar = p-$NO_2C_6H_4$

T/K :	493.0	505.0	508.1	513.7	518.4	522.7	540.1	544.8
10^4 k/s^{-1} :	1.33	3.29	4.02	5.95	8.13	10.90	34.20	46.40

Compound (3): G = *Ts*NH ; Ar = m-$NO_2C_6H_4$

T/K :	498.0	502.2	508.0	515.0	516.9	539.5	541.2	550.0
10^4 k/s^{-1} :	2.02	2.72	4.11	6.51	7.56	31.60	35.40	59.60

Compound (4): G = *Ts*NH ; Ar = p-ClC_6H_4

T/K :	496.2	506.4	516.8	519.7	532.0	539.9	547.0	
10^4 k/s^{-1} :	1.48	3.14	6.41	7.87	18.10	29.00	45.46	

Compound (5): G = *Ts*NH ; Ar = p-$CH_3OC_6H_4$

T/K :	501.4	518.6	522.1	525.6	530.2	534.0	558.6	
10^4 k/s^{-1} :	1.91	5.71	7.37	9.02	11.80	14.40	60.90	

Compound (6): G = *Ms*O ; Ar = C_6H_5

T/K :	350.0	357.0	362.6	367.0	372.1	375.1	381.3	
10^4 k/s^{-1} :	3.60	7.35	14.30	20.20	35.60	42.10	84.00	

Table 2. Arrhenius Parameters and Rates at 540 K for Pyrolysis of GN=CHAr.

Cpd	G	Ar	log A/s^{-1}	E_a/kJ mol^{-1}	10^4k/s^{-1} (at 540 K)	10^2 log k_{rel}	σ
(1)	*Ts*NH	C_6H_5	12.70	157.7	27.54	0.00	0.00
(2)	*Ts*NH	p-$NO_2C_6H_4$	12.29	152.6	33.11	8.00	0.78
(3)	*Ts*NH	m-$NO_2C_6H_4$	11.85	148.2	32.45	7.14	0.73
(4)	*Ts*NH	p-ClC_6H_4	12.17	152.0	28.84	2.00	0.22
(5)	*Ts*NH	p-$CH_3OC_6H_4$	11.01	140.8	24.55	-4.99	-0.29
(6)	*Ms* O	C_6H_5	12.96	109.9	21.38x10^5		

Benzaldoxime (**6**, Scheme: N–X = N–O bond) is 6.5 x 10^4 - 8.7 x 10^4 fold more reactive than the arenecarboxaldehyde hydrazones (**1-5**: N–X = N–NH bond). However, the rate of the most reactive hydrazone is only about 1.35-fold faster than that of the least reactive analogue. Benzaldoxime (6) is the methanesulphonyl (i.e. mesyl, *Ms*) derivative. The substrate to use for comparison purposes is evidently the p-methylbenzenesulphonyl (i.e. tosyl, *Ts*) compound. The latter, however, was found to be considerably faster than the former substrate under the conditions of pyrolysis. The rate factor of 6×10^4 - 9×10^4 represents, therefore, only a lower limit of rate-enhancement on replacing the hydrazone N–NH bond by the oxime N–O bond in the substrate molecular frame. The rate factor involved is conceivably in the order of a hundred thousand to a million-fold; an indication of the rate-controlling role of the polarity of the N–X σ-bond (Scheme). We have in previous studies analyzed the relative contribution to molecular reactivity from the polarization of the analogous –X –Y bond (X = O, NH; Y = ketone and thione moieties) in esters, anhydrides, and amides.[11,12]

The effect of the H-bond donor acidity of the hydrazone methine hydrogen and the contribution from its σ-electrons to the stability of the incipient cyanoarene moiety though moderate is nevertheless consistent. This is shown in the Hammett relation of Figure 1. Further, we have recently studied a number of heteroarene- and homoarenecarboxaldehyde hydrazones and assessed the effect which arene ring substituents have on reactivity due to the acidity of the hydrazone hydrogen. These studies also showed that development of aromatic character by an incipient ring fragment plays a significant role in directing the elimination pathway.[6,7]

