Gas-phase Pyrolytic Reactions. Part 5.[1] Rate Data for Pyrolysis of *N*-t-Butyl- and *N*-Acetyl-benzamide, *N*-Acetyl-*N*-methylacetamide, and *N*-Ethyl- and *N*-Prop-2-yl-thioacetamide

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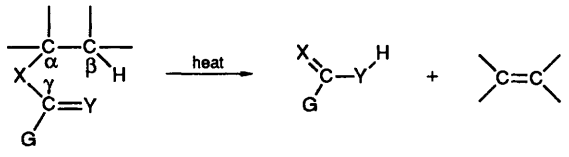
The rates of gas-phase elimination of *N*-t-butylbenzamide **1**, *N*-acetylbenzamide **2** and *N*-acetyl-*N*-methylacetamide have been measured in the ranges 674–734, 580–620 and 696–765 K, respectively. The compounds undergo unimolecular first order elimination reactions for which log A = 11.1, 13.7 and 10.5 s^{-1} and E_a = 172.6, 171.7 and 167 kJ mol^{-1}, respectively. At 600 K, the following reactivity ratios are observed: **1**: *N*-t-butylacetamide **3**, 260; *t*-butyl benzoate **4**: *t*-butyl acetate **5**, 2.3; *N*-acetylacetamide **6**: *N*-acetyl-*N*-methylacetamide, 290; and **2**:**6**, 3.6. These relative rate factors show that the phenyl group increases the rate of thermolysis due to its electron-withdrawing ability 250 times more for simple amides than for esters and diamides. These relative rate differences are highly affected by the nature of the C_α–X bond. The pronounced effect of the phenyl group on simple amides could be explained in terms of the low polarity of the C_α–NH bond relative to the more polar C_α–O bond in esters. On the other hand the pronounced deactivation effect of the methyl group in *N*-acetyl-*N*-methylacetamide is highly reflected in the reactivity ratio of 290 between **6** and *N*-acetyl-*N*-methylacetamide which could be explained in terms of the greater bond order of the C_α–X bond in the latter than in the former. Furthermore, the small reactivity ratio in the diamides **2** and **6** is consistent with the fact that resonance between the lone-pair of electrons on X and the α-carbonyl group increases the C_α–X bond order, thus rendering the C_α–X bond breakage more difficult. We have also measured the rates of thermolysis of *N*-ethylthioacetamide and *N*-prop-2-ylthioacetamide. The relative primary:secondary:tertiary rates at 600 K of 1:1.3:1.5 for the thioamides suggests that the transition state for this class of compound is much less polar than that for the thioacetates.

Our investigations on the rates of thermal elimination of amide and diamide systems have shown that they involve a six-membered transition state described in Scheme 1.[2] The effect of



Scheme 1. Cyclic transition state formulation of elimination pathway.

changing X from O (ester) to NH (amide) has been assessed for simple t-butyl systems.[3,4] The effect of changing Y from O (amide) to S (thioamide) has been recently described.[2] The results of the above investigations have shown the following.

(i) The relative rate ratio between t-butyl acetate **5** and *N*-t-butylacetamide **3** is 68 710. This has been attributed to the special importance of C_α–O and C_α–NH bond-breaking in the rate-determining step of the elimination pathway.

(ii) The relative rate ratio of 68 710 between **5** and **3** which has been reduced to 4066 between t-butylthioacetate and *N*-t-butylthioacetamide, has confirmed the fact that the reactivity differences diminish as C_α–X bond breakage becomes less important and C=Y attack on the β-hydrogen becomes correspondingly more important.

(iii) We have explained[2] the greater reactivity of diacetamide over *N*-acetylthioacetamide (by a factor of 173) in terms of delocalization of the lone-pair of electrons on the nitrogen atom onto two carbonyl oxygen atoms in the diamide system preferentially onto the carbonyl oxygen rather than the thiol sulphur.

