

Kinetics and mechanism of pyrolysis of sulphonyl hydrazones and oximes. Part 2—Structural effects and molecular reactivity

Nouria A. Al-Awadi,* Mohamed H. Elnagdi, Kamini Kaul, Swaminathan Ilingovan and Osman M. E. El-Dusouqui

Department of Chemistry, University of Kuwait, P.O. Box 5969, Safat 13060, Kuwait

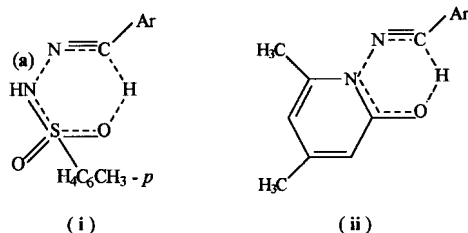
Received 25 October 1998; revised 23 1999; accepted 8 March 1999

ABSTRACT: The kinetics and products of the pyrolytic reaction of six tosyl arenecarboxaldoximes were studied over the temperature range ca 334 – 401 K to yield the following Arrhenius $\log A/s^{-1}$ and $E_a/kJ\ mol^{-1}$, respectively: 10.92 and 98.25 for tosyl benzaldoxime and 10.83 and 100.4 for *m*-nitro-, 10.66 and 97.53 for *p*-chloro-, 11.80 and 107.8 for *m*-chloro-, 11.60 and 101.5 for *p*-methyl- and 10.84 and 97.75 for *p*-methoxybenzaldehyde *O*-[(4-methylphenyl)sulphonyl]oxime. At 500 K, the oxime compounds were found to be 9.4×10^3 – 2.7×10^4 -fold more reactive than their hydrazone analogues. Copyright © 1999 John Wiley & Sons, Ltd.

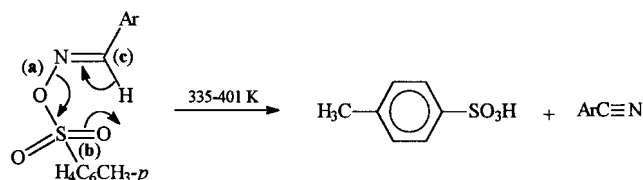
KEYWORDS: sulphonyl hydrazones; sulphonyl oximes; pyrolysis; kinetics; mechanism; structural effects; molecular reactivity

INTRODUCTION

In Part 1,¹ we reported the first kinetic and mechanistic study on the non-catalysed thermal elimination reaction of a number of tosyl arenecarboxaldehyde hydrazones. The reactions were found to be unimolecular and to involve a cyclic six-membered transition state. The study also featured Hammett correlation of the effects of substituents on the H-bond donor acidity of the hydrazone hydrogen [Scheme 1 (i)]. This analysis parallels an earlier finding from the pyrolysis of a heterocyclic hydrazone system where the development of aromatic character of an incipient pyridyl ring was considered to be an important factor in directing the elimination pathway [Scheme 1 (ii)].²



Scheme 1. Six-membered transition state



Scheme 2. Oxime elimination fragments

The mechanism of the present pyrolytic reaction of the arenecarboxaldoximes follows an identical pathway. The Arrhenius parameters and relative rates suggest that the polarity of the oxime N—O bond (a) and the concomitant charge development are the major contributors to the relatively high reactivity observed for these compounds, rather than the protophilicity of bond (b) or the H-bond donor acidity of (c) (see Scheme 2). It has been noted previously¹ that kinetic and mechanistic investigations on the pyrolysis of sulphonyl hydrazones are available but only for reactions in solution.^{3–5} This is also the case for the oximes.⁶

RESULTS AND DISCUSSION

First-order rate constants were calculated individually for tosyl benzaldoxime (1) and *m*-nitro- (2), *p*-chloro- (3), *m*-chloro- (4), *p*-methyl (5) and *p*-methoxybenzaldehyde *O*-[(4-methylphenyl)sulphonyl]oxime (6) over a range of temperature of ≥ 46 K. Each rate coefficient is an average

*Correspondence to: N. A. Al-Awadi, Department of Chemistry, University of Kuwait, P.O. Box 5969, Safat 13060, Kuwait.
E-mail: nouria@kuc01.kuniv.edu.kw
Contract/grant sponsor: Kuwait University; Contract/grant number: SC 088.

