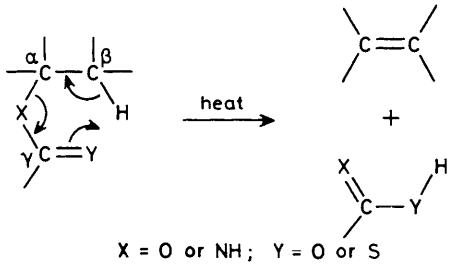
Gas-Phase Pyrolytic Reactions. Rate Data for Pyrolysis of *N*-t-Butylthioacetamide and *N*-Acetylthioacetamide: Role of Polarity of Transition State and γ-Carbonyl Group Protophilicity

Nouria A. Al-Awadi,* Rasha F. Al-Bashir, and Osman M. E. El-Dusouqui
Department of Chemistry, University of Kuwait, PO Box 5969 Safat, 13060 Safat, Kuwait

In the gas phase, both *N*-t-butylthioacetamide and *N*-acetylthioacetamide undergo unimolecular first-order elimination reactions for which log A = 11.58 s^{-1} and 10.64 s^{-1}, and E_a = 16.45 kJ mol^{-1} and 117.15 kJ mol^{-1}, respectively. The results are in accord with a reaction pathway involving a cyclic six-membered transition state, and show each compound to be more reactive than its oxygen-containing analogue. At 600 K, the statistically corrected reactivity ratios: t-butyl thioacetate (**1**)/t-butyl acetate (**2**); *N*-acetylthioacetamide (**3**)/diacetamide (**4**); and *N*-t-butylthioacetamide (**5**)/*N*-t-butylacetamide (**6**) are 83, 173, and 1 404, respectively. The above rate factors are consistent with the tenet that as C_α–X bond fission becomes less rate-contributing in these electrocyclic reactions, so attack by the C=Y bond upon the β-hydrogen atoms becomes more important. Thus, whereas t-butyl acetate at 600 K is some 68 700 times more reactive than *N*-t-butylacetamide, t-butyl thioacetate is only 4 060 times more reactive than *N*-t-butylthioacetamide.

The gas-phase thermal elimination of esters, amides, and anhydrides containing β-hydrogen atoms are thought[1] to involve pathways in which the transition states approximate to cyclic six-membered structures (Scheme 1).



Scheme 1. Cyclic transition state formulation of elimination pathway.

The effect of changing group X from O (ester) to NH (amide) has been assessed only for simple t-butyl systems.[2,3] The first-order rate coefficients at 600 K of 3.25 × 10^{-2} s^{-1} for t-butyl acetate (**2**), and 4.73 × 10^{-7} s^{-1} for *N*-t-butylacetamide (**6**) yield a relative rate of 68 710. This comparatively large relative rate factor is considered to be a manifestation of the special importance of C_α–O and C_α–NH bond-breaking in the rate-determining step of the elimination pathway.[4] If the same were true of the pyrolysis of t-butyl thioacetate (**1**) and *N*-t-butylthioacetamide (**5**), a similarly large relative rate factor might also be expected for this pair if no other factors were involved. In a series of papers, one of us has drawn attention to the spectrum of transition states that are evident in the pyrolysis of compounds that proceed *via* a six-membered electrocyclic mechanism.[5] For compounds in which the C_α–X bond is weakly polar, attack by the C=Y bond upon the β-hydrogen atoms assumes greater significance. Since the C=Y bond is weaker when Y=S than when Y = O, compounds in which S replaces O should be more reactive, and increasingly so the less polar the C–X bond. In order to provide additional evidence in support of this view we have prepared *N*-t-butylthioacetamide (**5**), and measured its rate of pyrolysis in order to compare this with the literature data on *N*-t-butylacetamide (**6**). Relative rates of elimination have previously been measured for diacetamide which was found to be only seven times less reactive than acetic anhydride, in contrast to the very large factor of 68 710 noted above for t-butyl acetate compared with *N*-t-butylacetamide.[4,6] This large difference in rate factors can also be attributed to the much greater importance of the γ-carbonyl group in the reactivity of the former class of compounds; and this being so, resonance between the lone pair on X and the C=Y bond would further diminish the relative reactivity factors between the O and NH compounds. To investigate further the importance of this structural effect, we prepared and pyrolysed *N*-acetylthioacetamide (**3**), and for consistency in comparative kinetic data we have also carried out a separate study on diacetamide (**4**) in our flow apparatus.