The effect of change in substituent on the carbonyl group on the elimination rate has been studied[3] in acetates, phenylacetates, benzoates, carbamates and carbonates. In all these systems X in the C_α–X bond is O. The present work is the first study of the same effect but on a C_α–NH bond. We have prepared *N*-t-butylbenzamide and *N*-acetylbenzamide and measured their rate of thermolysis in order to compare them with acetates and benzoates, respectively. It is also the first study of the electronic effect of a substituent on the nitrogen atom in amides. We have therefore prepared *N*-acetyl-*N*-methylacetamide and compared its reactivity with *N*-acetylacetamide in gas-phase thermolysis reactions. We have also compared the relative primary:secondary:tertiary rates at 600 K for *N*-alkylthioacetamides with that for thioacetates. We have therefore prepared *N*-ethylthioacetamide and *N*-prop-2-ylthioacetamide and measured their rates of gas-phase elimination.

Results and Discussion

In our analytical flow apparatus the compounds were each very well behaved kinetically, and gave excellent and reproducible first-order rate constants with a linearity of 95% reaction and with no deviation in the Arrhenius plots. Since a sixfold change in the amount of substrate used per kinetic run gave no significant change in rate coefficient, these reactions were deemed to be first-order processes. The data are summarised in Table 1. The Arrhenius parameters seem to be in agreement with the pathways proposed for these reactions. The kinetic

Table 1. Kinetic data and Arrhenius parameters for pyrolysis of amides **1**, **2**, *N*-acetyl-*N*-methylacetamide, **6** and *N*-ethylthioacetamide.

Compound	T/K	k/10^{-3} s^{-1}	log A/s^{-1}	E_a/kJ mol^{-1}	k/s^{-1} (600 K)
1	672.8	6.5	11.1 ± 0.7	172.6 ± 9.6	1.2×10^{-4}
	685.0	8.5			
	694.4	13.8			
	704.3	17.9			
	714.3	29.2			
	724.2	50.5			
	734.0	76.2			
2	580.7	24.0	13.7 ± 0.8	171.7 ± 11.5	5.6×10^{-2}
	592.4	38.0			
	599.5	54.0			
	604.2	71.1			
	607.9	93.5			
	611.6	123.0			
	615.4	161.8			
	619.2	212.8			
N-Acetyl-*N*-methylacetamide	696.2	9.4	10.5 ± 0.24	167.1 ± 3.4	8.7×10^{-5}
	706.0	13.4			
	715.5	18.1			
	735.5	41.4			
	756.9	90.2			
	765.6	121.9			
6	657.9	11.4	13.9 ± 0.6	199.1 ± 7.7	3.5×10^{-4}
	660.5	14.4			
	667.5	19.9			
	671.1	24.9			
	673.7	30.1			
	676.9	33.5			
	680.8	45.0			
	688.4	66.8			
	695.3	77.4			
N-Ethylthioacetamide	645.2	6.3	12.4 ± 0.4	179.7 ± 5.7	5.6×10^{-4}
	649.3	7.9			
	653.6	9.8			
	654.4	12.6			
	662.7	19.5			
	671.6	27.7			
	680.3	40.0			
	689.2	62.1			
	699.0	91.3			
	704.2	102.3			

Table 2. Rate coefficients and relative rates of MeCSXR.

X	Ethyl	Prop-2-yl	t-Butyl	k_{rel} 1°:2°:3°
NH	3.5×10^{-4}	5.6×10^{-4}	6.6×10^{-4} [a]	1:1.6:1.9
O	2.6×10^{-3} [b]	105×10^{-3} [b]	2700×10^{-3} [c]	1:40:1000

[a] Ref. 2. [b] Ref. 8. [c] Ref. 9.

consequences of changing G from a methyl to a phenyl group are recorded in Fig. 1. Comparison of the kinetic data reveals the following.

(i) Each of the phenyl-containing compounds is more reactive than its methyl-containing analogue due to the greater electron-withdrawing ability of the phenyl group which will assist in the breaking of the C_α–X bond.