Table 1. Kinetic data, rate coefficients (10^3 k/s^{-1}) at 380 K and Arrhenius parameters for pyrolysis of $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{N}=\text{CHAr}$ oximes

Compound	Ar	T/K	10^4 k/s^{-1}	$\text{Log } A/\text{s}^{-1}$	$E_a/\text{kJ mol}^{-1}$	$10^3 \text{ k/s}^{-1} (380 \text{ K})$
1	C_6H_5	335.0	0.40	10.92	98.25	2.60
		343.3	1.51	± 0.19	± 1.32	
		354.0	2.67			
		361.6	5.38			
		367.0	8.12			
		375.0	16.5			
		385.0	40.6			
2	$m\text{-NO}_2\text{C}_6\text{H}_4$	351.3	0.83	10.83	100.4	1.07
		367.6	3.54	± 0.01	± 0.05	
		373.9	6.58			
		378.0	8.74			
		384.7	15.5			
3	$p\text{-ClC}_6\text{H}_4$	397.2	45.1			1.80
		338.9	0.40	10.66	97.53	
		345.9	2.08	± 0.26	± 1.8	
		367.6	6.76			
		374.8	12.2			
4	$m\text{-ClC}_6\text{H}_4$	378.5	15.4			0.93
		385.0	24.8			
		353.1	0.68	11.80	107.8	
		369.0	3.49	± 0.24	± 1.7	
		384.4	14.3			
5	$p\text{-CH}_3\text{C}_6\text{H}_4$	392.1	24.5			4.44
		401.0	57.0			
		334.2	0.53	11.60	101.5	
		346.0	1.83	± 0.25	± 1.78	
		355.8	5.24			
6	$p\text{-CH}_3\text{OC}_6\text{H}_4$	360.5	8.10			2.53
		371.1	21.0			
		376.9	31.6			
		384.6	67.2			
		345.0	1.10	10.84	97.75	
		354.6	2.70	± 0.28	± 1.20	
		363.6	6.49			
		365.1	8.40			
		372.3	12.6			
		375.4	16.6			
		384.0	34.5			
		389.1	54.0			
		395.2	83.2			

of at least three kinetic runs with deviation $\leq \pm 2\%$. The rate constants and the temperatures at which the measurements were made are given in Table 1. Arrhenius plots of the kinetic data showed strict linearity for $\geq 95\%$ reaction. A representative plot was included in Part 1.¹ The $\log A/\text{s}^{-1}$ and $E_a/\text{kJ mol}^{-1}$ data are also given in Table 1; the values are correct to within ± 0.15 and ± 1.0 , respectively.

The present thermal elimination reactions were ascertained to be homogeneous, polar and unimolecular. It is noteworthy that the reactions are free from radical and catalytic pathways.⁷ The reactions were tested for their homogeneous first-order nature either by introducing a change of up to sixfold in substrate concentration or a change of up to 50% in reaction volume. The strict linearity of the Arrhenius plots over the reaction range

($\geq 95\%$) and temperature span (46–50 K) further substantiates the homogeneous first-order kinetics of the reactions.

