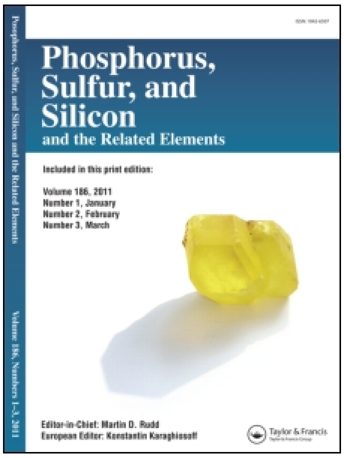

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M. M. Aly[a]; A. M. Fahmy[a]; A. M. Gaber[a]
[a] Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

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THERMOLYSIS AND PHOTOLYSIS OF SOME THIOUREA DERIVATIVES (PART I)

M. M. ALY, A. M. FAHMY and A. M. GABER
Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

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Thermolysis of *N*-benzoyl-*N*′-phenylthiourea (BPTU) on heating in air at 230°C gives NH_3, H_2S, benzaldehyde, benzil, aniline, azobenzene, benzamide, benzanilide, phenylisothiocyanate, phenylcyanamide, thiocarbanilide and benzoylisothiocyanate, whereas thermolysis of *N*-benzoyl-*N*′-benzylthiourea (BBTU) affords NH_3, H_2S, benzaldehyde, benzil, toluene, bibenzyl, stilbene, benzamide, cyanamide, benzylisothiocyanate, benzoylthiourea and benzoylisothiocyanate. Thermolysis of *N*-benzoyl-*N*′-α-naphthylthiourea (BNTU) under the same conditions gives NH_3, H_2S, benzaldehyde, benzil, benzamide, α-naphthylisothiocyanate, α-naphthanilide, α-naphthylcyanamide, benzoylisothiocyanate, α-naphthylamine and *N,N*′-di-α,α'-naphthylthiourea. Analogous results were also obtained on photolysis of (BPTU), (BBTU) and (BNTU) with the exception of NH_3 and the photodegradation products of phenylthiourea, benzylthiourea and α-naphthylthiourea respectively. The main feature of these pyrolyses is the homolysis of the amide and thioamide bonds providing free radicals that undergo different reactions involving H-abstraction, dimerization, coupling, fragmentation, rearrangement and disproportionation to yield the identified products.

Key words: Thermolysis; photolysis; thiourea derivatives.

INTRODUCTION

Aromatic and heteroaromatic thioureas are interesting both from the theoretical and the practical points of view as some of them are used as pesticides, preservatives, pharmaceuticals[1] and have many applications in photography, dye and textile industries.[2] Furthermore, thioureas can be conveniently employed as starting materials in the synthesis of various heterocyclic compounds.[2,3]

Decomposition of thiourea derivatives into the corresponding thiocyanate and amine are usually achieved by acid catalysis.[4]

The non-catalyzed thermal decomposition of thiourea and its derivatives in an aqueous medium received less attention.[5]

RESULTS AND DISCUSSION

The present work deals with the thermal and photodegradation of this class of compounds. Thermolysis of *N*-benzoyl-*N*′-phenylthiourea on heating under reflux in air at ~230°C for 10 hours gives ammonia, hydrogen sulfide, benzaldehyde, benzil, aniline, azobenzene, benzanilide, benzamide, phenylisothiocyanate, phenylcyanamide, thiocarbanilide, and benzoylisothiocyanate (Table I).

The formation of these products can be assumed to follow the series of reactions shown in (Scheme 1) which implies the preliminary homolysis of the amidyl function (route a) forming benzoyl and phenylaminothioamidyl radical

TABLE I

Thermolysis products of thiourea derivatives in gram (%)

