Egyptian Journal of Chemistry

Formation of Carbazole in ɤ- irradiated Aniline / Chlorobenzene mixtures

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Abstract

In this study, Gas chromatographic/mass spectrometric study indicated that carbazole (CARB) is formed in oxygen free ɤ-irradiation of aniline / chlorobenzene mixtures. It seems that ɤ-radiation induces the formation of CARB in these mixtures via intramolecular dehydrocyclization of diphenylamine (DPA). The yield of CARB estimated via gas chromatography (GC), was found to be dependent on aniline – chlorobenzene molar ratio. Where, the maximum CARB yield was found at 1:1 molar ratio of aniline – chlorobenzene. At this reactants molar ratio, the effect of absorbed radiation dose and dose rate on the yield of carbazole was studied. The yield of CARB increases, linearly, as the absorbed dose is increased up to about 50 kGy. The G-value ($5.8\mu M/J$) of CARB was determined. It was found that, the yield of CARB increase as the absorbed dose rate increases (0.226 -0.904kGy/h). So, it can be concluded that CARB is formed, mainly, in the spurs. The mechanism of the CARB formation was discussed.

Keywords: Carbazole; Aniline; Chlorobenzene; Diphenylamine; ɤ-Radiation; GC/MS.

1. Introduction

CARB belongs to a category of heterocyclic compounds with a great utilization during the recent years [1]. The carbazole structural unit is commonly present in several biologically active compounds [2]. Insecticides, pigments, drugs [3,4], polymers [5], dentistry, holography, microelectronics [6], and organic light emitting diodes [7] are areas where CARB and its derivatives have been utilized. Gas phase dehydrocyclization of diphenylamine (DPA) to CARB over Pt-based catalysts was studied at a temperature of 550 °C [8]. Since the work of Parker and Barnes [9], the intramolecular photocyclization of DPA and its derivatives to yield CARB and its derivatives has been the subject of extensive research in several laboratories [8,10-22,]. Debjani et al. [23] studied photochemical conversion of DPA to CARB, fluorometrically, in aerated aqueous and aqueous Beta-cyclodextrin solutions. The photocyclization reactions of DPA, N-methyldiphenylamine and triphenylamine have been studied in methanol by photolysis [18, 24]. Flash-excitation work, carried out by Grellmann et al., indicated that the photoconversion mechanism includes the formation of a triplet transient which is converted to another intermediate prior to the formation of CARB [11,12].

Moreover, CARB was formed during ɤ-radiolysis of DPA/ bromobenzene mixtures [25]. The goal of the current work is to study the effects of reactants molar ratio, absorbed radiation dose and dose rate on the yield of CARB in oxygen free ɤ- irradiated aniline / chlorobenzene mixtures. Moreover, a mechanism of CARB formation was proposed, according to the obtained results.

2. Experimental:
2.1.Sample Preparation and Radiolysis

Chlorobenzene (ClPh) (Sigma - Aldrich Analytical grade) was used as received without further purification. Aniline (sigma Aldrich analytical grade) was purified by vacuum distillation and the middle cut was used for sample preparation. Irradiation tubes (I.D. 13.7 mm and total volume 6 ml) were cleaned by soaking in chromic acid for 24 h, and rinsed with double distilled water before drying. Samples were prepared immediately prior to irradiation, were degassed by the freeze pump and thaw technique and sealed. Sample irradiations were carried out, at ambient temperature, by 60-Co source (India Gamma chamber4000 A).

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2.2.Analytical Procedures
2.2.1.Gas Chromatographic Analysis

CARB was quantitatively analyzed in irradiated samples by gas chromatograph (ATI-UNICAM 610) using helium (16 psi) as a carrier gas and 30m capillary column (DB-5). The following temperature program were applied: 300 °C flame ionization detector, 275 °C split/splitless injector, [50C (5min) to 250 °C at 8C/min(2min)] column oven. Split ratio was 1:55 and splitless time: 2 min (injected volume was 0.5 µL). The internal injection standard used was Anthracene. Estimation of the CARB *concentration* in the irradiated samples was carried out via *calibration* curve of CARB. Each sample was run 3 times, and average values were calculated for the relative CARB areas. The data were processed using the UNICAM 4880 data handling system.