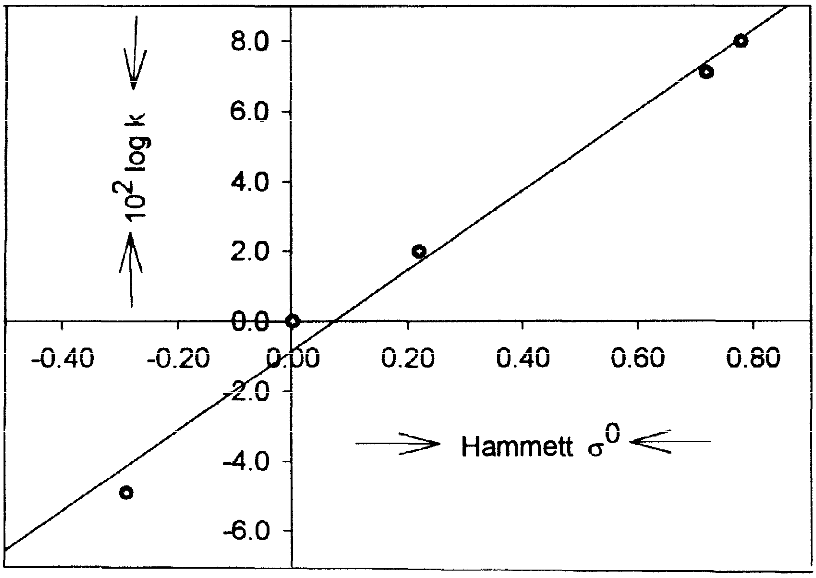


Figure 1. Correlation of log k with Hammett σ for Hydrazones 1-5.

EXPERIMENTAL

Synthesis

Mesyl (Ms) and Tosyl Benzaldoxime. **The benzaldoxime required in the synthesis was prepared using a standard procedure[13] , and was distilled prior to use. Typically, mesyl benzaldoxime (*Ms*ON=CHPh) was prepared by adding methanesulphonyl chloride (0.85 mL, 11 mmol) over a period of 5 - 10 minutes to a solution of benzaldoxime (1.21 g, 10 mmol) and triethylamine (2.1 mL, 15 mmol) in dichloromethane (50 mL) kept at -20 °C. The reaction mixture was stirred for 30 minutes at -20 °C and then transferred to a separatory funnel charged with dichloromethane. The solution was washed repeatedly with cold water, and dried over Na_2SO_4. On evaporation of the solvent and repeated washing of the solid residue with ether - petroleum ether, the NMR-pure mesylate was obtained in 70% yield as a low-melting white solid.**

Tosyl (Ts) Arenecarboxaldehyde Hydrazones. ***Ts*HNN=CHAr. Tosyl hydrazide was prepared from tosyl chloride obtained commercially and hydrazine monohydrate following literature procedure.[14] On reacting equivalent amounts of the hydrazide and the corresponding arenecarboxaldehyde, followed by normal work-up and subsequent recrystallization from absolute ethanol, the tosyl arenecarboxaldehyde hydrazones 1-5 were obtained in good yields.**

Characterization

All melting points are uncorrected.[15,16] NMR and IR spectra were obtained using Bruker AC 80 and a Perkin Elmer FT-IR 2000 spectrometers.

Benzaldehyde tosylhydrazone (**1**). *Ts*HNN=CHC_6H_5, m.p. 127 - 128 °C (Found: C, 61.17; H, 5.18; N, 10.19; S, 11.90. $C_{14}H_{14}N_2O_2S$ requires C, 61.31; H, 5.15; N, 10.21; S, 11.66 %); 4-Nitrobenzaldehyde tosylhydrazone (**2**). *Ts*HNN=CH$C_6H_4NO_2$-$\underline{p}$, m.p. 161 - 162 °C (Found: C, 52.56; H, 4.15; N, 13.30; S, 10.54. $C_{14}H_{13}N_3O_4S$ requires C, 52.66; H, 4.07; N, 13.16; S, 10.03%); δ_H (80 MHz; DMSO) 2.34 (3H, s, $C\underline{H}_3$), 7.81 (4Hx2, m, $C_6\underline{H}_4$), 11.70 (1H, s, $N\underline{H}$); 3-Nitrobenzaldehyde tosylhydrazone (**3**). *Ts*HNN=CH$C_6H_4NO_2$–$\underline{m}$, m.p. 164-165 °C (Found: C, 52.52; H, 4.01; N, 13.00; S, 10.44. $C_{14}H_{13}N_3O_4S$ requires C, 52.66; H, 4.07; N, 13.16; S, 10.03%); δ_H (80 MHz; DMSO) 2.37 (3H, s, $C\underline{H}_3$), 7.81 (4Hx2, m, $C_6\underline{H}_4$), 11.77 (1H, s, $N\underline{H}$); 4-Chlorobenzaldehyde tosylhydrazone (**4**). *Ts*HNN=CHC_6H_4Cl-$\underline{p}$, m.p. 150-151 °C (Found: C, 54.43; H, 4.26; N, 9.08; S, 10.68. $C_{14}H_{13}N_2O_2SCl$ requires C, 54.45; H, 4.21; N, 9.07; S, 10.37%); δ_H (80 MHz; DMSO) 2.37 (3H, s, $C\underline{H}_3$), 7.62 (4Hx2, m, $C_6\underline{H}_4$), 11.29 (H, s, $N\underline{H}$); 4-

