Gas-Phase Kinetics of Elimination Reactions of Pentane-2,4-Dione Derivatives. Part II [1]. Thermolysis of Derivatives and Analogues of 3-Phenylhydrazonopentane-2,4-Dione

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ABSTRACT: Six analogues and derivatives **(1–6)** of 3-phenylhydrazonopentane-2,4-dione **(7)** were subjected to gas-phase thermolysis. The Arrhenius log *A* (s^{-1}) and E*a* (kJ mol^{-1}) of the analogues **(1–5)** are, respectively: 10.42 and 140.8 for 1-cyano-1-phenyl-hydrazonopropanone **(1)**, 11.19 and 135.4 for 1-cyano-1-(p-nitrophenylhydrazono)-propanone **(2)**, 10.68 and 144.9 for 1-cyano-1-(p-methoxyphenylhydrazono)propanone **(3)**, 11.76 and 137.8 for 1-cyano-3-phenyl-1-phenylhydrazonopropanone **(4)**, and 11.29 and 145.9 for 1-cyano-1-phenylhydrazonobutanone **(5)**. The corresponding values for ethyl 3-oxo-2-phenylhydrazonobutanoate **(6)** are 11.90 s^{-1} and 143.3 kJ mol^{-1}. The rates of reaction at 600 K are compared with those of the title diketone **(7)** and of pentane-2,4-dione **(8)** and rationalized in terms of a plausible elimination pathway involving a semiconcerted six-membered transition state. © 1998 John Wiley & Sons, Inc. Int J Chem Kinet: 30: 457–462, 1998

INTRODUCTION

The rate of the gas-phase thermal elimination reaction of pentane-2,4-dione has been measured [1] and compared with the rates reported for acetic anhydride [2], diacetylsulphide [3], and diacetamide [4]. The mechanism adopted [4,5] to explain the kinetic data and

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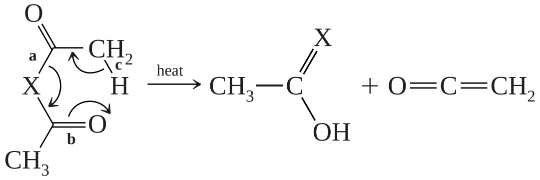
products of the elimination reaction of the present substrates and related compounds involves a semiconcerted 6-membered transition state (Scheme I). It is to be noted that ketene and acetone, acetic/thioacetic acid, or acetamide are the only products of fragmentation in these reactions.



Scheme I Generic elimination pathway: X = CH$_2$, O, S, and NH

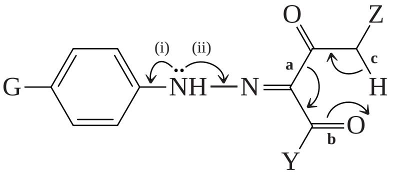
The rates of reaction at 600 K of pentane-2,4-dione **(8)**, acetic anhydride, diacetylsulphide, and diacetamide are in the ratio of $1:3 \times 10^2:6 \times 10^3:5 \times 10^4$, respectively. This increase in relative reactivity is the result of an increase in the polarity of the carbonyl C—X bond **(a)**, from the methylene (CH$_2$) unit in the dione **(8)** to O of the anhydride, to S of the sulphide, and to the NH unit of the diacetamide molecule (Scheme I). We have attempted to enhance the relatively low reactivity of the dione system by replacing the methyl moiety of the acetyl group with the electron-withdrawing CH$_3$O and CH$_3$CH$_2$O substituents, in order to increase the polarity of bond **(a)** and, hence, rates of reaction. However, this structural modification resulted in a change of mechanism of reaction to a pathway involving intermolecular elimination leading to cyclization and loss of alcohol [1]. Besides, our investigations have shown that it was possible to restore the elimination pathway of the dione reaction to the semiconcerted 6-membered transition state when an arylhydrazono (ArNHN=) group was incorporated into the dione frame in lieu of the methylene hydrogen atoms of the dione. We have accordingly prepared the series of compounds **(1–5)** examined here, in addition to compound **6** reported elsewhere [1]. It is instructive to note that all these substrates contain the hydrazono substituent.