(ii) A greater reactivity difference is observed between t-butylbenzamide **1** and t-butylacetamide **3**. This relative rate ratio of 260 decreases with increasing C_α–X bond polarity; this ratio is reduced to 2.3 for the corresponding oxygen-containing compounds, **5** and **6**. This effect could be attributed to the electron-withdrawing ability of the phenyl group which will aid the breaking of the less polar C_α–NH bond in benzamide more than it does for the C_α–O bond in benzoate.

(iii) The relative rate ratio between **2** and **6** is 3.6. This rate difference might have been even larger were it not for the lone-pair of electrons on X and the α-carbonyl group which will increase the C_α–X bond order, thus rendering C–X bond breaking more difficult; a small rate difference between **2** and **6** is thus observed.

The reactivity of *N*-acetyl-*N*-methylacetamide is highly affected by the electronic nature of the substituent on the nitrogen atom which will affect the resonance between the electron lone-pair on X and the α-carbonyl group. The reactivity ratio of 290 between *N*-acetylacetamide **6** and *N*-acetyl-*N*-methylacetamide is due mainly to the electron-donating nature of the methyl group which will positively affect the above-mentioned resonance making the C_α–X bond order in *N*-acetyl-*N*-methylacetamide greater than that for **6**. We are currently studying the effect of different aryl groups on the nitrogen atom in *N*-acetylacetamide.

The rate spread between the primary, secondary and tertiary thioacetamides given in Table 2 is much less than that for the thioacetates. Taylor[3] indicated that the most reactive ester types have the most polar transition states. However this study relates to the alkyl acetates and phenyl acetates, benzoates, carbamates and carbonates in which the increase in the electron-withdrawing effect at the α-carbon would assist in increasing the reactivity of the ester by increasing the polarity of the transition state. In this study we are comparing the relative

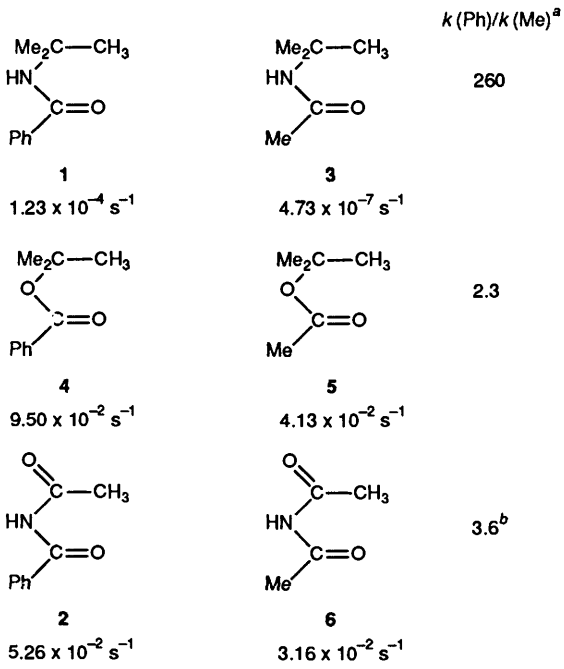


Fig. 1 Relative reactivities at 600 K of benzamide/acetamide, benzoate/acetate and *N*-acetylbenzamide/*N*-acetylacetamide. [a] At 600 K. [b] Statistically corrected for the β-hydrogen atoms available for elimination.

primary:secondary:tertiary rates for different types of amides and esters where there is a major difference in the polarity of the C_α–X bond which is reflected in the small rate ratio observed for primary, secondary and tertiary thioamides, and the relatively larger rate ratios (1:40:1000) for the relatively non-polar C_α–NH bond in the case of thioesters with the polar C_α–O bond.

Experimental

Kinetic Studies.—The particulars of the flow system used for measuring reaction rates, and the technique of kinetic data analysis have been described.[5] The pyrolysis gas chromatography used for the kinetic studies consisted of a Eurotherm 093 pyrolysis unit coupled to a Perkin-Elmer Sigma 115 gas chromatograph.

