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Photochemistry of 4-Chloroaniline in Solution. Formation and Kinetic Properties of a New Carbene, 4-Iminocyclohexa-2,5-dienylidene

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The photochemistry of 4-chloroaniline and related 4-halogenoanilines was investigated in solution by means of nanosecond transient absorption spectroscopy and steady-state photoproduct analysis. The main emphasis was the study of the mechanism of photoinduced reactions in aqueous solutions, motivated by the presence of 4-chloroaniline in the environment, following biodegradation of chlorophenylurea-based herbicides. Additional measurements were carried out in some organic solvents (aliphatic alcohols, acetonitrile, and *n*-hexane) in order to clarify the mechanism. The first transient detectable at nanosecond time resolution in aqueous solution was assigned to a carbene, 4-iminocyclohexa-2,5-dienylidene, produced by photoinduced heterolytic dehalogenation. The spectral and kinetic properties of this previously unknown species, as well as the products of its reactions, were studied in detail; it was found to react with O_2, giving an iminoquinone *O*-oxide, to abstract an H atom from aliphatic alcohols, giving an anilino radical cation, to add bromide, giving 4-bromoaniline quantitatively, and to react with H_2O quite slowly. This behavior, characteristic of a carbene with a triplet ground state, is fully analogous to that found in the well-studied photochemistry of 4-halogenophenols. There are a few characteristic differences in this system, however, most conspicuous being that the amino (or imino) group can accept a positive charge. For this reason, contrary to 4-chlorophenol, photolysis of 4-chloroaniline also produced the carbene in nonprotic polar solvents, such as acetonitrile. Furthermore, contrary to 4-chlorophenol and 4-chloroanisole, the reaction mechanisms of 4-chloro-*N*,*N*-dimethylaniline and 4-chloroaniline are the same. Finally, the product distribution from 4-chloraniline in the presence of O_2 was found to be different from that of 4-chlorophenol, and this was traced to the fact that the iminoquinone oxide is able to add to 4-chloroaniline.

Introduction

Chloroanilines are important intermediates in organic synthesis and they appear in the biodegradation of some herbicides derived from chlorophenylureas. They are toxic and classified as typical environmental pollutants.[1,2] Photodegradation may play an important role in their elimination from natural waters. The present work is focused on the photochemistry of 4-halogenoanilines, in particular 4-chloroaniline (4-ClA), in aqueous solutions, with auxiliary measurements in organic solvents designed to clarify the mechanisms involved.

The photochemistry of 4-ClA in organic solvents was investigated more than thirty years ago by Latowski, the main objective being the study of the influence of solvent polarity on the quantum yield of photodehalogenation; a photoionization step with concomitant formation of hydrated electrons was postulated to be the primary step in polar solvents.[3,4] Later, Miller and Crosby reported photooxidation of aqueous 4-ClA into 4-chloronitrosobenzene and 4-chloronitrobenzene.[5] The analysis of photoproducts from 4-ClA in H_2O/methanol mixtures has recently been reconsidered; benzidine was detected as a major product alongside with aniline.[6] This result was interpreted as indicating the intermediacy of anilino radicals in the photolytic mechanism, in contradiction to Latowski's original mechanism. A new mechanism was put forward[6] in analogy to the photochemistry of 4-halophenols,[7−12] which in the meantime had been shown to proceed by the intermediacy of a carbene, 4-oxocyclohexa-2,5-dienylidene, produced by photoinduced heterolytic dehalogenation. The spectral and kinetic properties of this carbene have been characterized by means of nanosecond transient absorption spectroscopy.[7] Very recently, photoheterolysis of 4-halo-*N*,*N*-dimethylanilines in acetonitrile could be evidenced by chemical trapping of the cation produced by dehalogenation.[13]

In the present work, we have investigated the photochemistry of 4-ClA and its methylated derivative, 4-chloro-*N*,*N*-dimethylaniline (4-ClDMA), using nanosecond transient absorption spectroscopy and product analysis. First, we wanted to test the hypothesis that 4-ClA and 4-chlorophenol indeed follow comparable photochemical mechanisms. Preliminary data had indicated that this was indeed the case.[14] In the present work, we present a full account of the observation and characterization

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of the previously undetected carbene, 4-iminocyclohexa-2,5-dienylidene. Particular emphasis is placed on the behavior in aqueous solutions.

Experimental Section

4-Chloroaniline (4-ClA) was obtained from Aldrich (>98%) and purified by steam distillation. 4-Chloro-*N*,*N*-dimethylaniline was prepared by methylating 4-ClA using dimethyl sulfate as methylation reagent, followed by separation using column chromatography. The other chemicals and organic solvents used were analytical grade. Water was either purified with a Milli-Q (Millipore) device or triply distilled.

Transient absorption experiments were carried out using a frequency-quadrupled Nd:YAG laser (Quanta-Ray DCR-1, 266 nm, pulse duration 10 ns). The procedures used for transient absorption spectroscopy measurements have been previously described.[15]

For continuous irradiations at 290 nm, a monochromator (Schoeffel) equipped with a xenon lamp was used. Actinometry was performed by means of potassium ferrioxalate. For the isolation of main photoproducts, solutions were irradiated in the range 290−350 nm with a device consisting of 6 lamps (Duke Sunlamp GL20), a cylindrical mirror, and a reactor made of Pyrex.