Expt. no.	(BPTU)	(BBTU)	(BNTU)
Expt. conditions	Reflux in air (10 h)	Reflux in air (10 h)	Reflux in air (10 h)
Products in gram (%)			
NH_3	evolved	evolved	evolved
N_2S	evolved	evolved	evolved
Benzaldehyde[a]	1.4(7.0)	1.8(9.0)	1.2(6.0)
Benzil[b]	0.65(3.25)	1.5(7.5)	1.5(7.5)
Aniline[c]	1.2(6.0)		
Azobenzene[d]	traces		
Toluene[e]		1.2(6.0)	
Bibenzyl[f]		0.8(4.0)	
Stilbene[g]		0.4(2.0)	
Anilide derivatives	5.3(26.5)[h]		4.5(22.5)[j]
Benzamide[k]	0.7(3.5)	1.4(7.0)	0.8(4.0)
Thiourea derivatives	1.0(5.0)[l]	1.5(7.5)[m]	1.9(9.5)[n]
Isothiocyanate derivatives	0.5(2.5)[o]	1.2(6.0)[p]	1.8(9.0)[q]
Cyanamide derivatives	0.5(2.5)[r]	0.4(2.0)[s]	0.5(2.5)[t]
Benzoylisothiocyanate[u]	0.8(4.0)	1.2(6.0)	0.8(4.0)
α-Naphthylamine[v]			1.3(6.5)
Residue (non-volatile)	2.0(10.0)	3.2(16.0)	2.1(10.5)

[a] Benzaldehyde, b.p. 75–85/10°C mm.Hg, estimated in the mixture as DNP derivative m.p. 230–232°C.

[b] Mixture m.p. 94°C, D.N.P. derivative mm.p. 185°C.

[c] B.P. 65–70/10°C mm.Hg; n_D^{20}: 1.5836; acetyl derivative mm.p. 113°C.

[d] Mixture m.p. 60°C.

[e] B.p. 40–45/10°C mm.Hg; 2,4-dinitro derivative mm.p. 72°C.

[f] Mixture m.p. 52°C; dinitro derivative mm.p. 180°C.

[g] Mixture m.p. 124°C.

[h] Benzanilide, mm.p. 161–163°C.

[j] α-Naphthanilide, mm.p. 165°C.

[k] Mixture m.p. 125°C.

[l] Thiocarbanilide, mm.p. 154°C.

[m] Benzoylthiourea, mm.p. 172°C.

[n] *N,N'*-Di-α,α'-naphthylthiourea, mm.p. 210°C.

[o] Phenylisothiocyanate; b.p. 100–110°C/10 mm.Hg., n_D^{20}: 1.6497.

[p] Benzylisothiolyanate; b.p. 115–120°C/10 mm.Hg., n_D^{20}: 1.6118.

[q] α-Naphthylisothiocyanate, mm.p. 55°C.

[r] Phenylcyanamide, mm.p. 47°C.

[s] Unsubstituted cyanamide, mm.p. 51°C.

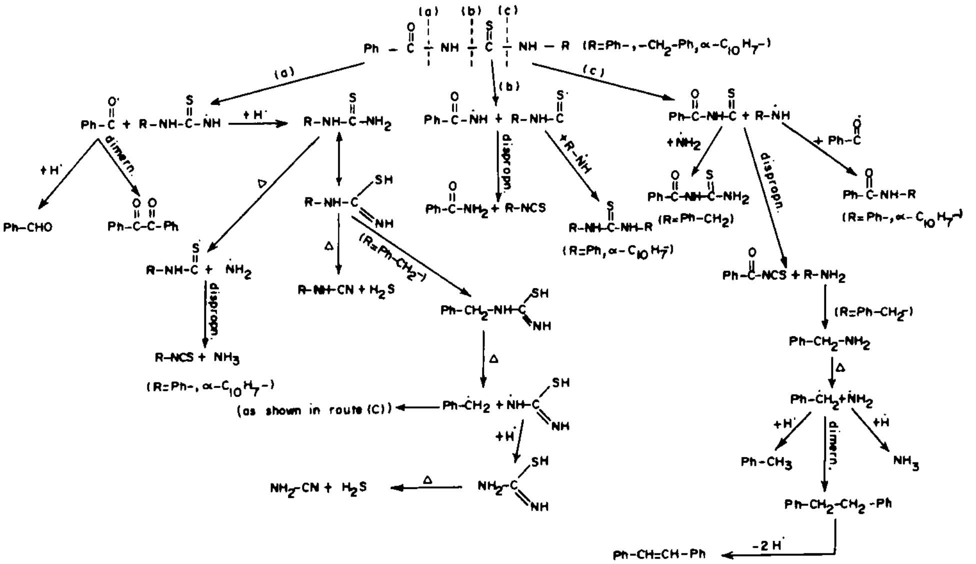
[t] α-Naphthyl cyanamide, mm.p. 134°C.

[u] B.p. 125–140°C/10 mm.Hg., n_D^{20}: 1.6334.