Further, we have measured the rates of reaction of these compounds and examined the influence of bonds **a**, **b**, and **c**, as well as the effects of groups G, Y, and Z on the reactivity of these substrates (Schemes I, II, and III).

RESULTS AND DISCUSSION

The kinetic data and Arrhenius log *A* (s^{-1}) and E$_a$ (kJ mol^{-1}) for the present series of compounds **(1–6)** are given in Table I, and to facilitate comparisons and correlation of reactivity to structure the rate coefficients at 600 K are recorded in Scheme III. The reactions of these substrates were confirmed to be homogeneous and unimolecular [1]. Rates were measured over a temperature range of >50 K, and the reported first-order rate constants represent average values of at least three kinetic runs which are in agreement to within ± 2%. The Arrhenius plots were strictly linear, and the magnitude of the log *A* (s^{-1}) values is as expected for such thermal gas-phase elimination processes [1,5,6]. A typical plot is shown in Figure 1 for 1-cyano-1-phenylhydrazonopropanone**(1)**. The products of reaction were analyzed and identified using FT–IR and NMR techniques [1].

The overall reactivities are the result of electronic synergism involving bonds **a**, **b**, and **c** and the stabilizing influences associated with the hydrazono substituents and the electronic and steric effects of groups Y and Z (Scheme II); Y would, of course, be absent when bond **(b)** is that of a C≡N moiety.



Scheme II Effective bond polarization and competitive (opposing) delocalization of lone pair of electrons on NH moiety

The present and reported kinetic data and relative rates (Table I and Scheme III) are discussed on the basis of the elimination pathway suggested for the reactions (Schemes I and II) as follows.

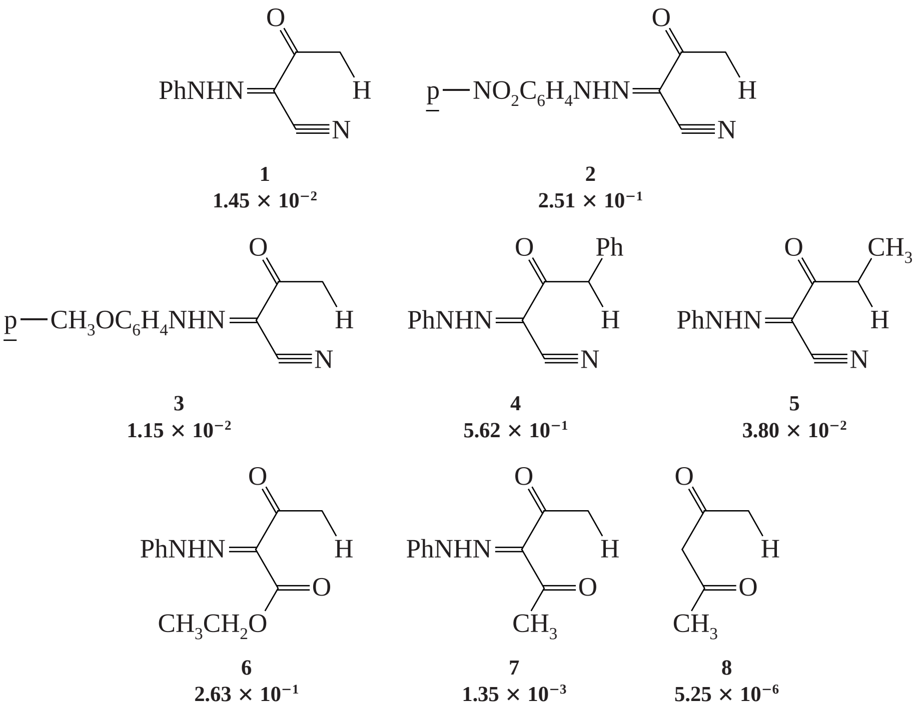
The reactivity of compound **(7)** exceeds that of **(8)** by a factor of 257. This rate enhancement is attributed to the influence which the phenylhydrazono (PhNHN) substituent has on the polarity of bond **(a)**, and to the protophilicity [4] of bond **(b)** through an extended conjugation involving the lone pair of electrons on the NH moiety of the phenylhydrazono group. It has already been noted above that when this group is incorporated into the molecular framework of a suitable substrate, the mechanism of the elimination process is restored to a semiconcerted six-membered transition state, thus, providing a uniform mechanistic base for comparison purposes [1]. The effect which the hydrazono substituent is exerting is further revealed when the rate of reaction of compound **(1)** is compared with that of substrates **(2)** and **(3)**: the rate factors involved are, respectively, 17 and 0.79. Reactivity is increased by the electron-withdrawing p-NO$_2$ group in **2** and slightly retarded by the mesomerically electron-do-