Methoxybenzaldehyde tosylhydrazone (5). *Ts*HNN=CHC$_6$H$_4$OCH$_3$-p, m.p. 115-116 °C (Found: C, 59.22; H, 5.41; N, 9.20; S, 10.99. C$_{15}$H$_{16}$N$_2$O$_3$S requires C, 59.20; H, 5.30; N, 9.20; S, 10.53%); δ_H (80 MHz; DMSO) 2.28 (3H, s, ArCH$_3$), 3.68 (3H, s, OCH$_3$), 7.32 (4Hx2, m, C$_6$H$_4$); **Benzaldehyde *O*-(methylsulphonyl)oxime (6).** *Ms*ON=CHC$_6$H$_5$, m.p. 85-86 °C (Found: C, 48.07; H, 4.59; N, 6.97; S, 16.85. C$_8$H$_9$NSO$_3$ requires C, 48.24; H, 4.52; N, 7.03; S, 16.08 %); δ_H (80 MHz, CDCl$_3$) 3.46 (3H, s, O$_3$SCH$_3$), 7.72 (5H, m, C$_6$H$_5$), 8.82 (1H, s, N = CH); ν_{max}/cm^{-1} 1651 (m, C = N), 1176 (s, –SO$_3$–).

Kinetics and Product Analysis

Kinetics. Reactor and reaction set-up , kinetic runs, and data analysis techniques have been described elsewhere.[17] An aliquot part (0.2 mL) of a dilute solution (ppm) of the neat substrate in acetonitrile as internal standard was allowed time to react to give 10-20 % substrate pyrolysis at the reaction temperature. The pyrolysate was analyzed using HPLC. The reaction was followed at 5-10 °C intervals until 90-95 % substrate pyrolysis was achieved, and the analytical data was used to calculate the rate coefficient at each reaction temperature. Arrhenius parameters were obtained from a plot of log k vs. 1/T (K). A typical plot is described for p-CH$_3$C$_6$H$_4$SO$_2$NHN=CHC$_6$H$_4$NO$_2$-p (2) in Figure 2.

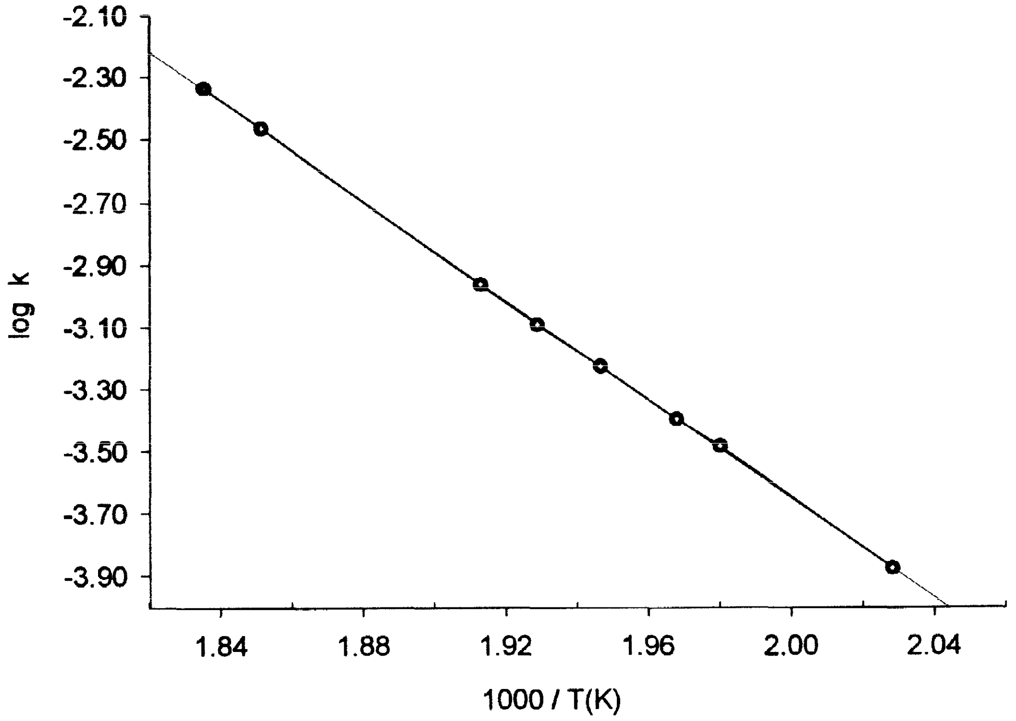


Figure 2. Arrhenius Plot for Compound (**2**)

The rate coefficients at T = 540 K were calculated using the kinetic relation: log k = log A - E_a/4.574 T; log A and E_a are the Arrhenius parameters obtained for the substrate.

Product Analysis. **The products of the gas-phase pyrolysis of the compounds under study were analyzed using both an on-line pyroprobe GC-MS and flow techniques. The techniques have been described in earlier communications.**[11,12,17]

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