Photochemical Reactions of Primary Aromatic Amines with Chloromethanes in Solution. II. The Products and Mechanisms of Partial Reactions of Aniline in Tetrachloromethane, Chloroform and Dichloromethane

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Photochemical Reactions, Primary Aromatic Amines, Chloromethanes

Major products of photochemical reactions of aniline in tetrachloromethane, chloroform and dichloromethane have been isolated and identified. The mechanisms of partial reactions have been discussed.

Introduction

Mixtures of aromatic amines with chloromethanes have been known to be photochemically active [1–6]. The UV radiation absorbed by an amine leads to the formation of hydrogen chloride and a variety of organic compounds resulting from thermal transformations of the products of primary photochemical reaction. For the primary photochemical reaction occurring in the N,N-dimethylaniline-chloromethane systems a mechanisms has been suggested wherein an electron from the first excited state of the amine molecule is transferred to a chloromethane molecule in its ground state, this resulting in heterolytic dissociation of the C–Cl bond to give an active $\dot{C}H_{3-X}Cl_X$ radical (where $X = 1, 2, 3$) and a thermodynamically stable chloride ion. Accordingly, among the products of this reaction one can find the radical cation of the amine, the polychloromethane radical and the chloride ion [7–12].

In the preceding paper [13], an attempt has been made to determine the nature of interactions between aniline and its derivatives with chloromethanes both in the ground and in the excited states. We have noted the formation of weak charge-transfer complexes. However, as a matter of fact, the radiation was absorbed mostly by "free" amine molecules. Again, the formation of the ex-CT complexes in the excited state is obviously facilitated by "ordering" of the solution in the ground state. The works of Land and Porter [14] and of Zechner and co-workers [15] have shown that an aniline radical rather than a radical cation of the amine is formed in the primary photochemical reaction.

Results and Discussion

Table I lists the identified products of photochemical reactions of aniline with the chloromethanes.

After elucidation of the nature of interactions of aniline with chloromethanes [13] and identification of the products of their reactions we wish to offer the following mechanism of the primary and secondary processes for the photochemical transformations of aniline (AH).

Table I. Products of photochemical reactions of aniline with CCl_4, $CHCl_3$ and CH_2Cl_2.

Compound	CCl_4	$CHCl_3$	CH_2Cl_2
Azobenzene (**1**)	*	*	*
Hydrazobenzene (**2**)	*	*	*
Phenylisonitrile (**3**)	*	*	
2-Aminodiphenylamine (**4**)	*	*	*
4-Aminodiphenylamine (**5**)	*	*	*
N-Dichloromethyleneaniline (**6**)	*		
1,2,3-Triphenylguanidine (**7**)	*		
N-Methyleneaniline (**8**)			*
Hexachloroethane (**9**)	*		
Chloroform (**10**)	*		
1,1,2,2-Tetrachloroethane (**11**)		*	
Dichloromethane (**12**)		*	
1,2-Dichloroethane (**13**)			*
Chloromethane (**14**)			*

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Primary processes:

$$AH + h\nu \rightarrow {}^1AH^*$$

$$(AH\cdots CH_{4-Y}Cl_Y) + h\nu \rightarrow {}^1(AH\cdots CH_{4-Y}Cl_Y)^*$$

$${}^1AH^* \rightarrow AH + h\nu_{fl}$$

$${}^1AH^* + CH_{4-Y}Cl_Y \begin{cases} \rightarrow {}^3AH^* + CH_{4-Y}Cl_Y \\ \rightarrow AH + CH_{4-Y}Cl_Y \\ \rightarrow {}^1(AH\cdots CH_{4-Y}Cl_Y)^*_{solv} \\ \rightarrow AH + {}^2\dot{C}H_{3-X}Cl_X + Cl({}^2P_{3/2}) \end{cases}$$

$$AH + Cl({}^2P_{3/2}) \rightarrow {}^2A^{\cdot} + HCl$$

$${}^1(AH\cdots CH_{4-Y}Cl_Y)^* \begin{cases} \rightarrow {}^3AH^* + CH_{4-Y}Cl_Y \\ \rightarrow {}^1AH^* + CH_{4-Y}Cl_Y \\ \rightarrow AH + CH_{4-Y}Cl_Y \end{cases}$$

$${}^1(An\cdots CH_{4-Y}Cl_Y)^*_{solv} \begin{cases} \rightarrow \{{}^2AH^{\cdot+};\ Cl^-;\ {}^2\dot{C}H_{3-X}Cl_X\} \\ \qquad\qquad \downarrow \\ \rightarrow \{{}^2A^{\cdot};\ HCl;\ {}^2\dot{C}H_{3-X}Cl_X\} \end{cases}$$

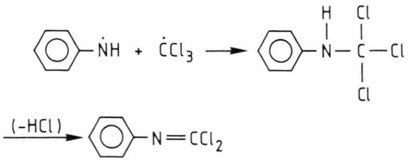
where $Y = 2, 3, 4$ and $X = 1, 2, 3$.