The formation of Cl^- was measured by capillary electrophoresis on a Waters Quanta 4000 instrument (column: $\phi = 75\ \mu m$, $l = 60$ cm). The analysis of organic photoproducts was carried out with a HPLC chromatograph (Waters) equipped with a photodiode array detector and a column C_{18} (250 mm × 4 mm). The eluent used was a 40:60 (v/v) H_2O/MeOH mixture. The aqueous solvent was buffered at pH 7.2 with phosphate buffer to prevent ionization of products. For the isolation of the main photoproducts, a 150 mm × 20 mm column was used and the eluent (H_2O/MeOH 45:55) was buffered with ammonium acetate (10^{-2} M).

GC-MS spectra were obtained on a Hewlett-Packard 5985 instrument equipped with a column Optima 5 (Machery-Nagel, 25 m, $\phi_i = 0.25$ mm) coated with siloxanes. The MS spectra of products P_1' and P_5 were recorded on a Hewlett-Packard 5989 instrument. NMR spectra were recorded on a Bruker AC400 instrument (direct introduction). Identification of the products P_5, P_6, and P_7 was based on the following data: 4′,5-diamino-2-chlorobiphenyl (P_5): δH (400 MHz; methanol-D4) 7.34 (2H, d, *J* 8.5, 2′-H and 6′-H), 7.30 (1H, d, *J* 8.5, 3-H), 6.94 (2H, d, *J* 8.4, 3′-H and 5′H), 6.86 (1H, d, *J* 2.8, 6-H), 6.79 (1H, dd, *J* 8.5 and 2.8, 4-H); *m*/*e* 218 ($M^{\bullet+}$, 100%), 220 ($M^{\bullet+}$, 33%), main fragments 182 (13%), 167 (8%), 154 (10%), 127 (8%), 109 (13%). 2,4′-Diamino-5-chlorobiphenyl (P_6): δH (400 MHz; acetone-D6) 7.13 (2H, d, *J* 8.7 and 2.5, 2′-H and 6′-H), 6.98 (1H, dd, *J* 8.5 and 2.5, 4-H), 6.94 (1H, d, *J* 2.5, 6-H), 6.76 (1H, d, *J* 8.4, 3-H), 6.73 (2H, d, *J* 8.6, 3′-H and 5′-H), 4.80 (2H, s, NH_2), 4.50 (2H, s, NH_2'); *m*/*e* 218 ($M^{\bullet+}$, 100%), 220 ($M^{\bullet+}$, 33%), main fragments 182 (64%), 167 (17%), 154 (34%), 127 (28%), 91 (78%). 4-Amino-4′-chlorodiphenylamine (P_7): δH (400 MHz; acetone-D6) 7.07 (2H, d, *J* 8.8, 3′-H and 5′-H), 6.95 (1H, s, NH), 6.89 (2H, d, *J* 8.6, 2-H and 6-H), 6.81 (2H, d, *J* 8.8, 2′-H and 6′-H), 6.65 (2H, d, *J* 8.6, 3-H and 5-H), 4.50 (2H, s, NH_2); *m*/*e* 218 ($M^{\bullet+}$, 100%), 220 ($M^{\bullet+}$, 33%), main fragments 182 (22%), 154 (11%), 107 (39%), 91 (17%).

Results and Discussion

1. Photophysical Properties. The aqueous spectroscopy, photophysics, and photochemistry of aniline are pH-dependent by virtue of the protonation of the amino group in acidic medium.[16] The halogenoanilines are expected to behave in a similar fashion. Indeed, the UV spectrum of 4-ClA is pH-dependent as shown in Figure 1. The S_1 and S_2 absorption maxima of the neutral form are located at 290 nm ($\epsilon = 1300\ M^{-1}\ cm^{-1}$) and 239 nm ($\epsilon = 10800\ M^{-1}\ cm^{-1}$); the cationic form has only a weak absorption at wavelengths longer than 225 nm. From the variation of absorption at 290 nm with the pH of the solution, shown in the insert of Figure 1, the pK_B of 4-ClA was evaluated as 4.0, which is similar to unsubstituted aniline.

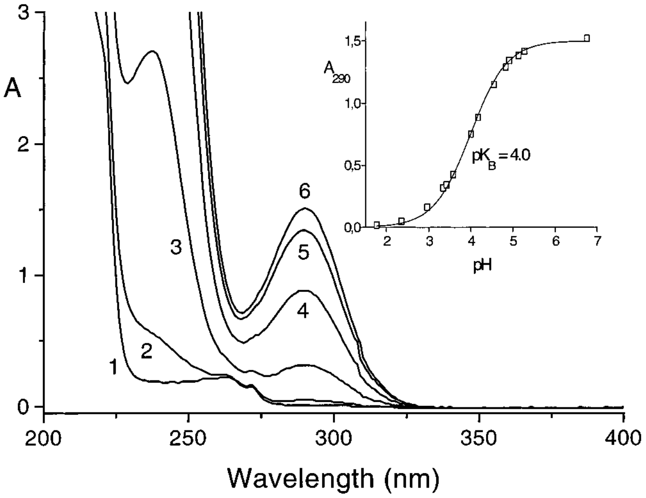


Figure 1. Absorption spectra of 4-ClA (1.1×10^{-3} M) in aqueous solution as a function of pH. Spectra measured at pH 1.77 (1), 2.36 (2), 3.34 (3), 4.16 (4), 4.96 (5), and 6.75 (6). *Insert*: Determination of pK_B from the absorbance values at $\lambda = 290$ nm.