Table I Rate Coefficients and Arrhenius Parameters for Thermolysis of Substrates **1–5**

Substrate	T/K	$10^{-4}k$ (s^{-1})	log A (s^{-1})	E_a (kJ mol^{-1})	$k_{600\ K}$ (s^{-1})
1	526.2	2.84	10.42 ± 0.16	140.8 ± 1.67	1.45×10^{-2}
	533.4	4.14			
	543.5	7.44			
	553.4	13.4			
	560.5	19.1			
	565.5	27.0			
	570.3	32.65			
	577.5	48.07			
2	480.5	2.99	11.19 ± 0.21	135.4 ± 2.05	2.51×10^{-1}
	488.1	4.66			
	495.5	8.19			
	500.5	12.4			
	508.1	17.7			
	513.0	25.1			
	520.5	39.62			
	527.6	60.36			
3	553.1	3.79	10.68 ± 0.13	144.9 ± 2.52	1.15×10^{-2}
	563.1	6.68			
	570.5	10.5			
	575.5	13.4			
	579.1	17.0			
	583.2	19.6			
	589.5	28.22			
	598.4	44.40			
4	458.3	1.08	11.76 ± 0.29	137.8 ± 2.65	5.62×10^{-1}
	475.3	4.05			
	485.2	9.26			
	493.3	14.6			
	498.1	19.0			
	503.0	27.1			
5	513.1	2.88	11.29 ± 0.21	145.9 ± 2.16	3.80×10^{-2}
	520.5	4.36			
	527.0	6.56			
	533.5	10.8			
	538.3	13.3			
	544.0	20.6			
	548.0	23.9			
	553.2	33.12			
	560.5	50.05			
6	503.4	0.10	11.90 ± 0.40	143.3 ± 3.90	2.63×10^{-1}
	520.5	3.10			
	525.4	4.70			
	533.0	6.40			
	547.8	15.1			
	554.9	22.5			

nating p-methoxyl substituent of compound **3**. One reason why the observed rate factors seem moderate might be associated with the opposing directions in which the lone pair of electrons on the NH moiety of the hydrazono substituent is being partitioned (Scheme II).

Dione **(6)** is 195 times more reactive than dione **(7)**. The rate factor involved is conceivably much higher than this, since the methyl group in **(7)** would have increased the reactivity of this compound by an increment not subjected to correction. The higher reactivity of compound **(6)** is a consequence of the effect which the methoxyl group has on the polarity of bond **(a)**; the importance of this structural effect in these elimi-



Scheme III Structures of Compounds **1–8** with rate constants **k/s^{-1}** at 600 K

nation processes has been noted in previous investigations [4].

