Photochemical and thermal decomposition of diphenylamine diazonium salts

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Abstract

The photochemical and thermal decomposition of diphenylamine-4-diazonium salt (DDS), *N*-methyl diphenylamine-4-diazonium salt (NMDDS), 3-methoxy diphenylamine-4-diazonium salt (MDDS), carbazole-3-diazonium salt (CDS) in ethanol and *N*-methyl-2-nitrodiphenylamine-4-diazonium salt (MNDDS) in water were studied. It was found that, in photochemical decomposition in ethanol, the major products (>70% of the total product) obtained for DDS, CDS, MDDS and NMDDS are diphenylamino-4-ethyl ether, carbazole-3-ethyl ether and the corresponding substituted diphenylamino-4-ethyl ethers. In thermal decomposition, the diphenylamine (DA), carbazole (CZ) and substituted DA were obtained as only one product in each case. For the decomposition of MNDDS, which has a strong electron-withdrawing nitro group on benzene nuclear at the meta site of the diazonium group, the decomposition products are identical, both in photochemical and in thermal decomposition. The mechanisms of photochemical and thermal decomposition for DDS, CDS and substituted DDS are discussed. © 1999 Elsevier Science S.A. All rights reserved.
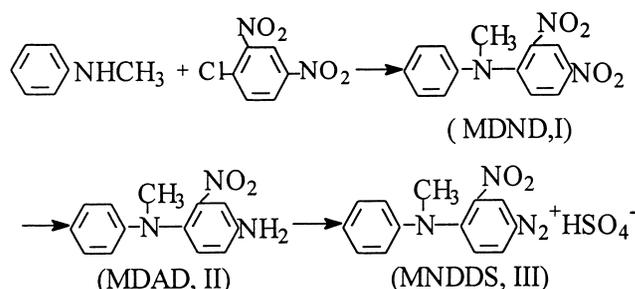
Keywords: Diphenylamine diazonium salt; Substituted diphenylamine diazonium salt; Photochemical decomposition; Thermal decomposition

1. Introduction

The photochemical and thermal decomposition of arene-diazonium salts have been studied extensively [1–17], but as we known, the investigation for photochemical and thermal decomposition of diphenylamine-4-diazonium salt (DDS), carbazole-3-diazonium salt (CDS) and substituted diphenyl-amine-4- diazonium salts (S-DDS), although the polycondensation products of DDS and S-DDS with formaldehyde are the most important photosensitive materials for fabrication of negative presensitized plate [18–25], has not been found in literature. In this article, we report on the photochemical and thermal decomposition of DDS, CDS and S-DDS in ethanol or in water. The results show that the products obtained from photochemical and thermal decomposition of DDS, CDS and S-DDS in ethanol is relatively simple as compare with most of the common arenediazonium salts, which usually produce considerable complex products, both in the photochemical [26,27] and thermal [28–30] decompositions. These results may be important to understand the decomposition mechanisms of arenediazonium salts.

2. Experimental

DDS was purified by reprecipitation from its ethanol solution with diethyl ether. MDDS was prepared according to the method described in Ref. [31]. NMDDS, CDS were prepared in our laboratory, described elsewhere[32]. MNDDS was synthesized according to the route we designed:

(MDND,I)

(MDAD, II) → (MNDDS, III)

The procedure of preparation of MNDDS is described as follows:

2.1. N-methyl 2,4-dinitro-diphenylamine (MDND, **I**)

2,4-Dinitro-chlorobenzene (40.4 g, 0.2 mol), sodium carbonate (23.3 g, 0.22 mol), absolute ethanol (200 ml) were

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charged in a 500-ml three-necked round bottom flask, *N*-methylaniline (23.5 g, 0.22 mol) was added dropwise into the reaction mixture under stirring at reflux temperature for 6 h and then filtered. MDND **I** was obtained with an orange color, the yield being 49 g, 90%. ^{1}HNMR (400 MHz, CDCl$_3$), (δ, ppm): 3.46, 3H (–CH$_3$); 7.09–8.62, 8H (aromatic).

