Heteroatom Chemistry
Volume 7, Number 6, 1996

The Mechanism of Thermal Elimination of Urea and Thiourea Derivatives. Part 1. Rate Data for Pyrolysis of N-Acetylurea, N-Acetylthiourea, N,N'-Diacetylthiourea, and N-Acetylthiobenzamide

Nouria Al-Awadi,* Mohamed Hilmy Elnagdi, Tommy Mathew, and Ibrahim El-Gamry

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

Received 29 January 1996; revised 11 June 1996

ABSTRACT

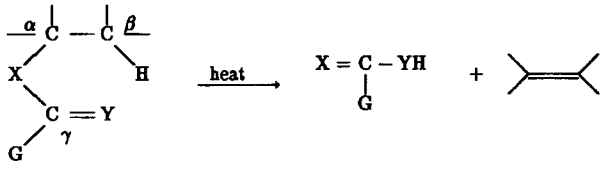
Rates of thermal decomposition of N-acetylurea (1), N-acetylthiourea (2), N,N'-diacetylthiourea (3), and N-acetylthiobenzamide (4) have been measured over a 45 K range for each compound. The molecules were found to undergo unimolecular first-order elimination reactions for which log A = 11.9, 11.6, 11.8, and 13.4 s^{-1}, and E_a = 181.2, 135.9, 128.3, and 130.3 kJ mol^{-1}, respectively. The reactivities of these compounds have been compared with those of amide derivatives and with each other. Product analysis together with the kinetic data were used to outline feasible pathways for the elimination reactions of the compounds under study. © *1996 John Wiley & Sons, Inc.*

INTRODUCTION

The gas-phase thermal elimination of amides containing β-hydrogen atoms are thought to involve pathways in which the transition state is approximated to a cyclic six-membered structure (Scheme 1) [1].

Previously, Al-Awadi et al. [2] showed that diacetamide undergoes unimolecular first-order thermal decomposition into acetamide and ketene in a reaction that is very similar to the thermal elimination of esters. Subsequently, the electronic effects of substituents on the nitrogen atom in amides [3] and diacetamides [4] were examined. The kinetic data revealed that N-aryldiacetamides are less reactive than the parent molecule. This observation was attributed to the mesomeric engagement of the lone pair of electrons on the nitrogen with either of the two carbonyl oxygen atoms or with the π-electron sextet of the aromatic ring.

In our effort to extend the investigation of this mechanistically interesting and potentially important structural effect, we now report work on struc-

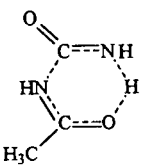


SCHEME 1 Cyclic transition-state formulation of elimination pathway.

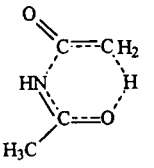
*To whom correspondence should be addressed.

1042-7163/96/060417-04

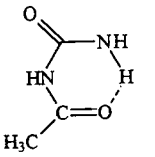
tures related to the acetamide and diacetamide systems, namely, N-acetylurea (1) and N-acetylthiourea (2), and, to provide comparative kinetic data, we have also prepared and pyrolyzed N,N'-diacetylthiourea (3) and N-acetylthiobenzamide (4). The present study describes the behavior of these molecules in gas-phase thermolysis reactions.



(I)



(II)



(III)

RESULTS AND DISCUSSION

Excellent and reproducible kinetic first-order rates for up to >95% of reaction were obtained for each of the compounds being investigated. The rate data (Table 1) gave very good Arrhenius plots, and the log A (s^{-1}) values (Table 2) are all of the order expected for the postulated electrocyclic mechanism.

N-Acetylurea (1). The rate data given in Table 2 confirm that, as in the case of diacetamide, a cyclic six-membered transition state seems to be a plausible option. Acetamide was the product of pyrolysis from (1), which can be formed through transition state (I). The rate coefficient at 600 K is 1.33×10^{-4} s^{-1}, which suggests that the elimination takes place 119 times slower than that of diacetamide [2], which proceeds through cyclic transition state (II); the rate factor is divided by 2 for a statistical consideration. We attribute the lower reactivity of N-acetylurea to hydrogen bonding (III), which does not exist in diacetamide.