2.2.2 Gas chromatographic - mass spectrometric (GC/MS) analysis

Finnigan mat SSQ 7000 GC/MS (Thermo instruments systems Inc. USA) was utilized for CARB detection. It was connected with the Dec 5000 data handling system. Mass spectra were recorded at an ionization potential of 70 eV (EI mode). Varian 3400 GC was used with the same conditions applied during the off-line GC analysis

3.Results and Discussion

CARB formed in oxygen free ɤ-irradiated aniline/chlorobenzene mixtures was identified by GC/MS and its yield was determined via GC. Fig.1 shows a partial GC chromatograme of oxygen free ɤ-irradiated aniline/ chlorobenzene mixture, including the peak2 corresponding to CARB. The mass spectrum (fig.2) corresponding to GC chromatographic peak2 is quite similar to that of CARB.
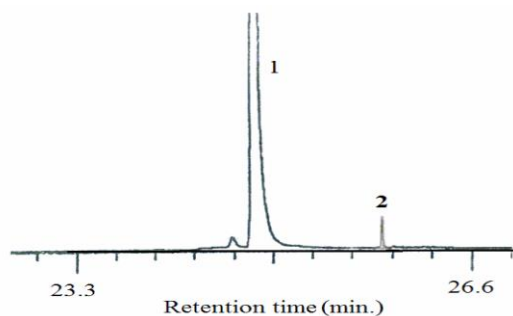

Fig.1. Partial GC chromatogram for analyses of ɤ-irradiated 1:1 molar ratio of aniline/chlorobenzene sample, 1 anthracene (internal standard), 2 CARB, [50C(5min) to 250C at 8C/min(2min)](Irradiated at: 24.3 kGy and 0.904 kGy/h).
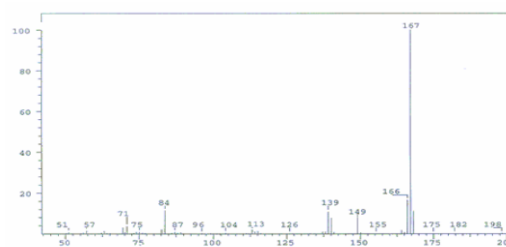
Fig.2.Mass spectrum (electron impact) of peak 2 in the GC chromatogram corresponding to CARB (M$^+$= 167) in ɤ-irradiated 1:1 molar ratio of aniline/chlorobenzene sample) (Irradiated at: 24.3 kGy and 0.904 kGy/h).
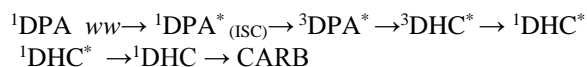
GC/MS analysis of ɤ-irradiated 1:1 molar ratio of aniline/chlorobenzene mixture showed the presence of DPA as a product. Moreover, It was reported that radiation induced cyclization of DPA to carbazole can be happened via either triplet state DPA [11,12], or free radical mechanism [26].

3.1. Cyclization of DPA to CARB via a triplet state DPA

Formation of carbazole via triplet state DPA ($^3DPA^*$) is a well known principal [11, 12]. So, formation of CARB in irradiated aniline/chlorobenzene mixtures can be summarised in the following equation:

$$\text{Aniline} + \text{ClPh } ww\rightarrow \text{ DPA} \qquad (1)$$
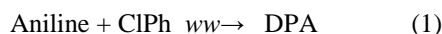
Grellmann, and Linschitz [11,12] reported that the mechanism of photoconversion of DPA to CARB includes the formation of a triplet transient DPA which is cyclized to dihydrocarbazole (DHC), and transformed finally to CARB. It should be mentioned that, DHC may either revert back to give DPA or can undergo CARB formation. The general scheme for the reaction can be summarized in scheme1:

$$^1DPA \; ww\rightarrow \; ^1DPA^*_{(ISC)} \rightarrow \; ^3DPA^* \rightarrow ^3DHC^* \rightarrow \; ^1DHC^*$$
$$^1DHC^* \rightarrow ^1DHC \rightarrow CARB$$

Scheme.1. the right hand star(*)corresponds *excited-state species,* and 1 and 3 in the left hand indicate the singlet and triplet states species respectively.

