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The Mechanism of Thermal Elimination of Urea and Thiourea Derivatives. Part 2. Rate Data for Pyrolysis of N-Acetyl-N′-phenylthiourea and N-Benzoyl-N′-arylthioureas

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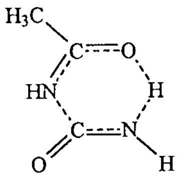
ABSTRACT

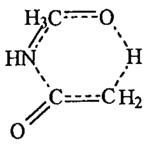
*The first-order rate constants of N-acetyl-N′-phenylthiourea (***1***), N-benzoyl-N′-phenyl-(***2a***), N-benzoyl-N′-(4-nitrophenyl)-(***2b***), N-benzoyl-N′-(3-chlorophenyl) (***2c***), N-benzoyl-N′-(4-chlorophenyl) (***2d***), and N-benzoyl-N′-(4-methylphenyl)thiourea (***2e***) were measured between 423 and 500 K. The reactions were homogeneous and unimolecular with log A* (s^{-1}) *= 12.0, 13.2, 13.8, 10.9, 11.8, and 12.7 and* E_a *kJ* mol^{-1} *= 130.3, 141.4, 134.6, 114.9, 124.1, and 141.1, respectively. The rate data gave good Hammett correlation with* σ^0 *values, and* ρ *is 1.99 at 450 K. © 1997 John Wiley & Sons, Inc.*

INTRODUCTION

In the preceding article [1], we have shown that N-acetylurea undergoes unimolecular first-order thermal decomposition through cyclic transition state (I) at a rate much lower than that of the thermolysis of diacetamide, and we attributed this finding to the hydrogen bonding being more extensive in the precursor of (I) compared to the precursor of (II).



(I)



(II)

The effect of substituting sulfur for oxygen was examined by studying the elimination reaction of N-acetylthiourea, which was found to decompose thermally to ketene and thiourea, as indicated by (IIIa) rather than (IIIb). This suggests that the protophilicity of the thione group ($C=S$), in (IIIa), is now more important than the H-bonding effect; otherwise, pathway (IIIb), which is equivalent to (I), would have been favored; perhaps the fact that the $C=S$ moiety is conceivably less electronegative than the $C=O$ group (an effect that, in part, makes it more protophillic) might have been a contributing factor in this respect.

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TABLE 1 Rate Coefficients k(s^{-1}) of YCONHCSNHX

Compound			
X	*Y*	*T/K*	*10^4 k(s^{-1})*
CH_3	C_6H_5	423.4	0.8
		433.7	1.3
		443.9	4.7
		452.6	8.2
		458.6	12.9
		463.4	18.3
		468.2	22.7
		473.0	35.5
C_6H_5	C_6H_5	443.5	3.3
		453.8	7.5
		458.3	11.8
		463.9	19.0
		468.6	24.5
		478.6	67.6
		489.9	122.3
		497.7	210.0
C_6H_5	4-$NO_2C_6H_4$	403.8	2.7
		413.3	4.2
		418.9	9.0
		423.3	16.5
		428.4	25.9
		436.5	48.7
		445.4	102.1
		455.3	224.7
C_6H_5	3-ClC_6H_4	423.4	5.4
		428.2	8.1
		433.4	10.6
		438.2	15.6
		443.4	24.6
		450.6	38.7
		459.7	71.2
		468.6	126.4
		477.5	219.7
C_6H_5	4-ClC_6H_4	423.5	3.2
		428.6	4.5
		433.5	6.4
		438.6	10.0
		443.4	15.0
		448.8	28.0
		457.5	41.5
		469.6	96.0
		475.5	142.3
C_6H_5	4-$CH_3C_6H_4$	455.5	3.1
		464.7	6.2
		474.2	14.5
		484.5	28.9
		488.9	37.6
		493.9	56.0
		505.7	124.8