N-Acetylthiourea (2). The rate data given in Table 2 also suggest that the pyrolysis of N-acetylthiourea likewise involves a cyclic six-membered transition state. Two alternative pathways (A and B in Scheme 2) could be suggested for the thermolysis of this compound.

However, ketene and thiourea were found to be the sole products from the pyrolysis of N-acetylthiourea, a finding compatible with mechanism (B). The rate coefficient of (2) is 58.7×10^{-2} s^{-1} at 600 K, which makes N-acetylthiourea 4144 times more reactive than N-acetylurea. This dramatic increase in rate is most likely due to the greater protophilicity of the thione sulfur atom in (2) compared to the carbonyl oxygen atom in (1), an effect already recognized elsewhere [2]. This reactivity also can be explained by assuming formation of transition state (IV), which is less energy demanding than formation of transition state (I) for N-acetylurea. The fact that the hydrogen bonding in acetylthiourea is weaker than that in acetylurea helps the molecule to attain the required geometry in transition state (IV).

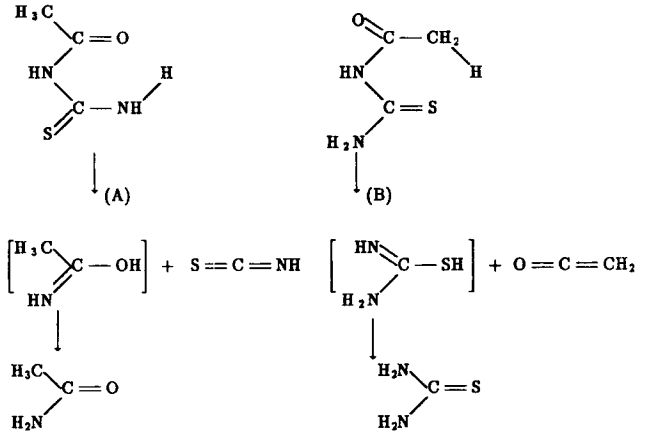
TABLE 1 Rate Coefficients of Compounds (1), (2), (3), and (4)

Compound	*(1)*		*(2)*		*(3)*		*(4)*	
	TK	$10^4 k$ (s^{-1})	*TK*	$10^4 k$ (s^{-1})	*TK*	$10^4 k$ (s^{-1})	*TK*	$10^4 k$ (s^{-1})
	608.0	2.3	463.3	2.5	420.3	0.9	388.2	0.7
	613.5	3.2	473.3	5.3	433.3	2.7	398.2	1.8
	623.3	5.7	478.4	7.7	443.4	6.9	408.1	5.9
	633.4	9.2	483.8	10.5	449.1	9.4	413.9	8.9
	641.1	14.6	488.4	13.6	454.3	14.1	418.9	14.5
	648.3	23.0	493.1	21.6	460.5	22.2	422.1	18.4
	658.0	35.3	503.1	41.6	464.0	27.3	428.0	26.6
			513.3	80.0	470.0	43.7	438.0	68.6

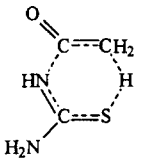
TABLE 2 Arrhenius Parameters and Rate Constants at 600 K for Pyrolysis of Compounds (1), (2), (3), and (4)

	(1)	(2)	(3)	(4)
log A (s^{-1})	11.9 ± 0.01	11.6 ± 0.20	11.8 ± 0.12	13.4 ± 0.01
E_a/kJ mol^{-1}	181.2 ± 0.03	135.9 ± 1.82	128.3 ± 0.10	130.0 ± 2.76
k^a (s^{-1})	1.33×10^{-4}	58.7 ± 10^{-2}	42.7×10^{-1}	113.8

[a]Rate data calculated from Arrhenius parameters.