2.2. N-methyl 2-nitro-4-amino-diphenylamine (MNAD, II)

MDND **I** (27.3 g, 0.1 mol), sodium carbonate (10.6 g, 0.1 mol), and 95% ethanol (80 ml) were added to a 500-ml three-necked round bottom flask, Na$_2$S·9H$_2$O (48 g, 0.2 mol in 80 ml water) was added dropwise into the mixture (in ca. 1 h) at reflux temperature and heated for another 1 h. The liquid was poured, when it is hot, into a 500-ml beaker and cooled. MNAD **II**, with an orange color, was precipitated and filtered. The filtrate was poured into the water to receive the product remained in filtrate. The yield is 16.9 g, 70%. The MNAD was converted to its bisulfate: 15 g **II** was dissolved in 50% H$_2$SO$_4$ (200 ml in hot), then added to 1.5 l boiling water. The bisulfate precipitated from the solution after cooling was filtered, the yield is 18.2 g, 86%. ^{1}HNMR (CDCl$_3$, δ, ppm): 3.26,3H (–CH$_3$); 4.13, 3H (–NH$_3$$^+$), 6.58/2H, 6.76/1H, 6.94/1H, 7.13–7.25/4H (aromatic).

2.3. N-methyl-2-nitro-diphenylamine-4-diazonium salt (HSO$_4^-$ as anion) (MNDDS, III)

Bisulfate of **II** (34.6 g, 0.1 mol) was added into the mixture composed of 130 ml 5% H$_2$SO$_4$ and 240 g crashed ice under stirring in 500 ml beaker which was cooled by an ice-water bath. NaNO$_2$ (8.3 g, 0.12 mol in 40 ml water) was added dropwise under stirring at 0–5°C, then the reaction was continued for 1 h and filtered. 54.4 g of ZnCl$_2$ (0.4 mol in 100 ml water) were added into the filtrate, the diazonium salt **III** as half the ZnCl$_2$ complex precipitated with a yellow color, the yield is 31.2 g, 80%. ^{1}HNMR (D$_2$O, δ, ppm): 3.68, 3H (–CH$_3$); 7.30–7.55/6H, 8.30–8.32/1H, 8.88/1H (aromatic).

2.4. Photochemical and thermal decomposition

The photochemical decomposition of diazonium salts was carried out in a column pyrex photoreactor ($\Phi = 40$, $l = 300$ mm), which has a ground-glass cover with a long glass tube ($\Phi = 10$ mm) attached at center of the cover, as an inlet, and a side tube as an outlet, for N$_2$. The reactor was installed in a 3-l beaker filled with ice water to capacity. A 300-W medium pressure mercury arc was placed at a distance of 30 cm from the reactor center, at which point the light intensity (360 nm) was determined to be 11.5 mW/cm^2. Fifty milliliters of ethanol solution of diazonium salt (0.027 mol/l) were added to the reactor and deaerated for 15 min with N$_2$. The photodecomposition was carried out in

an atmosphere of N$_2$ and magnetic stirring at pH 6.0–6.5 until the absorbance of the solution at 375 nm decreased almost to zero (ca. 2 h). Most of the solvent was then removed with an evaporator under reduced pressure, and the residue washed with water thrice to remove the trace diazonium salt. In order to better understand the decomposition, the decomposition products were used for analysis of ^{1}HNMR directly, without any purification. The ^{1}HNMR spectra of products from photodecomposition of DDS and MDDS are shown in Figs. 1 and 2 (the spectra of NMDDS and CDS are similar).

The decomposition of MNDDS was carried out in an aqueous solution because it is difficult to dissolve in ethanol.

The thermal decomposition of diazonium salts was performed in a three-necked bottle under stirring in an atmosphere of N$_2$ at 76°C in ethanol or 99°C in water: 50 ml of the solution (0.027 mol/l diazonium salt) were added to the bottle and deaerated with N$_2$ for 15 min, then heated at given temperature (in slight reflux). The decomposition was monitored by determining the absorbance of the solution, which decreases gradually with decomposition of diazonium salt. The decomposition was considered complete when the absorbance became close to zero (ca. 5 h), and then stopped. The solvent was then removed by an evaporator under reduced pressure, the residue washed with water thrice, then analyzed directly for ^{1}HNMR after drying. The ^{1}HNMR spectra of thermal decomposition products from DDS and MDDS are shown in Figs. 3 and 4 (the spectra of NMDDS and CDS are similar).