The reactions are deemed free of reactor-surface effects since an increase in the ratio of reactor surface-to-reactor volume of approximately ninefold did not produce any significant change in rate constants, within experimental error. The reaction surface was varied by using empty reaction tubes and tubes packed with glass helices. The Arrhenius $\log A/\text{s}^{-1}$ (11.3 ± 0.5) and $E_a/\text{kJ mol}^{-1}$ (103 ± 5) values are what might be expected for polar pyrolytic reactions. The polar nature of the reactions is further confirmed by the results of the Hammett correlation.¹ The first-order kinetics and product analysis of the reaction coupled with the expected thermodynamic stability of the incipient frag-

Table 2. Rate coefficients (k/s^{-1}) at 500 K and relative rates (k_{rel}) of oxime and hydrazone analogues: $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{XN}=\text{CHAr}$

Parameter	Ar C_6H_5	$m\text{-NO}_2\text{C}_6\text{H}_4$	$p\text{-ClC}_6\text{H}_4$	$p\text{-CH}_3\text{OC}_6\text{H}_4$
k/s^{-1} (oxime)	4.53	2.20	2.96	4.25
$10^4 k/s^{-1}$ (hydrazone)	1.68	2.33	1.95	1.99
k_{rel}	26 964	9 442	15 179	21 794

ments of pyrolysis point to a reaction which is unimolecular in nature. The quantitative estimation of the composition of the reaction mixture was carried out in presence of a thermally stable inert internal standard and using high-performance liquid chromatography (HPLC) with UV-visible detection. Further, parallel reactions were carried out in the presence and absence of free-radical scavengers. The rates were not changed by the addition of radical traps to the reaction mixture.

The elimination fragments in the pyrolysate were identified using on-line gas chromatography-mass spectrometry (GC-MS), Fourier transform (FT) IR pyroprobe and ^1H NMR spectroscopy. Each of the oximes **1–6** gave *p*-methylbenzenesulphonic acid and the corresponding cyanoarene compound (Scheme 2). All the reactions of the substrates under study were free from secondary decomposition processes.

To facilitate comparison of molecular reactivities, rates of reaction were calculated at 500 K for both the hydrazone and oxime series. The rate coefficients and relative rates of oximes **1, 2, 3** and **6** and their hydrazone counterparts are given in Table 2. The results in Tables 1 and 2 allow the following conclusions to be drawn.

The oximes are consistently more reactive than the hydrazones, showing large relative rate differences of $9.44 \times 10^3 - 2.70 \times 10^4$ -fold.

The greater reactivity of the oximes over the hydrazones is attributed to the differential in the polarity of the oxime (N—O) bond compared with the hydrazone (N—NH) bond. The relative contribution to the molecular reactivity of each of the three bonds involved in the electron flow described by the curved arrows in the elimination pathway (Scheme 2) has been documented in earlier studies.^{8–11} It has been noted in these studies that any one of bonds (a), (b) or (c) in Scheme 2 could be the prime contributor to molecular reactivity, or that the overall reactivity is a product of synergism of two or all three bonds. Non-synchronous bond breaking would be the reason for polarity of the concerted transition state, and an effective larger relative contribution from a particular bond might under favourable structural constraints lead to a linear Hammett correlation.^{11,12}

The effects of aryl substituents on the H-bond donor acidity of the aldehydic hydrogen is evident in the hydrazone series, and has provided a suitable set for a Hammett correlation analysis.¹ The value of the Hammett reaction constant for the pyrolysis of the hydrazone

compounds is $\rho = 0.125 \pm 0.025$. This observation might be the result of an appreciable contribution to overall molecular reactivity from bond (c).

The effect of structure on reactivity in gas-phase and vapour-phase pyrolytic reactions has been reviewed.¹³ Molecular reactivity in the oxime compounds is dominated by the greater polarity of the N—O σ -bond (a) and the associated residual charge developed across the bond.

In each analogous hydrazone-oxime pair where the structural difference between the two systems is associated with bond (a), the increase in reactivity of ca 10^4 -fold could be attributed primarily to the polarity of this bond. Where a change in reactivity of this magnitude or higher has been obtained in reactions of similar nature, the reason could be traced to a switch in the bond affecting the change^{9,11} and a non-linear Hammett correlation has been reported.¹¹ Failure to obtain a linear Hammett correlation for the present oxime series parallel to that reported for the hydrazone compounds might be due to this structural modification, where the contribution to reactivity from bond (a) is considered to dominate, thus superseding any effective contribution from H-bond donor acidity associated with bond (c). A review is available¹⁴ in which the relationship between non-linear Hammett structure-reactivity patterns and changes in effective molecular structure and associated reactivity, or change in the rate-controlling step of a reaction or change in the mechanistic pathway of the reaction is outlined and discussed.