So, $^3DPA^*$ can be formed by the direct or indirect action (Intersystem crossing, $_{ISC}$) of ɤ–radiation [25].

It is well known that amines have low ionization potentials (electron donor) and chlorobenzene have good electron affinity and oxidation potentials (electron acceptor). So, chlorobenzene and amines can form a good donor

acceptor ground state charge transfer complex (CTC) [27]. So, chlorobenzene and DPA can form a donor - acceptor CTC [28].
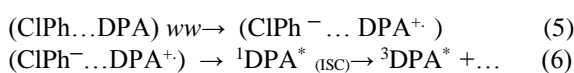
The excited CTC, between DPA (donor) and ClPh (acceptor), can dissociate to give $^3DPA^*$ [29]. It should be mentioned that, deactivation of the excited triplet CTC to ground state species will be faster in polar medium. Therefore, separation of $(ClPh…DPA)^{3*}$ to yield the $^3DPA^*$ is important in nonpolar medium (eq.2). Where, in non polar solvents, when charge transfer completed in CTC, the ion pair (ClPh $^-$ … DPA$^+$) undergoes fast charge recombination which can result in ground state or singlet or triplet states of the individual donor or acceptor molecules [29-31].

$$(ClPh…DPA) \, ww \rightarrow (ClPh…DPA)^{3*} \rightarrow \, ^3DPA^* \quad (2)$$

Where (ClPh…DPA) represents ground state CTC between ClPh and DPA, and (ClPh…DPA)^{3*} represents triplet excited state of this complex. Moreover, if DPA$^+$ were formed by the direct action of ɤ- radiation on DPA in nonpolar solvents (eq.3), it should be expected to decay by fast 2nd order kinetics with a law activation energy for recombination to form $^3DPA^*$(eq.4) [11, 30]:

$$DPA \, ww \rightarrow DPA^{+.} + e^- \quad (3)$$
$$DPA^{+.} + e^- \rightarrow \, ^3DPA^* \quad (4)$$
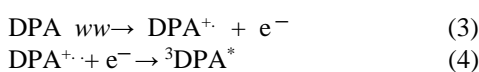
Moreover, in non- polar solutions, solute triplet states are believed to be formed mainly through neutralization of solute ions, or by formation of singlet solute which then converts to triplet by ISC (eq.5,6) [11, 29-35]:

$$(ClPh…DPA) \, ww \rightarrow (ClPh^- … DPA^{+.}) \quad (5)$$
$$(ClPh^-…DPA^{+.}) \rightarrow \, ^1DPA^*_{(ISC)} \rightarrow \, ^3DPA^* +… \quad (6)$$
Consequently, CARB can be formed by cyclization of $^3DPA^*$.
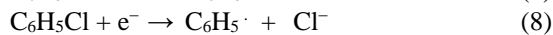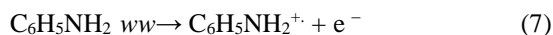
3.2. Cyclization of DPA to carbazole via a free-radical pathway

The formation of CARB in the current study can be happened, also, by a free-radical mechanism [26]. Where, free radicals such as, Cl and Ph can be formed by the DPA - sensitized cleavage of a C–Cl bond of chlorobenzenes, via quenching energy transfer [36-41]. Based on the previous consumption [26], these formed free radicals (Cl and Ph) can participate in CARB formation according to the following free radical mechanism:
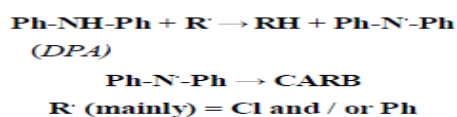
Ph–NH–Ph + R· → RH + Ph–N·-Ph
(DPA)
Ph–N·-Ph → CARB
R· (mainly) = Cl and / or Ph
Scheme.2.