Results and Discussion

In our analytical flow apparatus, *N*-acetylthioacetamide (**3**), diacetamide (**4**), and *N*-t-butylthioacetamide (**5**) behaved well and gave excellent Arrhenius plots over the temperature ranges of 472–524 K for (**3**), 565–615 K for (**4**), and 638–699 K for (**5**), respectively. Further, these plots revealed a notable absence of surface effects. Our rate data and Arrhenius parameters for diacetamide agree satisfactorily with those reported in the literature.[4] 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 kinetic data for the elimination reactions, and the rate coefficients at 600 K obtained in this investigation for the compounds under study, are given in the Table. The Arrhenius parameters seem to be in agreement with the pathways proposed for these reactions.[1]

Ketene and thioacetamide were detected as pyrolysis products from *N*-acetylthioacetamide (**3**), and thioacetamide from *N*-t-butylthioacetamide (**5**).

The kinetic data presented in Scheme 2 give the rates of a series of acid derivatives containing the C_γ=S moiety relative to the rates of their C_γ=O analogues. The important features evident from these results are as follows.

(i) All the sulphur-containing compounds are more reactive

Table. Kinetic data and Arrhenius parameters for pyrolysis of amides (**3**), (**4**), and (**5**).

Compound	T/K	10^3k/s^{-1}	log(A/s^{-1})	E_a/kJ mol^{-1}	Correlation coefficient	k^a/s^{-1}
(**3**)	472.8	4.60	10.64 ± 0.53	117.15 ± 5.34	0.998	2.73
	477.6	6.53				
	478.0	7.00				
	485.7	11.3				
	492.9	17.5				
	493.3	17.8				
	502.3	29.0				
	507.9	42.2				
	510.7	43.9				
	519.5	72.4				
	520.8	78.2				
	524.9	85.7				
(**4**)	565.3	4.97	11.86 ± 0.41	151.34 ± 2.68	0.999	3.16×10^{-2}
	575.0	8.26				
	576.0	8.81				
	582.7	12.5				
	591.3	20.8				
	592.4	21.8				
	599.5	31.3				
	599.8	32.4				
	608.6	48.1				
	615.3	65.6				
(**5**)	638.5	5.37	11.58 ± 0.31	169.45 ± 4.28	0.998	6.64×10^{-4}
	647.2	7.87				
	656.2	12.8				
	664.9	18.8				
	674.8	27.7				
	682.1	37.3				
	691.1	60.8				
	699.8	90.1				

[a] 600 K.

than the corresponding members of the oxygen-containing series; this observation relates to the relative thermodynamic stability and π-bond energy differences of the C=S and C=O bonds.[7]

(ii) Whereas t-butyl thioacetate (**1**) is only 83 times more reactive than t-butyl acetate (**2**), *N*-t-butylthioacetamide (**5**) is 1 404 times more reactive than *N*-t-butylacetamide (**6**). The latter rather large rate difference confirms the suggestion that in the transition state of amide pyrolysis, attack by the C=Y moiety upon the β-hydrogen atoms is of special importance, and that the transition state of the elimination process is more E_i-like than E_1-like.

(iii) *N*-Acetylthioacetamide (**3**) is 86.4 times more reactive than diacetamide (**4**). However, this reactivity difference must be doubled to allow for the fact that in the latter compound there are six β-hydrogen atoms available for elimination compared with only three in the former. This rate difference might have been even larger were it not for the fact that the lone-pair of electrons on the nitrogen atom is delocalized onto two carbonyl oxygen atoms in (**4**), whereas in (**3**) the electrons will be delocalized preferentially onto the carbonyl oxygen rather than the thione sulphur, and consequently the reactivity of the latter moiety is not enhanced to the degree that it might otherwise have been.

In Scheme 3, the kinetic consequences of changing X from O to NH are compared. Comparison of the kinetic data reveals the following.

(i) Each of the O-containing compounds is more reactive than its NH-containing analogue due to the greater ease of breaking the more polar C_α–X bond.

(ii) The reactivity difference diminishes as C_α–X bond-breaking becomes less important, and C=Y attack on the β-hydrogen correspondingly more important. Thus, the relative rate ratio of 68 710 between t-butyl acetate (**2**) and *N*-t-butylacetamide (**6**), where Y is O, is reduced to 4 066 between the corresponding S-containing compounds (**1**) and (**5**), because of the greater reactivity of the C=Y bond when Y = S than when Y = O.