In the presence of each of the chloromethanes, electronic excitation of the aniline molecule may, apart from deactivation processes, lead to the hydrogen atom transfer (or the successive electron and proton transfer) from the amine molecule to that of the chloromethane. Consequently, products of the primary reaction probably include the aniline radical, the $\dot{C}H_{3-X}Cl_X$ ($X = 1, 2, 3$) radical and HCl.

Secondary processes

Recombination of the aniline radical with that of $\dot{C}H_{3-X}Cl_X$ "in cage" gives respectively:

a) in the case of the $\dot{C}Cl_3$ radical (from CCl_4), N-dichloromethyleneaniline (**6**):



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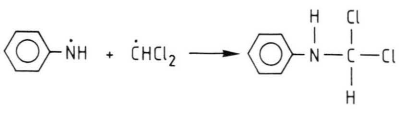
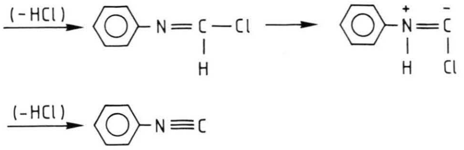
b) in the case of the $\dot{C}HCl_2$ radical (from $CHCl_3$), phenylisonitrile (**3**):





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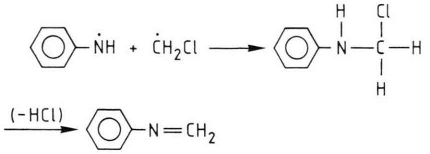
c) in the case of the $\dot{C}H_2Cl$ radical (from CH_2Cl_2), N-methyleneaniline (**8**):



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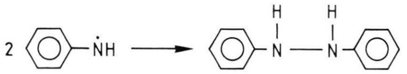
Recombination "outside the cage" of the aniline radicals affords hydrazobenzene (**2**):



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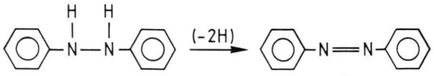
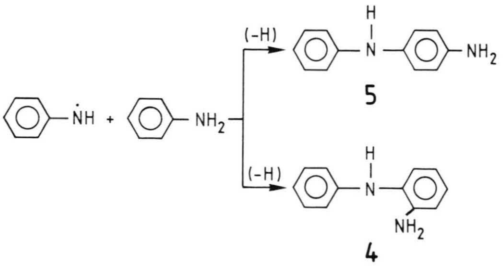
In each of the systems considered azobenzene **1** is formed as one of major products of the photochemical reactions. It probably originates from a facile oxidation of hydrazobenzene:

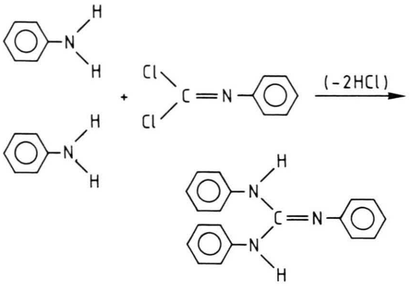


1

The products of the reaction of the aniline radical with the molecule of the amine are 4-aminodiphenylamine **5** and 2-aminodiphenylamine (**4**):



Compound **6** in the presence of aniline forms 1,2,3-triphenylguanidine (**7**):



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Recombination of the $\dot{C}H_{3-X}Cl_X$ radicals (X = 1, 2, 3) leads to hexachloroethane (**9**), 1,1,2,2-tetrachloroethane (**11**) and 1,2-dichloroethane (**13**):

$$2\,\dot{C}H_{3-X}Cl_X \rightarrow C_2H_{6-2X}Cl_{2X}$$

Again, in reactions of the $\dot{C}H_{3-X}Cl_X$ radical with a hydrogen donor, chloroform (**10**), dichloromethane (**12**) and chloromethane (**14**) are formed:

$$\dot{C}H_{3-X}Cl_X \xrightarrow{\text{H donor}} CH_{4-X}Cl_X$$

In the CCl_4 and CH_2Cl_2 media the yields of the major photoproducts are comparable (see Table II).

Only in $CHCl_3$, where the yield of phenylisonitrile is high, the yield of the aforementioned photoproducts distinctly declines, similar proportions being retained, however. Neither the nature nor the medium polarity have appreciable influence on the yields of the products (see Table III).

This result supports the correctness of the assumption of the radical character of these transformations.

