Brief Communications

Thermal decomposition of 2,6-di-*tert*-butyl-4-dimethylaminomethylphenol

L. Ya. Zakharova,* L. A. Khismatullina, and B. E. Ivanov

A. E. Arbuzov Institute of Organic and Physical Chemistry,
Kazan' Research Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420083 Kazan', Russian Federation.
Fax: 007 (843 2) 75 2253

Products of thermolysis of 2,6-di-*tert*-butyl-4-dimethylaminomethylphenol were determined qualitatively and quantitatively by GLC, UV, and ^{1}H NMR methods. The kinetics of the reaction was studied. The thermolysis products were studied as the inhibitors in thermopolymerization of monomers.

Key words: sterically hindered phenols, 2,6-di-*tert*-butyl-4-dimethylaminomethylphenol, quinomethides.

Sterically hindered phenols are widely used as inhibitors of radical processes.[1] We showed that systems based on 2,6-di-*tert*-butyl-4-dimethylaminomethylphenol (**1**) can be effectively used for inhibition of thermopolymerization of vinylic monomers.[2] The specific feature of this kind of systems is presumably their ability to form products at elevated temperatures that exhibit inhibitory activity.

We studied the thermal decomposition of **1** and its kinetics under various conditions to investigate the chemical transformations of aminophenol **1** under conditions of inhibition of monomer thermopolymerization and the role of the products of transformation in the inhibition process.

Results and Discussion

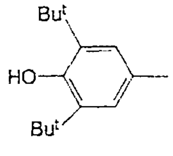
Compounds **2**, **3**, and **6**—**9** have earlier been identified among the products of thermal deamination of aminophenol **1** in chlorobenzene at 145 °C (Table 1).[3]

In a repeated study using TLC, GLC, UV, and ^{1}H NMR methods, we showed that along with the com-

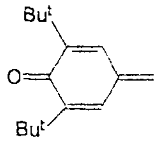
Table 1. Products of thermolysis of 2,6-di-*tert*-butyl-4-dimethylaminomethylphenol

Compound	The content of thermolysis products (%)	
	in xylene	in the presence of 10% stearic acid
$ArCH_2NMe_2$ (**1**)[a]	63.6	50.0
$ArCH_2Ar$ (**2**)	8.0	12.0
$ArCH_2CH_2Ar$ (**3**)	13.0	14.0
$Ar'{=}Ar'$ (**4**)[b]	0.4	1.5
$Ar'{=}CHNMe_2$ (**5**)	5.0	4.6
$ArCH{=}CHAr$ (**6**)	0.5	1.1
$Ar{-}CH{=}Ar'$ (**7**)	1.5	4.1
$(Me_2N)_2CH_2$ (**8**)	3.3	5.5
Me_2NH (**9**)	3.2	3.6

[a] Ar =



[b] Ar′ =



Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 1881—1883, October, 1997.

1066-5285/97/4610-1787 $18.00 © 1997 Plenum Publishing Corporation

pounds detected earlier, 3,5,3′,5′-tetra-*tert*-butyldiphenoquinone **4** and 3,5-di-*tert*-butyl-*N*,*N*-dimethylaminomethylenequinone **5** are formed in the thermolysis of compound **1**. When decomposition of aminophenol **1** is carried out in the presence of traces of water and atmospheric oxygen, the formation of 3,5-di-*tert*-butylbenzaldehyde is also observed.

In addition, we studied the decomposition of compound **1** in the presence of 10% stearic acid. Qualitatively, the composition of the products in the presence of acids within a certain pK_a range (from CF_3CO_2H to the higher aliphatic acids) remained unchanged. Comparison of the content of the decomposition products indicates that the yields of compounds **4**—**7** increase two- to threefold when an acid is added; this may be one of the reasons for the increase in the inhibitory activity of aminophenol **1** in the processes of monomer thermopolymerization.