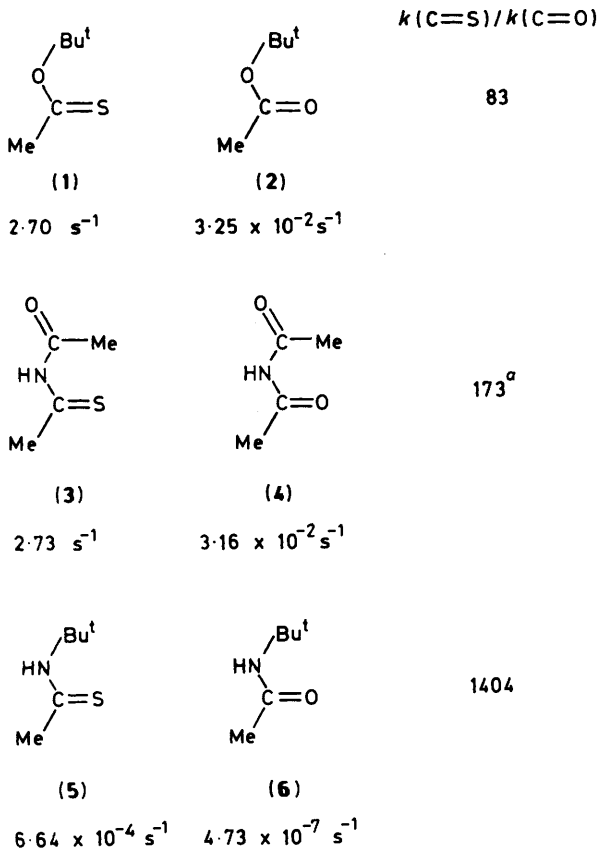
Likewise, the reactivity difference between acetic anhydride (**7**) and diacetamide (**4**) of *ca.* ×9 is very small. In this case, not only is it difficult for the C_α–X bond to polarize in the direction $C^{\delta+}$–$X^{\delta-}$, owing to electron-withdrawal by the carbonyl oxygen at C_α, but in addition, resonance between the lone-pair on X and the α-carbonyl group (Scheme 4) will increase the C_α–X bond order, thus rendering C–X bond-breaking more difficult. Thus attack by the C=Y moiety upon the β-hydrogen is the more important rate contributing factor, so that a small rate difference between (**4**) and (**7**) is observed.

Experimental

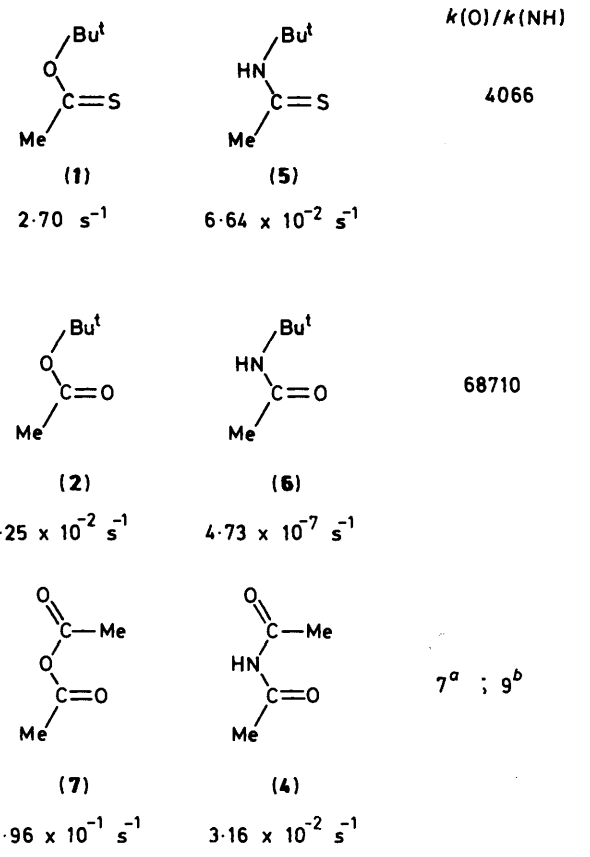
Kinetic Studies.—The particulars of the flow system used for measuring reaction rates, and the technique of kinetic data analysis have been described.[8] The pyrolysis gas chromatograph used for the kinetic studies consisted of a Eurotherm 093 pyrolysis unit coupling to a Perkin–Elmer Sigma 115 gas chromatograph.