3. Results and discussion

The photochemical and thermal decomposition of arenediazonium salts are among the oldest subjects to be studied intensively by organic and physical organic chemists [33,34], but there have been some disagreements both, in the products and in the mechanisms [35–37].

It was surprising, and unexpected, that in photochemical decomposition in ethanol, the DDS, MDDS, NMDDS or CDS principally produces the ethyl ether of corresponding diphenylamine as a major product, which was formed via heterolytic cleavage of the C–N bond of the diazonium salt, whereas in thermal decomposition, the diphenylamine (includes carbazole) or substituted diphenylamines was obtained as almost the only product via homolytic cleavage of the C–N bond. For MNDDS, the identical products were formed, both in photo- and in thermal decomposition. These results differ considerably as compared with the most of common arenediazonium salts reported in literature (the products reported sometimes are not coincident). Lee et al. [26] reported that in photochemical decomposition of 4-nitrobenzenediazonium salt in ethanol, 4-nitrobenzene, a homolytic product was obtained as a major product, but Detar et al. [38,39] reported that the heterolytic products from arenecation were obtained as major product in photo-
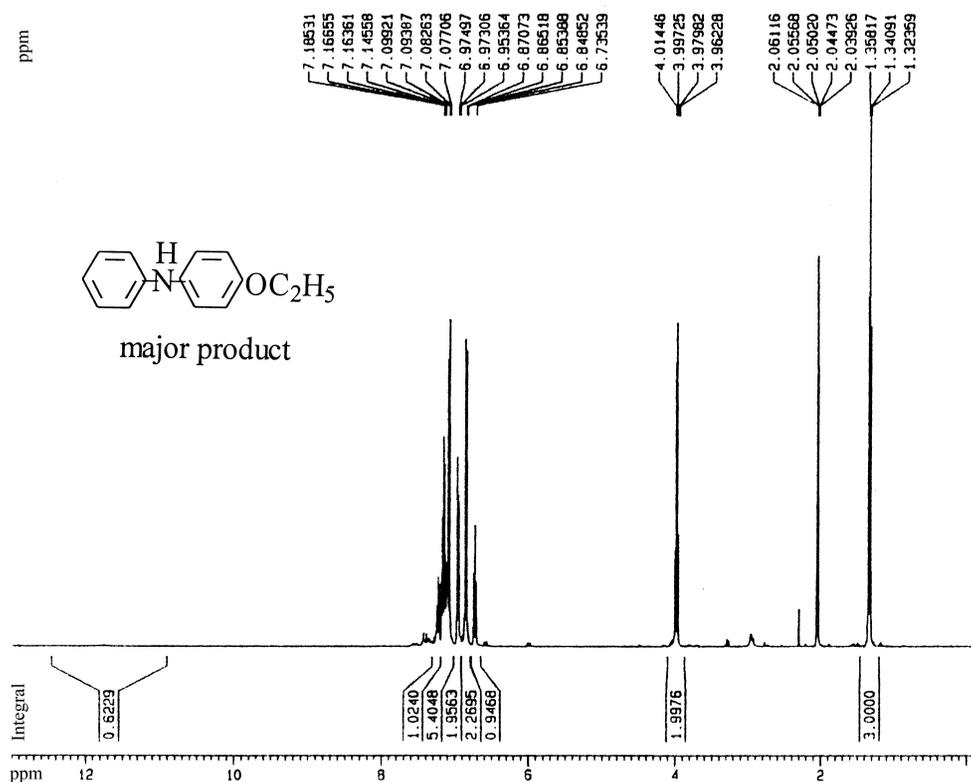
Fig. 1. The ^{1}HNMR of photodecomposition products of DDS in ethanol. Major product: $C_6H_5NHC_6H_4OC_2H_5$, aromatic, 9H (11.57*); OCH$_2$, 2H (1.998*); – CH$_3$, 3H (3.0*). *: Integral value.