SCHEME 2



(IV)

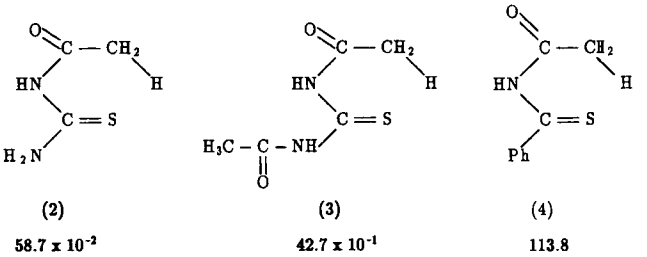
Scheme 3 shows the rate coefficients for elimination of (2), (3), and (4) at 600 K. The greater reactivity of (3) over (2) can be rationalized by the fact that the greater electron-withdrawing acetyl group in (3) has increased the elimination reaction rate by aiding C–N cleavage.

Ketene and thiourea were shown to be the only pyrolysis products from (3), which suggests that this compound pyrolyses via six-membered transition state to ketene and N-acetylthioura, and the latter will then decompose further to produce ketene and thiourea.

The pyrolysis of acetylurea and thiourea through transition states (I–IV) is assured to occur via a concerted way through synchronous reorganization of three electron pairs; i.e., essentially a hetero retro-ene reaction. It is reasonable to ascribe a "quasi-aromatic" character for these species; accordingly, they are favorably formed.

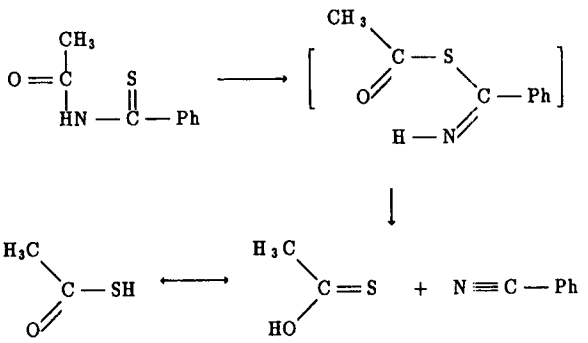
However, a four-center 4*e* system is antiaromatic, and a completely nonpolar transition violates the Woodward–Hoffman rules. It is thus believed that this transition state is highly dipolar.

The phenyl group in (4) is expected to reduce the reactivity of this system relative to (2) but only if both systems were to pyrolyze by equivalent pathways. This, however, is not observed. Besides, product analysis revealed that compound (4) decomposes



SCHEME 3 Rate coefficients k (s^{-1}) for elimination at 600 K.

to benzonitrile and thioacetic acid, an indication of a conceivable four-center mechanism [5] in which nucleophilic attack by the thione π bond upon the carbonyl carbon atom, and subsequent ring opening or concerted bond breaking finally leads to the observed reaction products (Scheme 4). The electron-withdrawing effect of the phenyl group might be a contributing factor in these transformations.



SCHEME 4 Pyrolysis of N-acetylthiobenzamide by four-center mechanism.

EXPERIMENTAL

Synthesis

N-Acetylurea. Urea (15 g) was heated for 1 minute with 15 g of acetic anhydride in the presence of 0.5 g aluminum trichloride at 185°C. Crystallization from water yields N-acetylurea (85%), mp 214–215°C; Ref. [6] mp 216–217°C.

N-Acetylthiourea. A sample was obtained from Aldrich and used as supplied.

N,N'-Diacetylthiourea. Thiourea was refluxed with excess acetic anhydride at 130°C followed by crystallization from a mixture of petroleum ether and acetone to yield N,N'-diacetylthiourea (80%), mp 149–150°C; Ref. [7] mp 151°C.

N-Acetylthiobenzamide. Thiobenzamide was refluxed with acetyl chloride at 100°C followed by crystallization from petroleum ether to yield N-acetylthiobenzamide (75%), mp 100°C, Ref. [8] mp 105°C, with decomposition.