EXPERIMENTAL

Synthesis

Benzaldehyde, *p*-chlorobenzaldehyde, *m*-chlorobenzaldehyde, *p*-methylbenzaldehyde and *p*-methoxybenzaldehyde *O*-[(4-methylphenyl)sulphonyl]-oxime.⁶ To a rapidly stirred solution of 3 mmol of benzaldoxime in 20 ml of dry diethyl ether, 3 mmol of powdered sodium amide were added and the mixture was stirred for about 5 h. The mixture was filtered and the precipitate was washed several times with diethyl ether. *p*-Toluenesulphonyl chloride (0.36 g, 2.5 mmol) in 5 ml of diethyl ether was slowly added to a rapidly stirred slurry of the sodium salt of the oxime in 5 ml of diethyl

ether. The salt produced was removed by filtration and 10 ml of hexane were added to the filtrate. On cooling, the oxime of the arenesulphonate crystallized out and was filtered. Recrystallization from 1:1 (v/v) mixture of diethyl ether and hexane gave the pure product in 55–60% yield.

***m*-Nitrobenzaldehyde *O*-[(4-methylphenyl)sulphonyl]oxime.** The sodium salt of *m*-nitrobenzaldoxime was prepared as described above. This salt is dissolved in 5 ml of 1:1 acetone–water mixture and then added slowly with stirring to a cooled solution of *p*-toluenesulphonyl chloride in 2 ml of acetone. From the mixture kept at -15°C , the oxime sulphonate ester separated out, was filtered, washed with 50% acetone solution and recrystallized from hexane–diethyl ether to give pure yield of about 50%.

Characterization

All melting-points are uncorrected.⁶ ^1H NMR spectra and results of the elemental analysis of the compounds under study are as follows.

Benzaldehyde *O*-[(4-methylphenyl)sulphonyl]oxime (1): m.p. $84\text{--}86^{\circ}\text{C}$ (found: C, 60.66; H, 4.86; N, 4.65; S, 11.65. $\text{C}_{14}\text{H}_{13}\text{NO}_3\text{S}$ requires C, 61.09; H, 4.72; N, 5.09; S, 11.63%); ^1H NMR (80 MHz; CDCl_3), δ 2.44 (s, 3H, CH_3), 7.26–7.98 (m, 9H, ArH), 8.23 (s, 1H, $\text{HC}=\text{N}$). *m*-Nitrobenzaldehyde *O*-[(4-methylphenyl)sulphonyl]oxime (2): m.p. $112\text{--}113^{\circ}\text{C}$ (Found: C, 52.02; H, 4.05; N, 8.47; S, 10.61. $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_5\text{S}$ requires C, 52.5; H, 3.75; N, 8.75; S, 10.0%); ^1H NMR (80 MHz; CD_3COCD_3), δ 2.46 (s, 3H, CH_3), 7.45–8.50 (m, 8H, ArH), 8.74 (s, 1H, $\text{HC}=\text{N}$). *p*-Chlorobenzaldehyde *O*-[(4-methylphenyl)sulphonyl]oxime (3): m.p. $109\text{--}110^{\circ}\text{C}$ (Found: C, 54.25; H, 3.82; N, 4.03; S, 10.99. $\text{C}_{14}\text{H}_{12}\text{NO}_3\text{SCl}$ requires C, 54.28; H, 3.87; N, 4.52; S, 10.34%); ^1H NMR (80 MHz; CDCl_3), δ 2.44 (s, 3H, CH_3), 7.25–7.99 (m, 8H, ArH), 8.19 (s, 1H, $\text{HC}=\text{N}$). *m*-Chlorobenzaldehyde *O*-[(4-methylphenyl)sulphonyl]oxime (4): m.p. $90\text{--}92^{\circ}\text{C}$ (Found: C, 54.08; H, 3.87; N, 4.15; S, 10.39. $\text{C}_{14}\text{H}_{12}\text{NO}_3\text{SCl}$ requires C, 54.28; H, 3.87; N, 4.52; S, 10.34%); ^1H NMR (80 MHz; CDCl_3), δ 2.44 (s, 3H, CH_3), 7.25–7.86 (m, 8H, ArH), 8.25 (s, 1H, $\text{HC}=\text{N}$). *p*-Methylbenzaldehyde *O*-[(4-methylphenyl)sulphonyl]oxime (5): m.p. $108\text{--}110^{\circ}\text{C}$ (Found: C, 62.49; H, 5.21; N, 4.52; S, 11.22. $\text{C}_{15}\text{H}_{15}\text{NO}_3\text{S}$ requires C, 62.28; H, 5.19; N, 4.84; S, 11.07%); ^1H NMR (80 MHz; CDCl_3), δ 2.35 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 7.18–7.99 (m, 8H, ArH), 8.18 (s, 1H, $\text{HC}=\text{N}$). *p*-Methoxybenzaldehyde *O*-[(methylsulphonyl)]oxime (6): m.p. $99\text{--}101^{\circ}\text{C}$ (Found: C, 59.26; H, 4.86; N, 4.21; S, 11.01. $\text{C}_{15}\text{H}_{15}\text{NO}_4\text{S}$ requires C, 59.02; H, 4.91; N, 4.59; S, 10.49%); ^1H NMR (80 MHz, CDCl_3), δ 2.43 (s, 3H, CH_3), 3.82 (s, 3H, H_3CO), 6.93–7.99 (m, 8H, ArH), 8.16 (s, 1H, $\text{HC}=\text{N}$).