Product Analysis.—Solutions of substrates **1**, **2**, *N*-acetyl-*N*-methylacetamide, *N*-ethylthioacetamide and *N*-prop-2-ylthioacetamide in chlorobenzene were passed down a reactor column packed with helices. The column was heated to temperatures comparable to those used in the kinetic investigations.[6] The products of pyrolysis were swept out using a stream of nitrogen gas, and the effluents were collected in cold traps. The product obtained from the pyrolysis of *N*-t-butylbenzamide was benzamide. Products from the pyrolysis of *N*-acetylbenzamide were benzamide and ketene; while the products from the pyrolysis of *N*-acetyl-*N*-methylacetamide were *N*-methylacetamide and ketene. All the products were trapped [2] and identified by NMR and IR spectroscopy. The only product which was identified from the pyrolysis of *N*-ethylthioacetamide and *N*-prop-2-ylthioacetamide was thioacetamide.

N-t-Butylbenzamide **1**.—Reaction of t-butylamine with benzoyl chloride in the presence of pyridine gave, after normal work-up, *N*-t-butylbenzamide (83%), m.p. 135–136 °C (light petroleum, b.p. 40–60 °C) (lit.,[7] 134 °C) $\delta_H(CDCl_3)$ 1.4 [9 H, s, $C(Me)_3$], 7.4–7.6 (5 H, m, Ph), and 9.8 (1 H, s, NH) (Found: C, 75.0; H, 8.5; N, 8.2. Calc. for $C_{11}H_{15}NO$: C, 75.0; H, 8.4; N, 8.5%).

N-Acetylbenzamide **2**.—Reaction of benzamide with acetyl chloride in the presence of pyridine gave, after normal work-up, *N*-acetylbenzamide (78.5%), m.p. 118 °C light petroleum, b.p. 40–60 °C (lit.,[8] 118°), $\delta_H(CDCl_3)$ 2.6 (3 H, s, Me) 7.5–7.8 (5 H, m, Ph) and 9.8 (1 H, s, NH) (Found: C, 66.0; H, 5.5; N, 8.4: Calc. for $C_9H_9O_2N$: C, 66.2; H, 5.5; N, 8.5%).

N-Acetyl-N-methylacetamide.—Reaction of *N*-methylacetamide with acetyl chloride in the presence of pyridine gave, after normal work-up, *N*-acetyl-*N*-methylacetamide (80%), m.p. 97.8 °C light petroleum, b.p. 40–60 °C, $\delta_H(CDCl_3)$ 2.3 [6 H, s, $(COCH_3)_2$] and 2.9 (3 H, s, CH_3) (Found: C, 52.0; H, 7.8; N, 12.4: Calc. for $C_5H_9NO_2$: C, 52.2; H, 7.8; N, 12.2%).

N-Ethylthioacetamide.—The reaction of *N*-ethylacetamide with P_2S_5 gave the *N*-ethylthioacetamide (40%), b.p. 98 °C at 2.0 mmHg, δ_H 1.25 (3 H, t, CH_2CH_3), 2.5 (3 H, s, CSMe), 3.6 (2 H, q, CH_2Me) and 7.9 (1 H, t, NH) (Found: C, 46.4; H, 8.5; N, 13.1. Calc. for C_4H_9NS: C, 46.6; H, 8.7; N, 13.5%).

N-Prop-2-ylthioacetamide.—The reaction of *N*-prop-2-ylacetamide with P_2S_5 gave *N*-prop-2-ylthioacetamide (53%), b.p. 92 °C at 20 mmHg, $\delta_H(CDCl_3)$ 1.3 [6 H, d, $HC(Me)_2$], 2.5 (3 H, s, CSMe), 4.7 [1 H, m, $HC(Me)_2$] and 7.9 (1 H, d, NH) (Found: C, 51.0; H, 9.3; S, 27.4; N, 11.5. Calc. for $C_5H_{11}NS$: C, 51.3; H, 9.4; S, 27.3; N, 11.9%).

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