The kinetics of the decomposition of compound **1** in xylene and DMF was studied both in the absence of acids and in the presence of either stearic or trifluoroacetic acids. We observed acceleration of the thermolysis of **1** in a more polar solvent, DMF. According to the literature data,[1] sterically hindered phenols cannot form self-associates because of steric hindrances: for example, 2,6-di-*tert*-butylphenol exists only in the form of isolated molecules. However, aminophenol **1** can form hydrogen bonds that involve the phenolic hydroxyl of one molecule and the amino group of another one. For this reason, compound **1** probably exists in the form of self-associates in a non-polar solvent. DMF has sufficiently high polarity and can form complexes with aminophenol **1** with a hydrogen bond that are less stable than those of the amine with the phenol. This affects the reactivity of compound **1** in various solvents. The rate of thermolysis also increases in the presence of acids, which protonate aminophenol **1** to block the formation of intermolecular hydrogen bonds (Table 2).

Compound **1** and the products of its thermolysis were tested as inhibitors of thermopolymerization of monomers (Table 3). We showed that aminophenol **1** exhibits the inhibitory activity only in combination with an acid in all ratios.[2] This may be due to the increase in the yields of the products **4**—**7**, which possess high inhibitory activity, in the presence of acids.

Table 2. Activation energies (E_a) and observed rate constants (k_{obs}) of the decomposition of compound **1**

Solvent	T/°C	E_a/kcal · mol^{-1}	$k_{obs} \cdot 10^4$/s^{-1}
Xylene	115	18.2	0.12
Xylene	125	18.2	0.26
Xylene	135	18.2	0.36
Xylene[a]	125	18.2	0.28
Xylene[b]	125	18.2	0.44
DMF	115	7.1	0.85
DMF	135	7.1	1.18
DMF	145	7.1	1.75

[a] 10% stearic acid was added. [b] 10% CF_3COOH was added.

Table 3. Inhibitory activity of aminophenol **1** and some of its thermolysis products

Compound	Content (%)	Monomer	Inhibition (%)
1	0.20	Isoprene	44.5
4	0.15	Isoprene	91.0
5	0.15	Isoprene	48.5
6	0.20	Isoprene	78.7
1	0.10	Styrene	—
1 + $C_{17}H_{35}COOH$	0.22	Styrene	100.0

Experimental

The thermolysis of aminophenol **1** was carried out in dry xylene (0.33 mol L^{-1}) under argon at 125 °C for 7 h. The thermolysis products were separated on a column with neutral Al_2O_3 (II activity). Petroleum ether, diethyl ether, their mixtures, and benzene were used as the eluants. All of the identified products (compounds **1**—**9**, see Table 1) were obtained by independent syntheses using well-known procedures.[4,5]

The quantitative composition of the reaction mixture was analyzed by GLC, UV, and ^1H NMR methods. The content of compounds **1**—**3** in a mixture was determined from the relative intensity of signals of methylene protons at δ 3.2, 2.7 and 3.7, respectively. ^1H NMR spectra were recorded in CCl_4 on a Tesla BS-467 (60 MHz) spectrometer; Me_4Si was used as the internal standard. UV spectra were recorded on a Specord UV-VIS spectrophotometer.

Qualitative and quantitative determination of the amines that formed in decomposition of aminophenol **1** was carried out by GLC. Amines **8** and **9** were blown out from the reaction mixture into a trap with acetone at −40 °C. GLC was carried out on a Tsvet-5 chromatograph (nitrogen as carrier gas, column 3000×3 mm, stationary phase 15% PEG-600 + 3% KOH on Chromosorb).

The kinetic measurements for the thermal decomposition of compound **1** were conducted both in xylene and in DMF (concentration of compound **1** was 0.33 mol L^{-1}) under argon at 115—145 °C using a well-known procedure.[6] To determine the effect of the addition of acids on the thermolysis of aminophenol **1**, the kinetics was studied in xylene under argon at 125 °C in the presence of 10% stearic or trifluoroacetic acids. The rate constants (k) were calculated by the following equation

$$-\ln C_t = k \cdot t + \text{const},$$

where C_t is the concentration of the substrate at the moment t. The activation energy (E_a) was determined using the Arrhenius equation

$$\log k_{obs} = \log A - \frac{E_a}{2.303\,R} \cdot \frac{1}{T}.$$

To determine the inhibitory ability of compounds, a monomer and the corresponding amount of an inhibitor were placed in a tube. The sample was degasses by successive freezing, evacuation, and thawing to a residual pressure of 10^{-3} Torr; the tube was filled with argon, sealed, and kept at 120 °C for 6 h. The polymer that formed was precipitated with ethanol and dried to constant weight.