TABLE 1: Fluorescence Quantum Yields (Q_F), Fluorescence Lifetimes (τ_F), and Quantum Yields of Triplet Energy Transfer to Anthracene (Q_T) for 4-Chloroaniline, 4-Chloro-*N*,*N*-dimethylaniline, 4-Fluoroaniline, and Aniline in Different Solvents

substance	solvent	Q_F	τ_F (ns)	Q_T
4-ClA	*n*-hexane	0.013	0.43	0.66
	ethanol	0.019	0.41	<0.02
	acetonitrile	0.015	0.29	
	water (pH 6)	0.021	0.42	
4-ClDMA	*n*-hexane	0.013	0.45	0.69
	ethanol	0.022	0.50	<0.02
	acetonitrile	0.016	0.51	
	water (pH 6)	0.028	0.75	
4-FA	*n*-hexane	0.10	1.89	0.69
	ethanol	0.14	2.96	<0.04
	acetonitrile	0.12	2.49	
	water (pH 6)	0.11	2.64	
aniline	*n*-hexane	0.17 [17]	4.42 [17]	0.63
	ethanol	0.13 [17]	3.14 [17]	0.72
	water (pH 6.5)	0.032 [18]	0.93 [18]	

Fluorescence data of 4-ClA, 4-ClDMA, and 4-FA are summarized in Table 1. 4-ClA and 4-DMClA were found to fluoresce very weakly in all solvents investigated (*n*-hexane, ethanol, acetonitrile, and water), with quantum yields not exceeding 0.03; the fluorescence lifetimes were in the range of a few hundreds of picoseconds. In contrast, the fluorescence of 4-FA was much more pronounced, with quantum yields over 0.1 and lifetimes in the nanosecond range. There was no marked solvent dependence of the fluorescence properties in either case. Literature data[17,18] on aniline are also shown in Table 1; for this molecule, both fluorescence quantum yield and lifetime are reduced in water as compared to *n*-hexane and ethanol, an effect that has been attributed to enhanced internal conversion in the aqueous environment.[18]

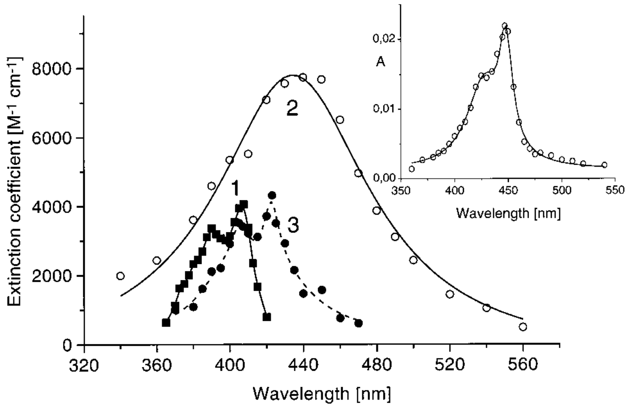


Figure 2. Transient spectra from the photolysis of 4-ClA in neutral aqueous solution. (1) Spectrum measured 50 ns after pulse end in deoxygenated solution; (2) spectrum produced by reaction of primary transient with O_2; (3) spectrum produced by reaction of primary transient with 2-propanol. *Insert*: Spectrum of 4-chloroanilino radical cation produced by one-electron oxidation of 4-ClA by sulfate radicals.

Formation of aniline and halogenoaniline triplet states was investigated by means of energy transfer to anthracene ($1-5 \times 10^{-4}$ M) in the solvents *n*-hexane and ethanol. The growth of the anthracene triplet−triplet absorption was monitored at 420 nm. The resulting triplet quantum yields, based on $\Phi_{isc} = 0.7$ for anthracene[19] are given in Table 1. In contrast to the fluorescence data, the results of the triplet energy transfer measurements were strongly solvent-dependent for all three halogenoanilines: substantial energy transfer to anthracene took place in *n*-hexane, whereas in ethanol the transfer yields were lower by a factor of 10 or more. This points to a correspondingly shorter lifetime of the halogenoaniline triplet states in ethanol. This solvent dependence was not observed for aniline.

2. Pulsed Laser-Induced Transients from 4-ClA in Neutral Aqueous Solution. The absorption spectrum of the transient species measured at pulse end (at a time resolution of about 50 ns) upon irradiation of an aqueous solution (pH 5−7) of 4-ClA is shown in Figure 2 (spectrum 1). At low to moderate pulse energies (<2 mJ/pulse, corresponding to 23.5 mJ × cm^{-2} in the geometry used), only one species was observed, characterized by a two-band spectrum with maxima at 407 and 390 nm. In the absence of additives, this transient decayed in the microsecond range (see Figure 3 for a typical oscilloscope trace) to give a secondary species with an absorption maximum around 450 nm. The decay at 407 nm and the growth at 450 nm exhibited the same kinetics, both getting faster with increasing 4-ClA concentration. This suggested a reaction of the 407/390 nm transient with 4-ClA to give the secondary species. This reaction, its pH dependence, and its mechanistic implications will be treated later.