Fig. 2. The ^{1}HNMR of photodecomposition product of MDDS in ethanol. Major products: $C_6H_5NHC_6H_3OCH_3OC_2H_5$, aromatic, 8H (8.8*); OCH$_3$ 3H (3.0*); OC$_2$H$_5$, 5H (3.83*). *: Integral value.
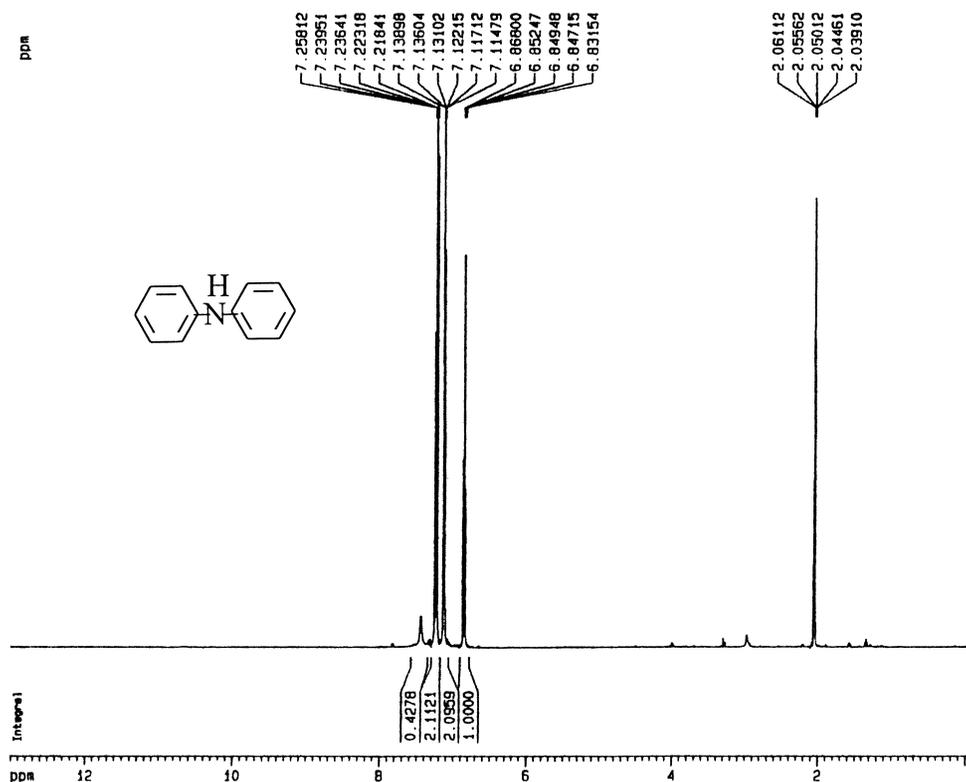
Fig. 3. The ^{1}HNMR of thermal decomposition product of DDS in ethanol $C_6H_5NHC_6H_5$, 10 H, aromatic.