Product Analysis.—Solutions of the amide 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.[9] 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 t-butylacetamide was acetamide (confirmed by n.m.r. and i.r. spectroscopy). The



Scheme 2. Relative reactivities at 600 K of *t*-butylamides, diamides and *t*-butyl esters, and their thione analogues. [a] Statistically corrected for the different numbers of β-hydrogen atoms.



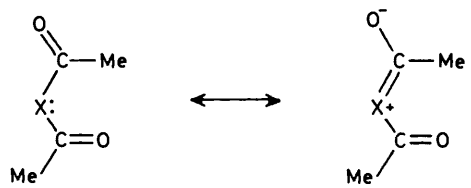
Scheme 3. Relative rates for pyrolysis at 600 K of ester/amide and anhydride/diamide analogues. [a] Computed from literature data. [b] From this work.

products from the pyrolysis of *N*-acetylthioacetamide were firstly passed through a trap in the form of a glass coil surrounded by a jacket of dry ice, and the effluent was passed into sodium hydroxide solution. The material collected on the walls of the trap was analysed using g.l.c., n.m.r., and i.r. spectroscopy, all of which confirmed the presence of only thioacetamide and chlorobenzene. The aqueous sodium hydroxide solution was acidified, extracted, and then analysed by g.l.c., n.m.r., and i.r. The only organic component revealed in the extract was acetic acid, produced by the hydrolysis of ketene.

N-*Acetylthioacetamide* (**3**).—Reaction of thioacetamide with acetyl chloride in the presence of pyridine[10] gave, after normal work-up, *N*-acetylthioacetamide (95.7%), m.p. 61 °C (from light petroleum, b.p. 80–100 °C) (lit.,[11] 62 °C); $\delta_H(CDCl_3)$ 2.23 (3 H, s, CH_3CS), 2.93 (3 H, s, CH_3CO), and 9.85 (1 H, s, NH) (Found: C, 41.3; H, 6.2; N, 12.0; S, 27.2. Calc. for C_4H_7ONS: C, 41.5; H, 5.9; N, 11.9; S, 27.3%).

Diacetamide (**4**).—Reaction of acetamide with acetyl chloride in the presence of pyridine gave diacetamide (82%), m.p. 76 °C (lit.,[5] 77 °C); $\delta_H(CDCl_3)$ 2.30 (6 H, s, CH_3) and 9.75 (1 H, s, NH) (Found: C, 47.6; H, 7.0; N, 13.8. Calc. for $C_4H_7O_2N$: C, 47.5; H, 6.9; N, 13.8%).

t-Butylthioacetamide (**5**).—The reaction of t-butylacetamide[11] with P_2S_5 gave *t-butylthioacetamide* (25%), m.p. 81 °C [from light petroleum (b.p. 80–100 °C)–ether]; $\delta_H(CDCl_3)$ 1.60 [9 H, s, $C(Me)_3$], 2.50 (3 H, s, CH_3), and 7.10 (1 H, 2, NH) (Found: C, 55.0; H, 9.9; N, 10.7; S, 24.5. $C_6H_{13}SN$ requires C, 54.9; H, 10.0; N, 10.6; S, 24.4%).



Scheme 4. Resonance interaction between C_α=O function and lone-pair on X.

Acknowledgements

We thank Mr. Adam Darwish for technical assistance. The support of the University of Kuwait, received through research grant SC032, is gratefully acknowledged.

References

1 R. Taylor, in 'The Chemistry of Functional Groups: Supplement B,' ed. S. Patai, John Wiley, Chichester, ch. 15, pp. 870, 871, and 880.
2 R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1025.
3 A. Maccoll and S. S. Nagra, *J. Chem. Soc., Faraday Trans. 1*, 1973, **69**, 1108.
4 R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1983, 89.
5 N. Al-Awadi and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1988, 177, and earlier papers in this series.
6 R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1983, 291.
7 N. Al-Awadi, D. B. Bigley, and R. E. Gabbott, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1223.
8 N. Al-Awadi and D. Bigley, *J. Chem. Soc., Perkin Trans. 2*, 1982, 773.
9 C. H. DePuy and R. W. King, *Chem. Rev.*, 1960, **60**, 436.
10 W. Walter and J. Krohn, *Liebigs Ann. Chem.*, 1973, 476.
11 J. Goerdeler and K. Stadelbauer, *Chem. Ber.*, 1965, **98**, 1536.

Received 26*th May* 1988; *Paper* 8/02118J