The formation of these free radicals, by the direct effect of radiation *can't* be denied. So, Cl and Ph can be formed during radiolysis (direct action of radiation on aniline and chlorobenzene):

$$C_6H_5NH_2 \, ww \rightarrow C_6H_5NH_2^{+.} + e^- \quad (7)$$
$$C_6H_5Cl + e^- \rightarrow C_6H_5^. + Cl^- \quad (8)$$
$$C_6H_5Cl^* \rightarrow C_6H_5^. + Cl^. \quad (9)$$

It should be mentioned that, these radicals can be formed by electron transfer quenching from the excited singlet and triplet complexes state of many aromatic amines to chlorobenzenes [36-41]. Up to our knowledge, the formation of CARB in ɤ-irradiated oxygen free Aniline / Chlorobenzene mixtures has never studied before. Therefore, in the present work the factors which affect the yield of CARB were studied. These factors are the reactants molar ratio, absorbed radiation dose and dose rate.

3.3.Effect of reactants Molar ratio

For studying the effect of aniline/chlorobenzene molar ratio on the CARB yield, samples with different aniline molar ratio from 0 to 1, were irradiated at the same dose (Fig.3). As the molar ratio of aniline increases from 0 to 1, the yield of CARB increases, up to a maximum at about 0.5 aniline molar ratio (1:1 reactants molar ratio), and then it gradually decreases at higher aniline molar ratios. It is known, that aniline is more polar (0.420) than chlorobenzene (0.188). So, when the less polar chlorobenzene predominates in aniline/chlorobenzene mixture, the formation of triplet state DPA is much probable [29,31].
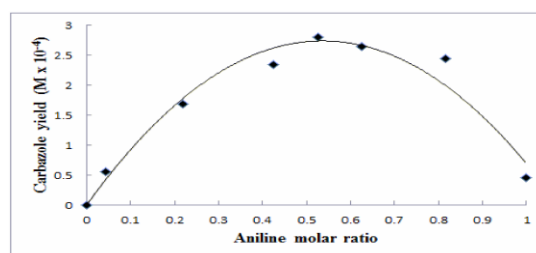

Fig.3. Effect of aniline Molar Ratio on the CARB yield (M x 10^{-4}) in ɤ - irradiated aniline / chlorobenzene mixtures (absorbed dose = 24.3 kGy at 0.904 kGy/h.

On the other hand when aniline predominates the mixture tends to be more polar. So, when molar ratio of aniline increases above 0.5 the mechanisms of carbazole formation, can be changed. Where, the formation of triplet state DPA is favored in non polar medium[42 ,43]. So, when aniline predominates carbazole can be, *also*, formed via a free-radical pathway [26]. Thus, an increase in aniline molar ratio can cause an increase in solvent

stabilization of the developing free radicals, resulting in an enhancement of formation of CARB via radical mechanism. Where, Cl radical can be complexed directly to the nitrogen atom of some nitrogenous compounds (pyridine). So, Cl formed from eq. (9) can be complexed with aniline, in the same way as pyridine [44]. Consequently, recombination of Cl with Ph will be hindered. So, Ph will get a good chance to participate in CARB formation via a radical mechanism (scheme 2). The decrease in the yield of CARB at higher aniline molar ratio than 0.5 can be related to the decrease of the yields of Cl and ph radicals formed from chlorobenzene.