Kinetic Studies

The reactor setup consists of (1) HPLC (Bio-rad model 2700) with UV-VIS detector (Bio-rad model 1740), HPLC column LC-8, 25 cm, 4.6 mm, 5 μm (Suppelco) and (2) CDS custom-made pyrolysis unit, where the elimination reactions were carried out. The pyrolysis tube is jacketed by an insulated aluminum block fitted with a platinum resistance thermometer and a thermocouple connected to a Comark microprocessor thermometer.

Kinetic Procedure

The kinetic rate was obtained by tracing the rate of disappearance of the substrate with respect to an internal standard. The latter was selected so as not to decompose at the reaction temperature, and it should not react with either substrate or product.

Estimation of the quantity of substrate in the reaction solution (very dilute solution of the pure substrate in ppm level, in acetonitrile and an internal standard) was related to the internal standard. The weight ratio between the substrate and the standard was calculated from the substrate peak area/standard peak area at reaction threshold (a_0) at T(K).

This solution (0.2 mL) was pipetted into the reaction tube that was then sealed under vacuum and placed inside the pyrolyzer for 600 seconds at a temperature where 10–20% pyrolysis is deemed to occur. The content of the tube was then analyzed using the HPLC probe.

The kinetic runs were repeated for each 5–10°C rise in temperature of the pyrolyzer and for the same time interval until 90–95% pyrolysis was achieved. For each run, the ratio of substrate to standard was calculated.

The kinetic rates were obtained from the first-order expression $kt = \ell n\, a_0/a$. The Arrhenius parameters were computed from a plot of log k versus 1/T(K).

Product Analysis

Flow Technique. Solutions of substrates in chlorobenzene were passed down a 1 m reactor column packed with helices [9]. The column was heated to temperatures comparable to those used in the kinetic investigations. The products of pyrolysis were swept through the column using a stream of nitrogen gas, and the effluents were trapped in a glass coil surrounded by a jacket of Dry Ice. The material collected on the walls of the trap (glass coil) was crystallized and analyzed by NMR spectroscopy. The product from the pyrolysis of compounds (2) and (3) were first passed through a trap in the form of a glass coil surrounded by a jacket of Dry Ice, and the effluent was passed into a sodium hydroxide solution. The aqueous sodium hydroxide solution was acidified, extracted, and then analyzed. The organic component revealed in the extract was acetic acid, produced by the hydrolysis of ketene [2].

On-line Pyroprobe GC-MS. Pyroprobe (CDS Analytical Model 2000), which is a multiple-step platinum filament pyrolysis instrument, is interfaced to the GC-MS system by means of a heated chamber that houses the pyrolysis filament rod. A minute amount of the compound to be pyrolyzed was placed in a quartz tube inside the coil probe. The probe was placed inside the interface and sealed into the interface using a septum with 1/4" hole. The temperature programing of the interface and probe were so adjusted to achieve 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 effect a good separation of the pyrolysates and for the proper identification of its constituents.

ACKNOWLEDGMENT

The support of Kuwait University through research Grant SC 067 is gratefully acknowledged.

REFERENCES

[1] R. Taylor: in S. Patai (ed): *The Chemistry of Functional Groups: Supplement B,* John Wiley, Chichester, Chap. 15. p. 860 (1979).
[2] N. Al-Awadi, R. F. Al-Bashir, O. M. El-Dusouqui, *J. Chem. Soc., Perkin Trans. 2,* 1989, 579.
[3] N. A. Al-Awadi, *J. Chem. Soc. Perkin Trans. 2,* 1990, 2187.
[4] N. A. Al-Awadi, F. A. Al-Omran, *Int. J. Chem. Kinetics, 26,* 1994, 951.
[5] J. March: *Advanced Organic Chemistry: Reactions, Mechanisms and Structure,* John Wiley, New York (1992).
[6] R. W. Stoughton, *J. Org. Chem., 2,* 1938, 514.
[7] A. E. Dixon, J. Taylor, *J. Chem. Soc.,* 1920, 720.
[8] J. Goerdeler, H. Horstmann, *Ber. Dtsch. Chem. Ges., 93,* 1960, 671.
[9] C. H. Depuy, R. W. King, *Chem. Rev., 60,* 1960, 436.