[v] Mixture m.p. 47°C.

pairs. The benzoyl radicals may abstract hydrogen from the medium to give benzaldehyde or undergo dimerization into benzil, whereas the phenylaminothioamidyl radical may abstract hydrogen to give phenylthiourea which subsequently decomposes into ammonia and phenylisothiocyanate.[6]

Phenylthiourea may undergo rearrangement into phenylisothiourea which decomposes on heating into H_2S and phenylcyanamide.[7] The formation of benzamide and thiocarbanilide can be assumed to proceed through the homolysis of the thioamidyl function (route b) to phenylamidyl and anilinothione radical



SCHEME 1

pairs which on disproportionation give benzamide and phenylisothiocyanate. Moreover, the anilinothione radical may couple with anilino radical to give thiocarbanilide.

The formation of aniline, azobenzene, benzanilide and benzoylisothiocyanate may be suggested to take place through homolysis of the other thioamidyl function (route c) to give anilino and phenylamidylthione radical pairs which on disproportionation give rise to aniline and benzoylisothiocyanate, whereas the aniline radicals may couple with benzoyl radicals to give benzanilide or undergo dimerization to form azobenzene.

Similarly, thermolysis of *N*-benzoyl-*N*′-benzylthiourea (BBTU) under the same condition gives rise to ammonia, hydrogen sulfide, benzaldehyde, benzil, toluene, bibenzyl, stilbene, benzamide, cyanamide, benzylisothiocyanate, benzolthiourea and benzoylisothiocyanate following the same pathways as mentioned previously.

Moreover, the formation of ammonia, toluene, bibenzyl, stilbene and benzoylthiourea can be assumed to proceed through the homolysis $\overset{\overset{S}{\|}}{C}$—N bond (route c) forming benzylaminyl radical and phenylamidylthione radical. The former may abstract hydrogen forming benzylamine which subsequently decomposes on heating into ammonia and benzyl radical.[8] The benzyl radical can be considered to be the precursor of toluene bibenzyl and stilbene through processes of H-abstraction, dimerization followed by dehydrogenation, whereas the phenylamidylthione radicals undergo coupling with aminyl radicals to form benzoylthiourea.

Analagous results were also obtained in case of thermolysis of *N*-benzoyl-*N*′-α-naphthylthiourea under the same conditions which gives rise to ammonia,

TABLE II

Photolysis products of thiourea derivatives in gram (%)

	(BPTU)	(BBTU)	(BNTU)
Products in gram (%)			
NH_3	—	—	—
H_2S	—	—	—
Benzaldehyde	0.09(9.0)	0.07(7.0)	0.06(6.0)
N,N'-Di-α,α'-naphthylthiourea			0.11(11)
Benzamide	0.07(7.0)	0.1(10)	0.05(5.0)
Benzil	0.1(10)	0.07(7.0)	0.04(4.0)
Amine derivatives	0.17(17)[a]	0.14(14)[b]	0.2(20)[c]
Anilide derivatives	0.22(22)[d]	—	0.26(26)[e]
Thiourea derivatives	0.1(10)[f]	0.12(12)[g]	0.1(10)[h]
Bibenzil		0.17(17)	
Stilbene		0.1(10)	
Isothiocyanate derivatives	0.02(2.0)[i]	0.08(8.0)[j]	0.08(8.0)[k]
Benzoylthiourea		0.06(6.0)	
Benzoylisothiocyanate	0.05(5.0)	0.01(1.0)	0.05(5.0)
Residue	0.03(3.0)	0.08(8.0)	0.05(5.0)

[a] Aniline

[b] Benzylamine; n_D^{20}: 1.5424.

[c] α-Naphthylamine.

[d] Benzanilide.

[e] α-Naphthanilide.

[f] Phenylthiourea, mm.p. 154°C.

[g] Benzylthiourea; mm.p. 164°C.

[h] α-Naphthylthiourea; mm.p. 190°C.

[i] Phenylisothiocyanate.

[j] Benzylisothiocyanate.

[k] α-Naphthylisothiocyanate.

hydrogen sulfide, benzaldehyde, benzil, benzamide, α-naphthylisothiocyanate, α-naphthylcyanamide, α-naphthanilide, α-naphthylamine, benzoylisothiocyanate and *N,N'*-di-α-α'-naphthylthiourea.

The formation of these products can be explained on similar grounds as mentioned previously.