In a solution saturated with O_2, the primary transient was rapidly transformed into a different secondary species with a broad unstructured band having an absorption maximum at 440 nm (Figure 2, spectrum 2). This new transient disappeared in a pseudo-first-order reaction with 4-ClA with a rate constant of $5 \times 10^{8}\ M^{-1}\ s^{-1}$.

The effect of the addition of 2-propanol to a neutral solution of 4-ClA was again the transformation of the primary transient into a secondary intermediate, which in this case had a two-band spectrum with maxima at 423 and 405 nm (Figure 2, spectrum 3). Other aliphatic alcohols induced the same reaction.

Addition of bromide (at concentrations around 10^{-3} M) or of chloride (at concentrations around 0.1 M) accelerated the decay of the 407/390 nm transient without concomitant growth of a secondary species.

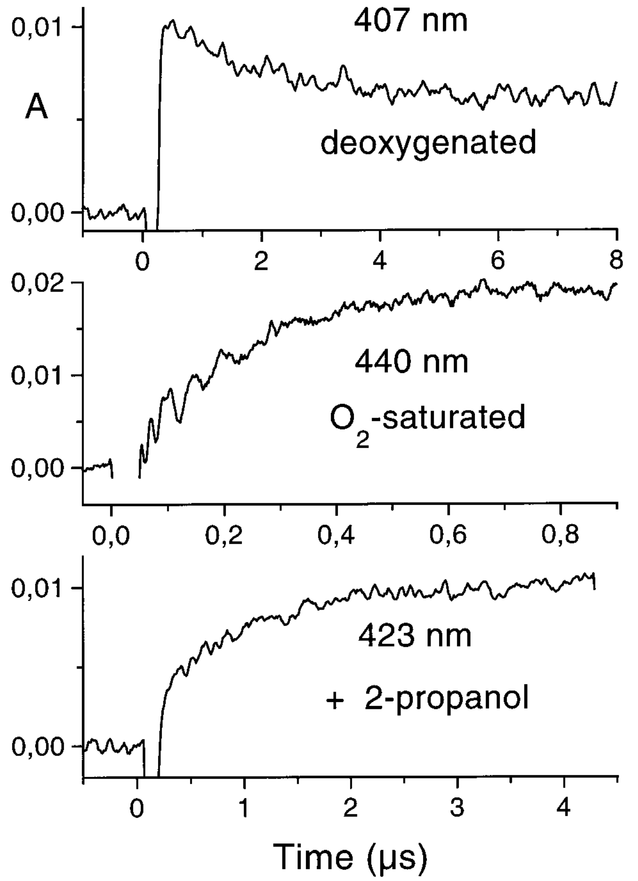


Figure 3. Oscilloscope traces of transients corresponding to spectra 1−3 in Figure 2.

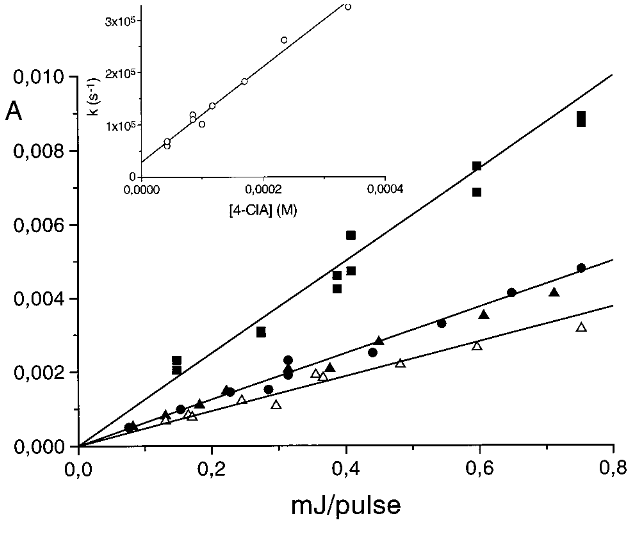


Figure 4. Dependence of transient absorbance on laser pulse energy in aqueous solutions of 4-ClA at constant absorbance at the excitation wavelength ($A_{266} = 0.1$). Squares: pH 6, solution saturated with O_2, absorbance of secondary transient computed from kinetic fit (see text); full triangles: pH 6, deoxygenated solution containing 0.34 M 2-propanol, absorbance of secondary transient measured 4 μs after the pulse; open triangles: same as full triangles, pH 2. Dependence of decay rate at $\lambda = 407$ nm on 4-ClA concentration (pH 6, deoxygenated solution).