Kinetic and product analysis

Instrumentation. The pyrolyser was a CDS custom-made unit. It consisted of an insulated aluminium block to ensure a low temperature gradient and resistance to high temperature, a Pyrex reaction vessel to fit in a groove along the cylindrical axis of the block, a platinum resistance thermometer and a thermocouple connected to a microprocessor. The temperature of the block was controlled by means of a Eurotherm 093 precision temperature regulator. The temperature setting was achieved with a digital switch which allows temperature read-out accurate to $\pm 0.5^{\circ}\text{C}$. The actual temperature of the reactor groove was measured by means of a Comark microprocessor thermometer. Comparative quantitative analyses of reaction mixtures were carried out using HPLC with an LC-8 column (25 cm $\times$ 4.6 mm. i.d.) and a UV–visible detector (Bio-Rad, Shimadzu SPD-10AV). Samples were injected using a Supelco 5 μm precision syringe.

Characterization of the substrates and the constituent fragments of the pyrolysates included elemental analysis, GC–MS, FT-IR and ^1H NMR spectroscopic analysis. The GC–MS Instrument was a Finigan MAT INCOS XL quadrupole mass spectrometer. FT-IR spectra were measured using a Perkin-Elmer model 2000 spectrometer, ^1H NMR spectra were recorded on a Bruker AC-80 spectrometer and the elemental analyser was a LECO CHNS-932 unit.

Kinetic runs and data analysis. Dilute (ppm) standard solutions of the substrates in a suitable solvent (e.g. acetonitrile) were prepared and an internal standard (e.g. chlorobenzene) was added to each solution. Care was taken to ensure that both the solvent and the internal standard were not pyrolysable under the conditions of the reaction. Further, the standard solutions used in the kinetic runs always comprised a mixture where the substrate gave a peak which was one third higher than that of the internal standard in the analytical HPLC trace. Preparation of a standard solution allows several kinetic runs to be performed on the same reaction mixture.