Photolysis of (BPTU), (BBTU) and (BNTU) in acetone solution at 254 nm and 25°C in presence of benzophenone as a sensitizer for different periods 90, 60 and 120 h respectively was carried out. Photolysis of (BPTU) gives the same products as in the thermolysis with the exception of the photodegradation products of phenylthiourea namely; NH_3, H_2S and phenylcyanamide. A result which indicates the photostability of phenylthiourea under the given conditions as shown experimentally. Similarly, photolysis of (BBTU) affords the same products as on its thermolysis with exception of the photodegradation products of benzylthiourea namely; NH_3, H_2S and cyanamide, whereas in the case of (BNTU) the same products are obtained as on thermolysis with the exception of the photodegradation products of α-naphthylthiourea namely; NH_3, H_2S and α-naphthyl cyanamide as (Table II).

EXPERIMENTAL

All melting points are uncorrected. The IR spectroscopic analyses were carried out on a Pye-Unicam IR spectrophotometer, Model Sp.3-100. G.L.C. was carried out using Perkin–Elmer Sigma-3B apparatus and the columns used are 4 ft × 4mm packed with 30% SE 30 on chromosorb W (35–80 mesh), or 10% SE 30 on celite (60–80 mesh) at 180°C, using nitrogen as a carrier gas. Ultraviolet irradiation was carried out using the low pressure U.V. lamp Model GL-58 multiband U.V.

254/366 nm and the solutions were contained in open-topped pyrex beakers. The solvents used were of analar grade. Thin-layer chromatography was carried out on glass plates covered with silicagel (25–40 mesh) and eluted with acetone-pet.ether (1:4 v/v). Thiourea derivatives were prepared by standard methods in the literature.[9]
N-Benzoyl-*N*'-phenylthiourea m.p. 148–150°C.
N-Benzoyl-*N*'-benzylthiourea m.p. 142–145°C.
N-Benzoyl-*N*'-α-naphthylthiourea m.p. 170°C.

Thermolysis of thiourea derivatives. The thioureas (20 g) were heated under reflux in air at 230°C for 10 hours. The gases evolved were detected by standard chemical means (NH_3 by Nessler's reagent and H_2S by lead acetate). The pyrolysate was first distilled under normal pressure up to 120°C, where the volatile materials such as benzaldehyde and toluene were collected and identified. The remaining oil was separated into its constitutents by means of column chromatography over silicagel using gradient elution technique and by fractional distillation under reduced pressure. The separated products were identified by physical constants; bps, mps, TLc, GLc, IR as compared with authentic samples. The results are shown in Table I.

Photolysis of thiourea derivatives. A solution of BPTU, BBTU or BNTU (1 g) in dry acetone (50 ml) was irradiated at room temperature (25°C) for 90, 60 and 120 hrs respectively in presence of little amount of benzophenone as a sensitizer. The photolysate was separated as indicated in a previous work[10] into neutral and basic products and analyzed by GLC as compared with authentic samples using nitrobenzene as internal standard and separated into their constituents by column chromatography over silicagel using gradient elution technique. The results are summarized in (Table II).

Preparation of Reference Compounds.
1. Bibenzyl:[11] crystals from ethanol, m.p. 52°C, 4,4'-dinitroderivatives, m.p. 180°C.
2. *trans*-Stilbene:[12] crystals from ethanol, m.p. 124°C.
3. Thiocarbanilide:[13] crystals from ethanol, m.p. 154°C.
4. Benzylisothiocyanate:[14] b.p. 140°C/17 mm.Hg; as colourless oil, n_D^{20}: 1.605.
5. Benzoylisothiocyanate:[15] b.p. 137°C/18 mm.Hg, as yellow oil, n_D^{20}: 1.6354.
6. Phenylcyanamide:[16] White crystals, m.p. 45°C.
7. α-Naphthylcyanamide:[16] White crystals, m.p. 130–131°C.
8. α-Naphthanilide:[17] Crystals from ethanol, m.p. 160–161°C.
9. α-Naphthylisothiocyanate:[6] White needles, m.p. 54°C.
10. α-Naphthylthiourea:[18] Crystals from ethyl alcohol, m.p. 190°C.
11. *N*-Benzylthiourea:[19] Crystals from ethyl alcohol, m.p. 165°C.
12. *N*-Benzoylthiourea:[20] Yellow crystals from ethyl alcohol, m.p. 171°C.
13. *N,N*'-Di-α,α'-Naphthylthiourea:[21] Pale rose needles from nitrobenzene, m.p. 210°C.

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