3.4.Effect of absorbed radiation dose

The effect of absorbed radiation dose, on the yield of CARB in ɣ- irradiated aniline / chlorobenzene mixture (1:1 molar ratio) was studied up to 154 kGy (fig.4). From fig.4, it can be seen that as the absorbed radiation dose increases the yield of CARB, linearly, increases up to about 50 kGy. The G-value of CARB (5.8µM/J) was calculated using the slope of the linear part of the curve, according to the following equation:

$$\text{G-value} = \frac{\mu\text{mole}}{\text{Gy} \times \text{Kg (sample)}}$$
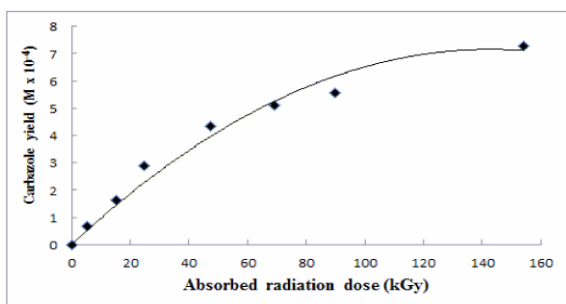

Fig.4 Effect of absorbed radiation dose (kGy) on the yield of CARB (M x 10^{-4}) in ɣ-irradiated (1:1) aniline/chlorobenzene mixture (Dose rate = 0.9039kGy/h).

3.5.Effect of absorbed radiation dose rate

Ions, electrons, and excited-state species are formed in spurs via irradiation. It is well known that the rate of energy deposition determines the concentration of these intermediates in the irradiated medium. Ion recombination and free radical reactions were proposed to be included in the CARB formation process. Therefore, the concentration of the ions and

free radicals should affect the yield of CARB. At law absorbed dose rates, spurs will be apart from each other in the irradiated medium. Consequently, ions and electrons escaping these regions will diffuse and react with a solute or become uniformly distributed. At higher dose rates the distance between the spurs is closer and the expanding spurs will overlap [45-47]. Such overlap of spurs yields a denser concentration of ions and free radicals. Consequently, the probability of recombination of ions, and, consequently, excited species will increase [33,48]. Also, free radical reactions will be favorable at higher dose rates. Fig.5. shows that the yield of CARB linearly increases with increasing the absorbed dose rate. Which, points to the role of free radical mechanism in carbazole formation. Moreover, ion recombination reactions, which are the precursor of triplet excited states, are favored at higher dose rates. Such observation could be related to the formation of CARB in spurs mainly.
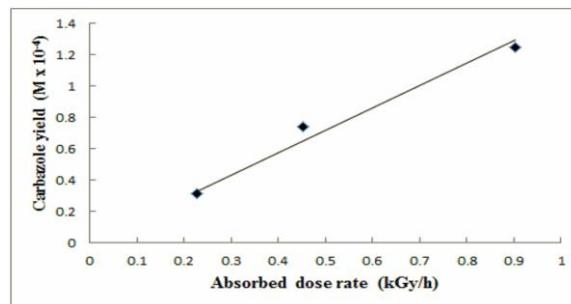

Fig.5 Effect of absorbed radiation dose rate (kGy/h) on the yield of CARB (M x 10-4) in ɣ-irradiated (1:1) aniline/chlorobenzene (absorbed radiation dose=10.77 kGy).

4.Conclusion

Carbazole (CARB) is formed in ɣ-irradiated aniline/chlorobenzene mixtures, via radiation induced cyclization of DPA. Radiation induced cyclization of DPA to CARB can be happened via either ^{3}DPA*, or free radical mechanism. Molar ratio of the reactants affects the polarity of the medium and, consequently, determines the mechanism, through which CARB is formed. So, DPA in the triplet state comes to play, almost, when the less polar, chlorobenzene, predominates. Where, the ISC rates increase and ^{3}DPA* yield improved in nonpolar medium. On the other hand, when the more polar aniline predominates, free radical mechanism becomes more effective. The maximum yield of CARB was found at 1:1 aniline: chlorobenzene molar ratio. The yield of CARB increases as the dose rate increase due to increase of ions and free radical concentrations. Which, points to the role of free radical mechanism in

carbazole formation. Moreover, ion recombination reactions, which are the precursor of triplet excited states, are favored at higher dose rates.

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