The polar and hyperconjugative effects of the methyl group in substrate **(7)** act to increase the protophilicity of bond **(b)** and, therefore, also the overall rate of elimination. Nevertheless, the rate of reaction of compound **(1)** is ca. 11 times higher than that of **(7)**. This factor, therefore, represents only a lower limit, since bond **(b)** in **(1)** is now part of the C≡N moiety. The present results suggest that the rate-enhancing effect of the C≡N bond exceeds that of the C═O bond, since the two labile and protophilic π-bonds of the C≡N moiety are being compared with only one π-bond in the case of the C═O function.

The relative rates of the two substrate pairs **(4/1)** and **(5/1)** are, respectively, 39 and 3.93 (2.62 without statistical correction). The former rate factor is rationalized in terms of the electron-withdrawing effect of the phenyl group on the acidity of the incipient proton, which indicates a hydrogen-bond donating effect of bond **(c)**, and to a resonance stabilizing influence on the incipient ketene fragment. The origin of the small rate-enhancing factor of 3.93 associated with the methyl group of compound **(5)** is not consistent with the effect which the electron-donating methyl group is expected to have on the acidity of the incipient proton. However, the formation of ketene from **(1)** and methylketene from **(5)** involves an increase in bond angle from the tetrahedral to the digonal and to the trigonal angles of the adjacent double bonds in question. Any steric relief associated with this change in bond angles would be expected to be more important for **(5)** than for **(1)**.

EXPERIMENTAL

Materials

Synthesis. The preparation and characterization of compounds **4** and **5** have been reported [7,8]. Compounds **1, 2**, and **3** were prepared using an essentially similar procedure as follows. A solution of 3-aminocrotononitrile (0.1 mL) in ethanol (100 mL) was treated with sodium acetate (20 g). The appropriate aromatic diazonium salt was then added gradually with stirring to the mixture; the diazonium salt being prepared according to standard literature procedures from the corresponding aromatic amine (0.1 mL), concentrated hydrochloric acid, and sodium nitrite. After complete addition of the diazonium salt, the reaction mixture was kept at room temperature for one hour. The resulting solid product was filtered and dissolved

Table II Melting Points (m.p.) and C, H, and N Analysis of Compounds **1–5**

Compound	m.p. (°C)	Calculated (%) C	Calculated (%) H	Calculated (%) N	Found (%) C	Found (%) H	Found (%) N
1	176	64.17	4.85	22.46	64.30	5.06	22.54
2	270	51.72	3.47	24.13	51.64	3.61	24.22
3	132	60.82	5.10	19.35	60.78	4.97	19.30
4	137	72.98	4.98	15.97	73.23	4.97	16.04
5	129	65.67	5.51	20.88	65.71	5.70	20.85

in acetic acid (50 mL), and the solution was treated with concentrated hydrochloric acid (30 mL). The mixture was refluxed for 10 min, allowed to cool, and then poured into water. A yellow solid was obtained, which was isolated and recrystallized from ethanol.

Characterization. The melting points (uncorrected) and the results of element analysis of compounds **1–5** are reported in Table II. IR spectra were recorded on samples in KBr disks using a Shimadzu IR-740 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-80 spectrometer using [^{2}H]DMSO as solvent and TMS as internal standard. **IR** spectra of compounds **1, 2**, and **3**: 3305–3215 (NH), 2205 (CN), and 1652–1661 (CO). The **^{1}H NMR** spectra of compounds **4** and **5**: δ 4.20 (s, 2H, CH_2), 7.27–7.56 (m, 10H, 2Ar-H), and 12.30 (br, 1H, NH) for compound **4**; δ 1.20 (*t*, 3H, CH_3), 2.90 (s, 2H, CH_2), 7.10–7.40 (m, 5H, Ar—H), and 9.65 (br, 1H, NH) for compound **5**. The glc purity of all the compounds was ascertained, and their HPLC retention data were collected for use in the kinetic and reaction product analysis.