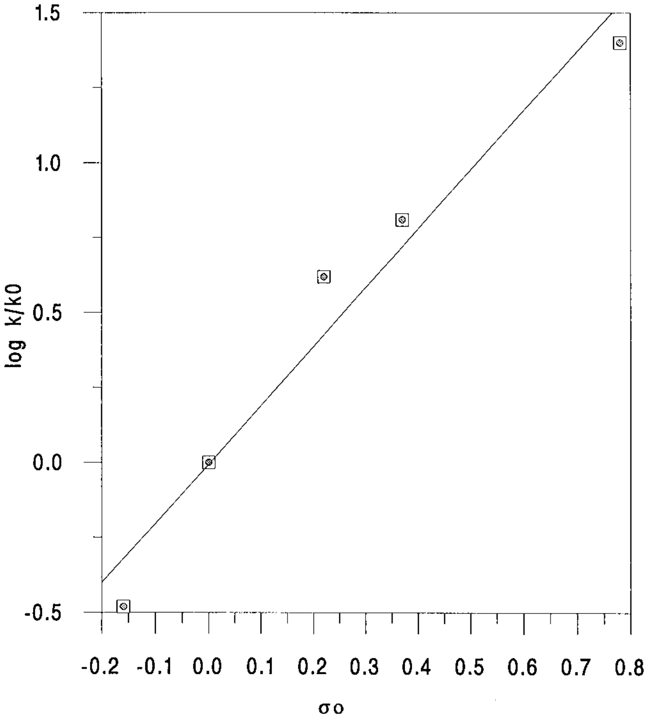
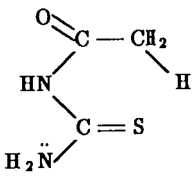
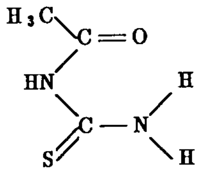


FIGURE 1 Log k/k_0 vs. σ^0 substituent constants for gas-phase pyrolysis of N-phenyl-N′-arylthioureas.



(IIIa)



(IIIb)

The present study further reports on the kinetic and mechanistic implications of introducing a phenyl/aryl substituent as part of the NH_2 function, and of constraining the elimination pathway by replacing the acetyl group with a benzoyl group in (III). Here we have prepared compounds (**1**) and (**2a–e**) and have studied their thermal elimination reactions. These systems offer suitable models for assessing the importance of the acidity of the β-hydrogen atom.

RESULTS AND DISCUSSION

All the compounds under study gave excellent reproducible kinetics, first order to the 95% reaction range. The kinetic data (Table 1) gave excellent Arrhenius plots with no deviant points. The rate data and product analysis confirm that, as in the pyrolysis

TABLE 2 Arrhenius Parameters and Rate Data for Pyrolysis of $C_6H_5CONHCSNHX$ at 450 K

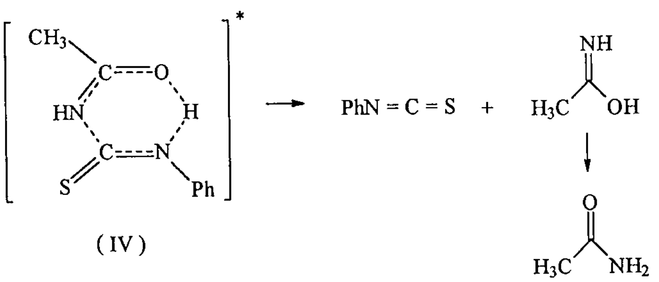
Compd	*X*	*log A(s^{-1})*	*E_a (kJ mol^{-1})*	*10^4 k(s^{-1})*	*log $k_{rel.}$*	*σ^0*
2a	C_6H_5	13.2 ± 0.3	141.4 ± 2.8	5.7	0.0	0.0
2b	4-$NO_2C_6H_4$	13.8 ± 0.5	134.6 ± 4.3	148.0	1.4	0.78
2c	3-ClC_6H_4	10.9 ± 0.1	114.9 ± 1.1	37.0	0.81	0.37
2d	4-ClC_6H_4	11.9 ± 0.1	124.1 ± 1.3	24.0	0.62	0.22
2e	4-MeC_6H_4	12.7 ± 0.2	141.1 ± 1.7	1.9	−0.48	−0.16