chemical decomposition of benzene or substituted benzenediazonium tetraflouroborate in methanol. In thermal decomposition, 2,4,6-trimethyl-benzene diazonium salt decomposed in hexaflouoropropanol produces 2,4,6-trimethylbenzene hexafluoropropyl ether-a heterolytic product [40], and the predominate product is phenyl ethyl ether in thermal decomposition of benzene diazonium tetrafluoroborate (ethanol as solvent) [28], whereas 4-chlorobenzene diazonium salt or 4-methylbenzene diazonium salt produces 4-chlorobenzene or toluene [41].
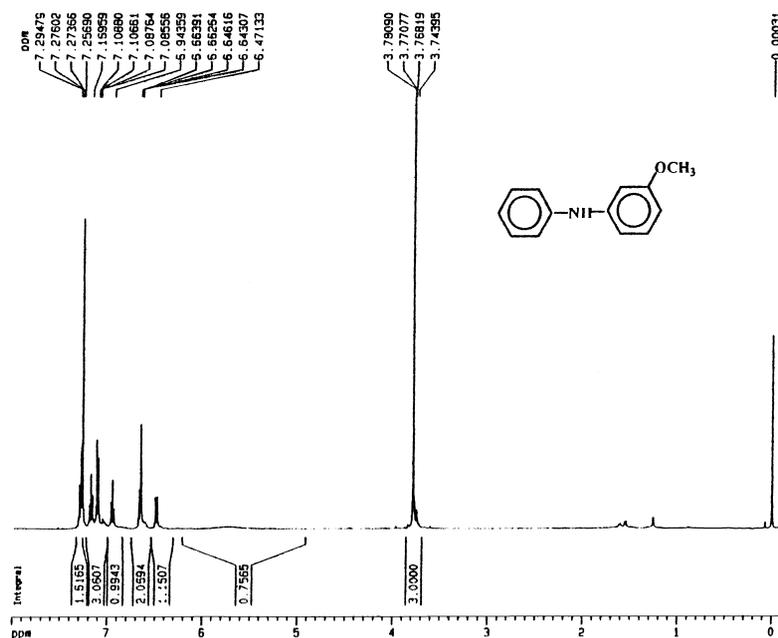

Fig. 4. The ^{1}HNMR of thermal decomposition product of MDDS in ethanol $C_6H_5NHC_6H_4OCH_3$, aromatic, 9H (8.85*); OCH$_3$, 3H (3.00*). *: Integral value.
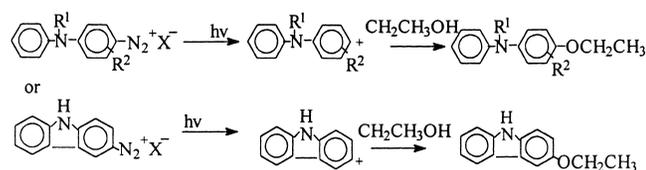
Table 1
The products of photo- and thermal decompositions of substituted benzene diazonium salts in ethanol ([7]), $R\alpha C_6H_4-N_2^+X^-$ (X = Cl or HSO_4^-)

R	Products in photodecompositiom (wt%)		Products in thermodecomposition (wt%)	
	$R-C_6H_5$	$R-C_6H_4OC_2H_5$	$R-C_6H_5$	$R-C_6H_4OC_2H_5$
$-NO_2$	60	0	60	9
$-Cl$	60	0	4	50
$-CH_3$	40–50	20–30	0	62
$-OCH_3$	40–50	20–30	2	30

The most cited results (Table 1) relating the photo- and thermal decomposition of arenediazonium salts have been reported by Honer et al. [7]. From the data of Table 1, obviously, both photochemical and thermal decompositions of arenediazonium salts are not single process, the products formed usually being rather complex, with no dominant product being obtained.
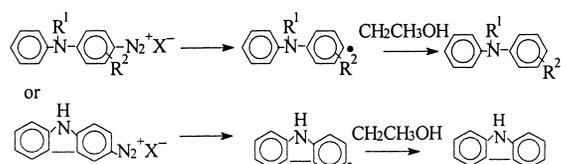
In the photochemical decomposition of DDS, CDS, MDDS, NMDDS in ethanol, the diphenylamino-ethyl ether (DAE), carbazole-3-ethyl ether (CE) or substituted diphenylamino-ethyl ether (SDAE) should be formed via a heterolytic cleavage of C–N bond of the diazonium salt, the arenecations produced in cleavage process then react with ethanol to form the product:

where R^1 represents H or CH_3; R^2 represents H or OCH_3; and X represents Cl or HSO_4.
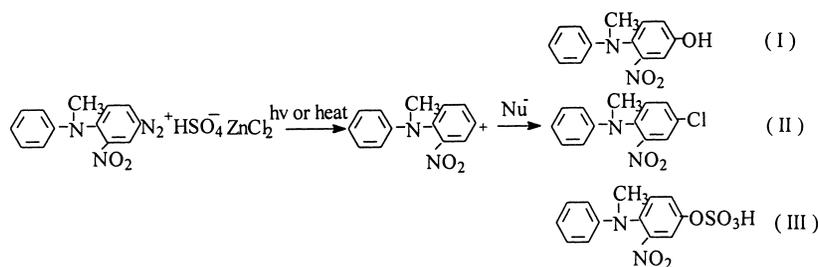
From Figs. 1 and 2, the integral of aromatic H, which is slightly higher than the calculated value, we can evaluate ca. 10–20% diphenylamine (DA) or substituted diphenylamine

In thermal decomposition of DDS, MDDS, NMDDS or CDS in ethanol, the diphenylamine (DA), carbazole (CZ) or substituted diphenylamin (SDA) should be formed via the homolytic cleavage of C–N bond of the diazonium salt, the areneradical produced in cleavage process then reacts with ethanol to form the product:

where R^1 represents H or CH_3; R^2 represents H or OCH_3; X represents Cl or HSO_4.

For MNDDS, which is difficult to dissolve in ethanol, the decomposition was carried out in water. In order to better understand the decomposition, the product was also analyzed by elementary analysis directly, without any purification and the results are presented in Table 2. We can see that in case of both, photo- and thermal decompositions, the products were obtained in the same composition of chloride, hydroxyl and sulfonic compounds of the corresponding diazonium salts. The decomposition of MNDDS, therefore, both in photochemical and in thermal decompositions, follows the same mechanism, proposed as follows.

(SDA) formed from homolytic cleavage of C–N bond, was mixed among the major product. The DA or SDA can be separated by recrystallization in ethanol –H_2O (usually 2 : 1 by volume). An elementary analysis of the purified product ($C_6H_5NHC_6H_4OC_2H_5$, DDS decomposition product as example) gives the following: $C_{14}H_{15}NO$, Calculated: C (78.87%), H (7.04%); N (6.57%); Experimental: C (78.63); H (6.98); N (6.51).

Table 2
The elementary analytic data of products formed in photochemical and thermal decompositions of MNDDS in water

	Elementary analytic data (wt%)			
	C	H	N	Cl
Photodecomposition product	61.95	4.95	11.10	1.11
Thermal decomposition product	61.92	4.85	11.11	1.01

where Nu^- represents the OH^- from water, Cl^- from $ZnCl_2$ and HSO_4^- ($^-OSO_3H$).

From the elementary analytic data of Table 2, the percentages of **I**, **II** and **III** in the total decomposition product can be calculated to be 76.4, 8.2 and 15.2%, respectively.

The same cleavage mode of C–N bond of MNDDS in photochemical and thermal decompositions should be ascribed to that of the strong electron-withdrawing $-NO_2$, attaching itself on the meta site of the diazoniun group, is favorable to forming MNDDS cation, which reacts with OH^-, Cl^- and HSO_4^- to form **I**, **II** and **III**, respectively.

It is well known that DDS and S-DDS have been utilized to prepare diazoresin—a polycondensation product of DDS or S-DDS with formaldehyde in sulfuric acid. The diazoresin is the most important photosensitive material in the manufacture of negative presensitized plate. Therefore, it is important to understanding the mechanisms of diazoresin in photochemical and thermal decomposition. The preliminary study shows that the mechanisms and products of diazoresin decomposed in UV irradiation or in heat are very similar to that of its monomer (DDS or S-DDS). The further investigations are in progress.

4. Conclusion

The photochemical and thermal decompositions of DDS, MDDS, NMDDS, CDS in ethanol and MNDDS in water were investigated. The results show that, for DDS, MDDS, NMDDS and CDS in ethanol, the major photo-decomposition products are the corresponding ethyl ethers formed from C–N heterolytic cleavage of diazonium salts, whereas in thermal decomposition, the corresponding diphenylamine (including carbazole) was obtained as only one product via homolytic cleavage of the C–N bond of diazonium salts. For MNDDS, the products are the same, both in photochemical and in thermal decompositions.

Acknowledgements

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