Kinetics

Reaction Set-up. The flow-system configuration used in the kinetic investigations consisted of: (a) HPLC chromatograph (Bio-rad Model 2700) housing a UV/VIS detector (Bio-rad Model 1740); the HPLC accessories included an LC-8 chromatography column, 25 cm, 4.6 mm, and 5 μm (Suppelco) and (b) CDS custom-made pyrolysis unit for the gas-phase thermolysis. The pyrolysis tube used to investigate the elimination reactions was insulated by an aluminium block fitted with a resistance thermometer and a thermocouple connected to a Comark microprocessor thermometer.

Kinetic Runs and Data Analysis. Aliquot parts (0.2 ml) of very dilute solutions (ppm) of neat substrates in acetonitrile as internal standard were pipetted into the reaction tube, and the tube was sealed under vacuum and placed inside the pyrolyzer for 600 s at a reaction temperature where 10–20% pyrolysis was deemed to occur. The contents of the tube were then analyzed using HPLC. Data from sets of three kinetic runs were recorded when the set runs were in agreement to within experimental error, and the reaction was followed at 5–10°C temperature intervals until 90–95% pyrolysis was observed. The rates of reaction of each substrate were followed over a temperature range of ca. 50 K within the temperature domain of 480–600 K. The rate coefficients were calculated using the rate equation: $kt = ln\ a_0/a$, and the Arrhenius parameters were obtained from a plot of log k against $1/T$ (K) [1]. A typical plot is given in Figure 1 for 1-cyano-1-phenylhydrazonopropanone **(1)**. The rate co-

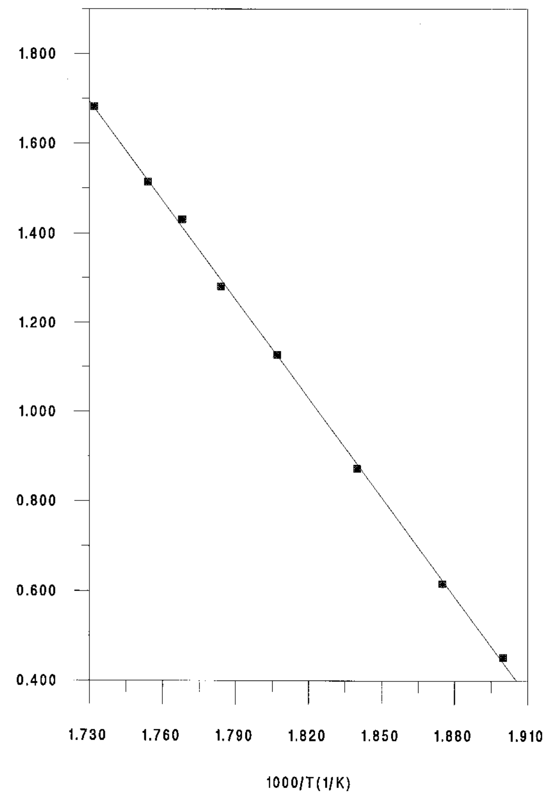


Figure 1 Arrhenius plot for compound (1).

efficients at $T = 600$ K were obtained using the relation: $\log k = \log A - Ea/4.574\ T$.

Product Analysis

Using On-Line Pyroprobe GC-MS. Pyroprobe CDS Analytical Model 2000 is a multiple step platinum filament pyrolysis instrument interfaced to the GC–MS system by means of a heated chamber which houses the filament rod during pyrolysis. A minute amount of the compound to be pyrolyzed was placed in a quartz tube inside the coil probe. The probe is placed inside the interface and sealed into the interface using a septum with $\frac{1}{4}''$ aperture. The temperature programming of the interface and probe were adjusted to allow an efficient pyrolysis of the compound. The pyrolysates are swept into the GC-MS system by the carrier gas. The conditions of the GC and the MS were adjusted to affect a good separation of the pyrolysates and to allow proper identification.

Using Flow Technique. This technique has been described in an earlier communication [4].

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