TABLE 3 Melting Point and Element Analysis of Compounds **2a–2e**

		Elemental Analysis					
		Calculated (%)			*Experimental (%)*		
Compound	*Mp (°C)*	*C*	*H*	*N*	*C*	*H*	*N*
2a	146–147	65.63	4.19	10.94	65.00	4.30	11.04
2b	191–193	55.81	3.65	13.95	55.93	3.70	14.10
2c	133–134	57.84	3.79	9.64	57.4	3.80	9.71
2d	142–143	57.84	3.79	9.64	57.5	3.77	9.74
2e	158–159[a]	66.67	5.19	10.39	66.36	5.06	10.44

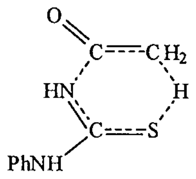
[a] Ref. [5] mp 158–159 °C.

of N-acetylthiourea, a cyclic six-membered transition state [2] is most probably involved in the thermal elimination reaction of N-acetyl-N′-phenylthiourea (**1**). Further, the products of reaction (acetamide and phenyl isothiocyanate) suggest that this pyrolysis reaction takes place via concerted transition state (IV) and that a synchronous reorganization of three electron pairs takes place, essentially a hetero retro-ene reaction. It is reasonable to ascribe a quasi-aromatic character to this species, which would account for its favorability.



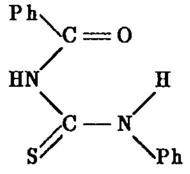
(IV)

Although pyrolysis of N-acetyl-N′-phenylthiourea may also proceed through cyclic transition state (V) similar to the one observed for the thermolysis of acetylthiourea [1], transition state (IV) is more favored here as the phenyl moiety induces further stability to this species; moreover, formation of phenyl isothiocyanate from (IV) is less energy demanding than formation of the isothiocyanic acid from (V).


(V)

The introduction of the phenyl group (accepted as an electron-withdrawing substituent) into the NH_2 function seems to influence the protophilicity of the C = S moiety to an extent that has restored the H-bonding facility of the acetyl C = O group, and to have further increased the acidity of the remaining hydrogen of the amino group, thus enhancing its interaction with the carbonyl function.

We have also prepared and measured the rate of the thermal elimination reaction of N-benzoyl-N′-phenylthiourea (**2a**). The only elimination pathway for this system is that as indicated through (VI).


(VI)

This is confirmed by product analysis, as benzamide and phenyl isothiocyanate were the only products detected in the thermal elimination reaction of this compound.

In order to determine the importance of the acidity of the β-hydrogen atom involved in this thermal elimination reaction, a series of N-benzoyl, N′-arylthioureas (**2a–e**) were prepared and reacted. The relative rates of 450 K (Table 2) gave a satisfactory Hammett correlation (Figure 1) using σ^0 substituent constants [3] and a reaction ρ constant of 1.99. This result confirms that the reactivity of each compound (**2a–e**) toward thermal elimination is highly dependent on the extent of the electron withdrawal (or supply) by the substituents on the aryl group and the electronic nature of the transition state of this reaction. The linearity of the Hammett plot further confirms the structural and electronic balance between the mesomeric effect of the NH_2 function, the protophilicity of the thione center, the acidity of the β-hydrogen, and the influence of H. . .N hydrogen bonding.

EXPERIMENTAL

Synthesis

N-Methyl-N′-phenylthiourea. This compound was prepared by a standard literature method [4], mp 171°C; Ref. [4] mp 169–170°C.

N-benzoyl-N′-arylthiourea. These thiourea derivatives were prepared according to the literature methodology [5] by the reaction of an acid chloride with ammonium thiocyanate in dry acetone for 10 minutes, with subsequent addition of the corresponding arylamine, and heating for 15 minutes longer, to give 60–75% yields of the derivatives of thiourea. Melting points and the results of C, H, and N analyses are shown in Table 3.

Kinetic Studies

The experimental setup and the analytical procedures are explained in the preceding article [1].

ACKNOWLEDGMENT

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