The dependence of transient absorption on laser pulse energy is displayed in Figure 4. The absorbance values were determined in the following ways: for transient 1, the decay trace (see Figure 3) was extrapolated to $t = 0$ (corresponding to the laser pulse); the absorbance of transient 2 was determined by means

TABLE 2: Rate Constants of Reactions of Protonated 4-Iminocyclohexa-2,5-dienylidene in Aqueous Solution with Selected Substrates[a]

reactant	k ($M^{-1}\,s^{-1}$)	method
O_2	2.3×10^9	A
methanol	2.3×10^6	B
Ethanol	7.3×10^6	B
2-propanol	2.2×10^7	B
tert-butanol	7.6×10^5	B
H_2O	5.3×10^2	C
OH^-	3.1×10^{10}	C
Br^-	6.9×10^8	C
Cl^-	8.4×10^5	C
p-chloroaniline	9.0×10^8	C

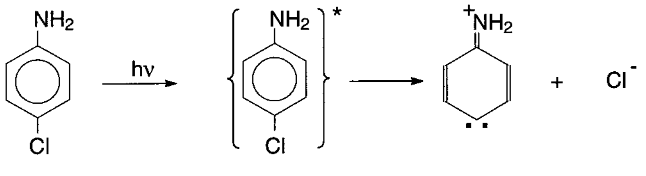
[a] Methods employed: (A) build-up of iminoquinone *O*-oxide at $\lambda = 440$ nm; (B) build-up of aniline radical cation at $\lambda = 423$ nm; (C) decay of 4-iminocyclohexa-2,5-dienylidene at $\lambda = 407$ nm.

of a kinetic fit based on two consecutive reactions describing its formation and decay; the absorbance of transient 3 was directly read at $t = 4\ \mu s$ after the pulse, the decay of the transient being sufficiently slow to allow this approach. As shown in Figure 4, the behavior is linear for all species, in agreement with a one-photon photolysis process. The slopes of the straight lines obtained were subsequently used for the determination of the quantum yields of transient formation (see below).

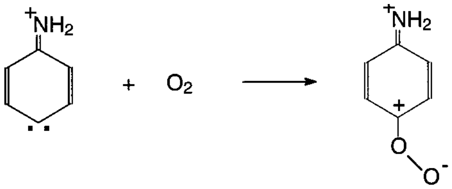
The kinetics of the reactions of the 407/390 nm transient with the mentioned compounds were determined by following either its decay or the formation of the product at various reactant concentrations. As an example, the insert in Figure 4 shows the dependence of the first-order decay rate, measured at $\lambda = 407$ nm, on the concentration of 4-ClA in neutral aqueous solution. The data yield a positive *y*-axis intercept which can be interpreted as resulting from the reaction of the 407/390 nm species with H_2O. The rate constants measured in this and related experiments are listed in Table 2.

3. Interpretation of Reaction Behavior in Neutral Aqueous Solution. The spectral and kinetic behavior obtained upon photoexcitation of neutral aqueous 4-ClA is in complete agreement with that of the previously studied 4-chlorophenol.[7] On the basis of the comparison between the two systems, the following reactions can be identified and assigned:

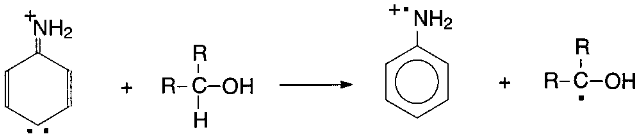
(a) Initial formation of a transient with a two-band absorption reminiscent of that of the anilino radical cation,[20] but shifted to shorter wavelengths by about 15 nm. A related result was previously obtained in the photoinduced dehalogenation of 4-chlorophenol;[7] in this system, the absorption spectrum of the initial transient is similar to that of the phenoxyl radical. On the basis of the identification of the carbene, 4-oxocyclohexa-2,5-dienylidene, as the initial intermediate in the 4-chlorophenol system,[7] it can be surmised that its counterpart, protonated 4-iminocyclohexa-2,5-dienylidene, is formed in the case of 4-ClA. The assumption that this species is protonated is based on the similarity of its absorption with that of the anilino radical cation, and is confirmed by the results obtained in the solvent acetonitrile, as will be shown below.



(b) The assignment of this carbene is further strengthened by its characteristic reactivity. First, rapid diffusion-controlled addition of O_2 is observed to form a product which based on its spectrum can be identified with a 4-iminoquinone *O*-oxide.[7,21] It should be noted that there is no experimental evidence available to decide whether the imino group of this species is protonated, because its absorption properties are not expected to depend very much on this condition; the structure written below thus corresponds to one of two possibilities:



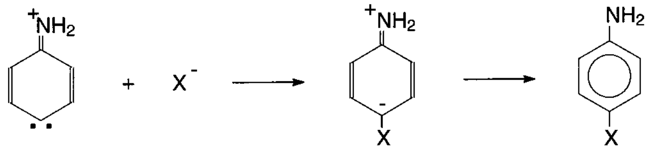
Second, reaction with aliphatic alcohols generates a transient which, based on its absorption features (maxima at 423 and 405 nm), can be identified as the anilino radical cation.[20] This observation is analogous to that of the formation of phenoxyl radicals in the reaction of 4-oxocyclohexa-2,5-dienylidene with aliphatic alcohols[7] or with cyclohexane,[22] which had been interpreted as arising from an hydrogen atom transfer to the carbene. If the H atom donor is an alcohol (ROH), a C-centered hydroxyalkyl radical will most probably be produced together with the anilino radical cation:



The characteristic feature of this reaction is that dehalogenation of 4-ClA precedes formation of the radical cation. To ascertain the correctness of this mechanism, the absorption spectrum of the halogenated radical cation, 4-$ClA^{\bullet+}$ was measured in a separate experiment; this was necessary since this species might be produced by laser-induced electron ejection from 4-ClA. We generated 4-$ClA^{\bullet+}$ by one-electron oxidation of 4-ClA by sulfate radicals from the photolysis of peroxodisulfate; the transient spectrum obtained is shown in the insert of Figure 2. The 4-ClA radical cation produced in this reaction had absorption maxima at 447 and 425 nm; its extinction coefficient was determined as $\epsilon_{447} = 4400\ M^{-1}\ cm^{-1}$ based on $\epsilon_{450} = 1600\ M^{-1}\ cm^{-1}$ for the sulfate radical.[23] The radical cations of aniline and 4-chloroaniline thus can be clearly distinguished by their absorption spectra; it can be concluded that only the former are produced upon photoexcitation of 4-ClA in the experimental conditions used.

(c) Both reactions, with O_2 as well as with alcohols, point to a carbene with a triplet ground state. The trend observed in the rate constants for H abstraction from the alcohols, which increases in the order *tert*-butyl alcohol < methanol < ethanol < 2-propanol (Table 2), is the same as that observed for H atom reactions[24] and confirms the biradicaloid character of the carbene ground state.

(d) A further characteristic property of the carbene is that its reaction with bromide is efficient whereas reaction with chloride is slow (Table 2). No secondary transients absorbing in the visible or near-UV spectral ranges are produced in these reactions, in agreement with a mechanism involving direct addition of the halides to the carbene. This behavior can be understood by considering that the reaction initially occurs on the triplet surface; the intersystem crossing step necessary to generate the final product may be promoted by a heavy-atom effect in the halide adduct:



(e) Similar to 4-oxocyclohexa-2,5-dienylidene,[7] the imino carbene studied here has a very low rate constant for reaction with H_2O. In the former case, this behavior was rationalized by arguing that reaction with H_2O is likely to proceed by an insertion mechanism on the singlet surface, similarly to other carbenes. A radical-type reaction on the triplet surface would have to be slow on account of the high energy required to break the H−OH bond. Furthermore, semiempirical calculations indicated that a specific carbene−H_2O interaction could additionally induce an orientational hindrance.[7]

Assuming quantitative transformation of the carbene into the 4-ClA radical cation at sufficiently high concentrations of alcohols, the quantum yields of carbene formation and its extinction coefficient, as well as the extinction coefficient of the quinone *O*-oxide could be determined relative to the value $\epsilon_{423} = 4110\ M^{-1}\ cm^{-1}$ for the anilino radical cation.[20] The extinction coefficients, determined from the slopes of the linear relationships of transient absorbance versus laser pulse energy (see Figure 3) are given in Figure 4; the quantum yield of carbene formation was found to be 0.53 ± 0.05 in neutral aqueous solution.

4. pH Dependence of Carbene Formation and Reactivity. Photoexcitation of protonated 4-ClA in acidic medium (pH 1−2) yielded the same 407/390 nm primary transient as in neutral solution, indicating initial carbene formation in this case too. The comparatively low UV absorption of protonated 4-ClA allowed the measurement of transient spectra in the far-UV region; a further absorption band of the carbene was detected with a maximum at 250 nm. Reaction of the carbene with the substrate molecules is slower in acidic than in neutral medium, suggesting a different reaction mechanism (see below). The carbene reactions with O_2, alcohols, and halides were in all respects similar to those observed in neutral solution. The quantum yield of carbene formation in acidic medium was found to be 0.40 ± 0.05 (see Figure 4). The protonation state of 4-ClA thus does not alter the photochemical behavior, but appears to influence the quantum yield of carbene formation to a small, but measurable extent. It may be speculated that this difference is related to the requirement of a deprotonation step for generation of the carbene from protonated 4-ClA, which is absent if the amino group is unprotonated.

In moderately alkaline solution (pH around 10), the decay of the carbene is accelerated according to a reaction with OH^- (Table 2). The observed decay of the absorbance at 407 nm most probably reflects the OH^- − induced deprotonation of the imino group of the carbene. The resulting nonprotonated carbene is expected to have lower absorbance than its protonated counterpart, in analogy to the neutral anilino radical,[20] and therefore escapes detection. As will be detailed below, the finding that the carbene derived from 4-ClDMA did not undergo this reaction supports this interpretation.