The authors express their gratitude to V. P. Nefedov and T. A. Zyablikova for the investigations of the reaction mixture by GC and ^{1}H NMR spectroscopy.

References

1. V. V. Ershov, G. A. Nikiforov, and A. A. Volod'kin, *Khimiya prostranstvenno-zatrudnennykh fenolov* [*Chemistry of Sterically Hindered Phenols*], Khimiya, Moscow, 1972 (in Russian).
2. USSR Invention Certificate No. 819078, *Byul. Izobret.*, 1981, No.13.
3. A. Schmidt and H. Brunetti, *Helv. Chim. Acta*, 1976, **59**, 522.
4. C. D. Cook, N. G. Nash, and H. R. Flanngan, *J. Am. Chem. Soc.*, 1955, **77**, 1783.
5. S. Kharash and B. S. Joshi, *J. Org. Chem.*, 1957, **22**, 1435.
6. B. E. Ivanov and L. A. Valitova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 768 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1968, **17** (Engl. Transl.)].

Received November 12, 1996;
in revised form May 13, 1997

Reactivity of ytterbium in liquid ammonia

1. Synthesis of the complex with the ytterbium—iron bond

***A. Z. Voskoboinikov*[a]* *and I. P. Beletskaya*[b]**

[a]*State Research Center of the Russian Federation "State Scientific and Research Institute*
of Chemistry and Technology of Organoelement Compounds,"
38 sh. Entuziastov, 111123 Moscow, Russian Federation.
Fax: 007 (095) 273 1323
[b]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
Vorob'evy Gory, 117912 Moscow, Russian Federation.
Fax: 007 (095) 939 1854

A solution of metallic ytterbium in liquid ammonia reacts readily with various carbonyl complexes of metals to form the corresponding lanthanide carbonylmetallates. The reaction of an excess of Yb in liquid NH_3 with $[CpFe(CO)_2]_2$ gave $(THF)_4Yb[Fe(CO)_2Cp]_2$ in 42% yield. It was suggested that the resulting complex contains two equivalent Yb—Fe bonds.

Key words: ytterbium, metal carbonyls.

It is known that ytterbium, samarium, and europium dissolve readily in liquid ammonia to form solutions of typical blue color (the color of solvated electrons).[1] The resulting product should be an active reducing agent of different organic and organometallic substrates, and its application is, apparently, a convenient method for the synthesis of a number of scarcely available organic derivatives of lanthanides. Recently, it has been demonstrated that $Fe(CO)_5$ is readily reduced by a solution of ytterbium in liquid ammonia to afford a polymeric heterometal complex having Yb—Fe bonds and an additional interaction with the participation of two isocarbonyl ligands per Yb atom.[2]

In this work, we report on the successful use of ytterbium in liquid ammonia as the reagent for selective reduction of $[CpFe(CO)_2]_2$ and for the preparation of the complex of divalent ytterbium having Yb—Fe bonds and in which no additional coordination with the bridging carbonyl ligands occurs.

Procedures for the synthesis of completely substituted metal carbonyl derivatives of lanthanides have been studied recently in detail.[3—5] Apparently, the reaction of the corresponding metallic rare-earth elements with dimeric carbonyl complexes of metals of composition $[M(CO)_nL_m]_2$ (M = Co, Cr, Mo, W, Mn, or Re; and L = Cp or PR_3) in THF is the most promising one. This procedure gave good results when readily reducible carbonyl derivatives of metals were used. On the contrary, hardly reducible complexes, such as $[CpM(CO)_2]_2$ (M = Fe or Ru),[6] do not enter into this reaction.

As part of the studies on the reactivity of a solution of ytterbium in liquid ammonia, it was demonstrated

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1883—1885, October, 1997.