The photochemical reactions of aniline in the presence of chloromethanes, described here, afford products which were also found following chemical and electrochemical oxidation of aniline. For instance, azobenzene was formed, amongst others, during oxidation of aniline with phenyl iodoacetate [16], lead (IV) acetate [17] sodium peroxoborate [18], manganese dioxide [19] and cupric chloride [20]. The mechanism of formation of the azo-compound during oxidation of aniline with these reagents involves hydrogen abstraction from the amine nitrogen, dimerization of the radicals formed to hydrazobenzene and oxidation of the hydrazine derivative to the azo-compound. A similar mechanism has been suggested by us for the formation of azobenzene in the photochemical reactions under consideration. Anodic oxidation of aniline affords benzidine and 4-aminodiphenylamine depending on the medium and conditions used [21, 22].

Table II. Percent yields of the loss of amine and of the formation of major products in photochemical reaction of aniline in CCl_4, $CHCl_3$ and CH_2Cl_2.

Products	CCl_4	$CHCl_3$	CH_2Cl_2
Aniline	21.2	16.1	11.7
Azobenzene	21.2	12.5	18.6
Hydrazobenzene	3.1	traces	traces
2-Aminodiphenylamine	31.8	18.4	25.8
4-Aminodiphenylamine	18.4	10.5	15.6
Phenylisonitrile	traces	30.2	–

Table III. Percent yields of the loss of amine and of the formation of major products in photochemically induced reactions of aniline and CCl_4 in 1,4-dioxane and methanol.

Products	1,4-Dioxane	Methanol
Aniline	22.6	20.0
Azobenzene	19.6	12.8
2-Aminodiphenylamine	33.4	30.2
4-Aminodiphenylamine	23.2	18.0

Experimental

Aniline (analytical grade reagent; POCh, Gliwice) was purified by repeated vacuum distillation over zinc dust. Tetrachloromethane, chloroform and dichloromethane were purified as described elsewhere [2, 3]. The solution for preparative irradiation (0.05 M aniline solution in appropriate chloromethane) was placed in a Pyrex flask fitted with an adapter enabling de-oxygenation of the photolyte with a slow stream of argon. The solution was placed in a water bath (15 °C) and exposed to the radiation of a Q-400 mercury burner for 24 h. As the Pyrex glass cuts off the radiation below 285 nm, this was absorbed mainly by the amine. After termination of the irradiation, the hydrogen chloride formed was neutralized with ammonia gas. The precipitate of ammonium chloride was filtered off and washed with small amounts of diethyl ether. The filtrate was concentrated at ambient temperature *in vacuo*. Preliminary analysis of the products was accomplished by thin-layer chromatography. The separation of the reaction mixture was performed by column chromatography on silica gel using a petroleum ether–diethyl ether developing system. The separation was also carried out by liquid chromatography using micropreparative columns. The isolated components were identified by ^1H NMR, IR and mass spectrometry as well as by elemental analysis. Volatile products were identified by gas chromatography (column packing was 15% UCON LB-550-X on Chromosorb P AW – 60/80 mesh, carrier gas – helium – 50 cm^3/min, the temperature of thermostat – 100 °C, thermal conductivity cell) by comparison with standards. The yields of the loss of aniline and of the formation of the major products of the photochemical reactions of aniline in CCl_4, $CHCl_3$ and CH_2Cl_2 were calculated on the basis of liquid chromatographic assays. The masses of the products were determined from calibration graphs constructed for each component.

Spectroscopic characteristics of some photochemical reaction products:

2-Aminodiphenylamine (**4**): ^{1}H NMR (CCl_4/TMS) δ ppm: 3.50 (s, 2H, NH_2), 5.00 (s, H, N–H), 6.30–7.60 (m, 9H_{arom}). – IR (Nujol): 3570, 1620, 1525 cm^{-1}.

4-Aminodiphenylamine (**5**): ^{1}H NMR (CCl_4/TMS) δ ppm: 3.30 (s, 2H, NH_2), 5.20 (s, H, N–H), 5.90–7.20 (m, 9H_{arom}). – IR (Nujol): 3590, 1620, 1525 cm^{-1}.

N-Dichloromethyleneaniline (**6**): ^{1}H NMR (CCl_4/TMS) δ ppm: 6.70–7.60 (m, H_{arom}). – IR (Nujol): 1680, 1620, 1505, 760 cm^{-1}.

1,2,3-Triphenylguanidine (**7**): ^{1}H NMR CD_3OD/TMS) δ ppm: 5.05 (s, 2H, N–H), 7.00–7.50 (m, 15H_{arom}). – IR (Nujol): 3470, 1680, 1600, 1520 cm^{-1}.

N-Methyleneaniline (**8**): ^{1}H NMR (CCl_4/TMS) δ ppm: 4.7 (s, 1H, $=CH_2$), 4.9 (s, 1H, $=CH_2$), 6.60–7.40 (m, 5H_{arom}). – IR (Nujol): 1670, 1610, 1510 cm^{-1}. – MS (EI, 70 eV) *m/e*: 105 $C_6H_5NCH_2^+$.

Analysis for C_7H_7N (105.14)

Calcd	C 80.0	H 6.7	N 13.3,
Found	C 79.8	H 7.0	N 13.2.

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