The spectra of the secondary species formed by reaction of the carbene with neutral and protonated 4-ClA are shown in Figure 5. In neutral solution, the spectrum measured 20 μs after the pulse exhibits a maximum at 447 nm, similar to that of the 4-ClA radical cation (Figure 2). Assuming that the part of the spectrum at $\lambda > 440$ nm is due to this species, a second transient contributing to the overall absorption can be extracted which is shown as a broken line in Figure 5. This transient is characterized by a weak broad band with a maximum around 390 nm that is reminiscent of the neutral anilino radical ($\epsilon_{400} = 1250\ M^{-1}\ cm^{-1}$ [20]). The observation that the ratio of the absorbances of the two bands (Figure 5) is close to that of the extinction coefficients of the assigned species strengthens this assumption. The formation of these transients is therefore consistent with a reaction between a protonated carbene and an unprotonated 4-ClA molecule that formally corresponds to transfer of an electron:

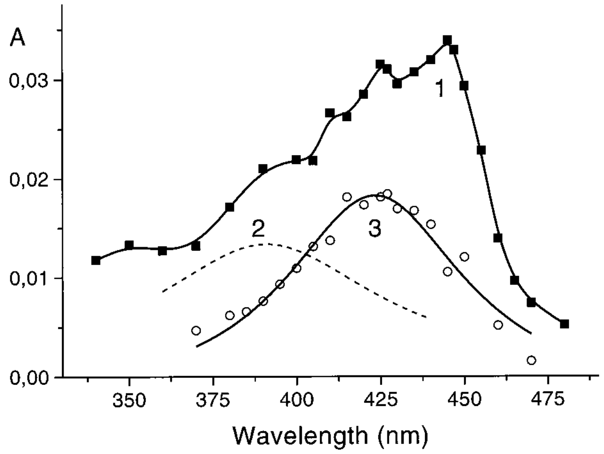
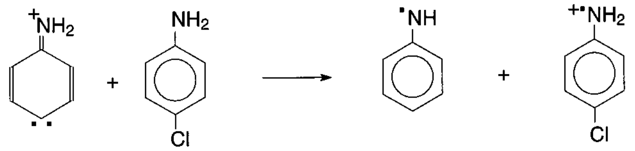
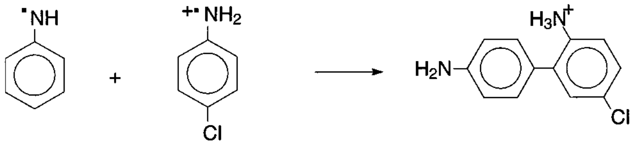


Figure 5. Secondary transients formed by reaction of protonated 4-iminocyclohexa-2,5-dienylidene with 4-ClA in neutral, respectively, acidic solutions. (1) Spectrum measured 20 μs after the laser pulse in a solution of 4-ClA (2.35×10^{-4} M; 0.8 mJ/pulse) at pH 6; (2) spectrum obtained by subtracting the spectrum of the 4-ClA radical cation from spectrum A; (3) spectrum measured 80 μs after the laser pulse in a solution of 4-ClA (2.3×10^{-3} M; 0.2 mJ/pulse) at pH 2.



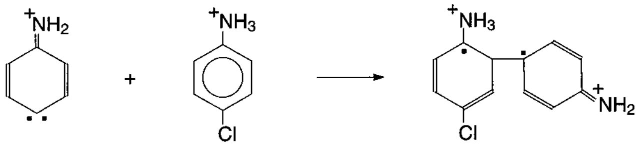
The actual mechanism of this reaction may involve electron transfer followed by H atom migration from the amino group to the para carbon.

The anilino radical and 4-ClA radical cation formed in this reaction may be expected to have a high probability for in-cage combination. One possible reaction among others would consist in ortho-para coupling:



As will be shown later, this mechanism is fully supported by the results of product analysis, which also indicate that meta−para coupling occurs as a minor process.

In acidic solution, the carbene−substrate reaction is slower by more than 1 order of magnitude compared to its value in neutral solution (Table 2). This can be understood by considering that, contrary to neutral 4-ClA, electron transfer from protonated 4-ClA to the protonated carbene is impossible. The reaction might therefore proceed by addition; a triplet biradical species can be suggested as a possible intermediate responsible for the observed transient (Figure 5):



5. Transients from Other Haloanilines. The pulsed laser-induced transients from 4-fluoroaniline (4-FA) and 4-bromoaniline (4-BrA) were studied in aqueous solutions under the same conditions utilized with 4-ClA. Their photochemical behavior was found to be completely analogous to that of 4-ClA. The only significant difference was in the quantum yields of carbene formation, which were found to decrease in the order 4-FA > 4-ClA > 4-BrA. As will be shown below, this result is confirmed by the steady-state measurements. There is no single obvious reason for this trend in quantum yields. We may note, however, that it supports the heterolytic bond cleavage mechanism since a homolytic mechanism would be expected to show the opposite trend. Moreover, it is tempting to associate the lower yield found for 4-BrA as compared to 4-ClA with the much higher rate constant for reaction of the carbene with Br^- (see Table 2), which might increase the probability of in-cage recombination.