A sample (0.2 ml) of the standard solution was placed in a reaction tube (9 ml) and the contents were sealed under vacuum. The tube was placed swiftly in the pyrolyser, which had been preheated to a threshold temperature that together with a convenient reaction time would allow only 10–20% pyrolysis. The contents of the reaction tube were then analysed using HPLC. For each substrate, the rate coefficient represents an average from triplicate runs with rate agreement to within $\pm 2\%$. Rates were measured at regular intervals of $5\text{--}10^{\circ}\text{C}$ over a 46–50 K temperature range and up to $\geq 95\%$ reaction.

Rates were reproduced using empty reaction tubes and tubes packed with glass helices in order to increase the reactor surface by up to about ninefold. This precaution was to test for reactor surface effects. Further, rates were

measured in the presence and absence of free-radical scavengers (e.g. cyclohexene) to confirm the non-involvement of free-radical pathways.

The rate coefficients were calculated using the expression $kt = \ln a_0/a$ for first-order reactions. The Arrhenius parameters were obtained from a plot of $\log k$ vs $1/T$ (K), an example of which was shown in Part 1.¹ The elimination rate constant at T (K) is given by

$$\log k = \log A(s^{-1}) - E_a(kJ\ mol^{-1})/4.574\ T(K)$$

Product analysis. The products analysed were for pyrolyses conducted at temperatures commensurate with those of the kinetic measurements. No secondary decomposition was observed for any of the compounds studied. In both the kinetic runs and product analysis, the initial conversion of 10–20% and reaction extent of $\geq 95\%$ pyrolysis have been maintained.

Acknowledgements

The support of Kuwait University through research grant SC 088 and the facilities of Analab and SAF are gratefully acknowledged.

REFERENCES

1. N. A. Al-Awadi, M. H. Elnagdi, K. Kaul, S. Ilingovan and O. M. E. El-Dusouqui, *Tetrahedron* **54**, 4633–4640 (1998).
2. N. A. Al-Awadi, M. H. Elnagdi, T. Mathew, I. El-Gamry and M. Abdel Khalik, *Int. J. Chem. Kinet.* **28**, 741–748 (1996).
3. F. Bellesia, R. Grandi, U. M. Pagnoni and R. Travi, *J. Chem. Res. (S)* **4**, 112 (1981); *Gazz. Chem. Ital.* **111**, 511–513 (1981).
4. A. M. Gaber, A. A. Atalla and A. M. K. El-Dean, *Phosphorous, Sulfur, and Silicon* **112**, 131–136 (1996).
5. E. J. Corey, G. H. Posner, R. F. Atkinson, A. K. Wingard, D. J. Halloran, D. M. Radzik and J. J. Nash, *J. Org. Chem.* **54**, 389–393 (1989).
6. R. J. Crawford and C. Woo, *Can. J. Chem.* **43**, 1534–1544 (1965).
7. N. A. Al-Awadi, M. H. Elnagdi and T. Mathew, *Int. J. Chem. Kinet.* **27**, 517–523 (1995).
8. N. A. Al-Awadi, R. F. Al-Bashir and O. M. E. El-Dusouqui, *J. Chem. Soc., Perkin Trans. 2* 579–581 (1989).
9. N. A. Al-Awadi and O. M. E. El-Dusouqui, *Int. J. Chem. Kinet.* **29**, 295–298 (1997).
10. N. A. Al-Awadi, M. H. Elnagdi, H. A. Al-Awadhi and O. M. E. El-Dusouqui, *Int. J. Chem. Kinet.* **30**, 457–462 (1998).
11. N. A. Al-Awadi, O. M. E. El-Dusouqui and T. Mathew, *Int. J. Chem. Kinet.* **29**, 289–293 (1997).
12. N. A. Al-Awadi, R. F. Al-Bashir and O. M. E. El-Dusouqui, *Tetrahedron Lett.* **30**, 1699–1702 (1989).
13. G. G. Smith and F. W. Kelly, *Prog. Phys. Org. Chem.* **8**, 75–234 (1971).
14. J. O. Schreck, *J. Chem. Educ.* **48**, 103–107 (1971).