It is noteworthy that photochemistry is most efficient for 4-FA although this molecule has a significantly longer fluorescence lifetime than 4-ClA (see Table 1). Together with the solvent dependence of the yield of triplet energy transfer to anthracene (Table 1), this result supports a model according to which photochemistry occurs on the triplet and not on the singlet surface. It may be noted here that the 4-haloanilines were not suitable for investigating this hypothesis in more detail. Their triplet states could not be experimentally accessed in polar solvents, neither directly by spectroscopic observation nor indirectly by looking for an effect of triplet quenchers or heavy atoms on carbene yields; we tried to detect an effect of triplet quenchers on the yield of photochemistry in ethanolic solutions, but even at the highest quencher concentrations that could be used at $\lambda_{exc} = 266$ nm (5×10^{-4} M anthracene or 5×10^{-3} M acrylamide) there was no measurable reduction. As in the case of 4-chlorophenol,[7] the reason might be that on one hand the intersystem crossing yield in the parent molecule is high whatever the nature of the halogen substituent (thus precluding any measurable effect of heavy atom addition), and on the other hand the triplet lifetime is very short in polar solvents due to fast dehalogenation (thus requiring unrealistically high concentrations of triplet quenchers to induce a measurable effect on photochemistry). In this respect, other haloaromatics with measurably longer triplet lifetimes are better suited for study; indeed the results of studies of the photochemistry of 5-chloro-2-hydroxybenzonitrile[12] and 4-chlorosalicylic acid[25] are consistent with dehalogenation occurring from the lowest haloaromatic triplet state.

6. Pulsed Laser-Induced Transients from 4-ClA in Nonaqueous Solvents. Laser flash photolysis of a solution of 4-ClA in ethanol gave the transients shown in Figure 6. The intermediate obtained at pulse end is characterized by maxima at 426 and 408 nm. Its spectrum was very similar to that of the anilino radical cation in aqueous solution (compare Figure 2), and could therefore be assigned to this species. It may be concluded that the initial photochemistry of 4-ClA proceeds in the same way in aqueous and in ethanolic solution. The same observation had previously been made for 4-chlorophenol.[7] Not surprisingly, the initially formed carbene is absent in the transient spectrum, since its reaction with ethanol is too fast to be resolved in time when the alcohol is used as the solvent; the anilino radical cation is therefore the first species seen after the laser pulse. At longer times, the transient spectrum shifts to longer wavelengths as a secondary species with an absorption maximum around 450 nm is formed (Figure 6). This observation is consistent with the earlier detection, by means of Raman spectroscopy, of benzidine radical cations resulting from the decay of aniline radical cations.[20]

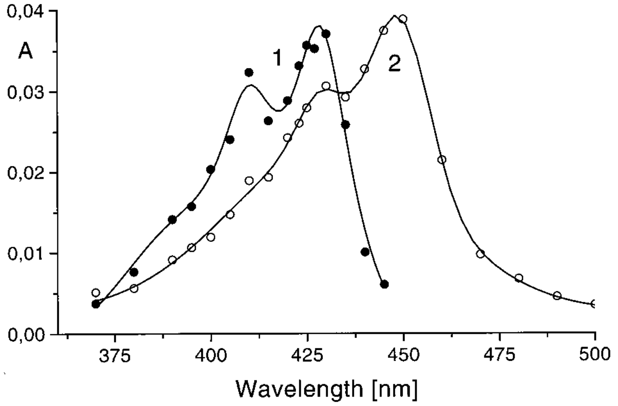
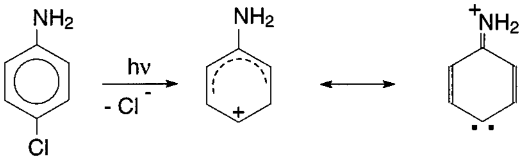


Figure 6. Transient spectra obtained in a deoxygenated solution of 4-ClA (10^{-3} M) in ethanol. (A) 100 ns after pulse end; (B) 8 μs after pulse end.

The photochemistry of 4-chlorophenol in acetonitrile was characterized by the fact that no transients were detectable on a nanosecond time scale.[7] This behavior was rationalized by pointing out that formation of a carbene by dehalogenation of the neutral molecule is likely to be a two-step process, with initial formation of a carbocation by halide elimination and subsequent deprotonation of the carbocation to generate the carbene; in a nonprotic solvent, the second step is not possible. In the case of 4-ClA, the situation is different since the initally produced carbocation and the protonated carbene are tautomeric, and consequently a deprotonation step is not necessary in order to generate the carbene:



The photochemistry of 4-ClA in acetonitrile can therefore serve as a test of the proposed mechanism. The transients obtained in this system are shown in Figure 7.

The transient spectra obtained from 4-ClA in acetonitrile solution are a clear demonstration of rich photochemistry occurring in this solvent. This was expected on account of the recent observation that a cation photogenerated from 4-ClDMA in acetonitrile can be chemically trapped.[13] The initial transient (1 in Figure 7) was again the familiar two-peaked band of the carbene, in confirmation of the mechanism outlined in reaction 7. This species subsequently transformed in secondary species (2 and 3) with band locations that shifted to longer wavelengths in the course of the reaction. An intermediate with $\lambda_{max} = 425$ and 410 nm was transiently observed 1 μs after the pulse, giving way to another species characterized by a spectrum with $\lambda_{max} = 447$ and 425 nm. This was reminiscent of the behavior observed in ethanolic solution (Figure 6) with the difference that the carbene now was observable on account of the much smaller rate constant for H abstraction from acetonitrile compared to ethanol.[7] Furthermore, a new feature in the transient spectrum was found at longer wavelengths, where a weak long-

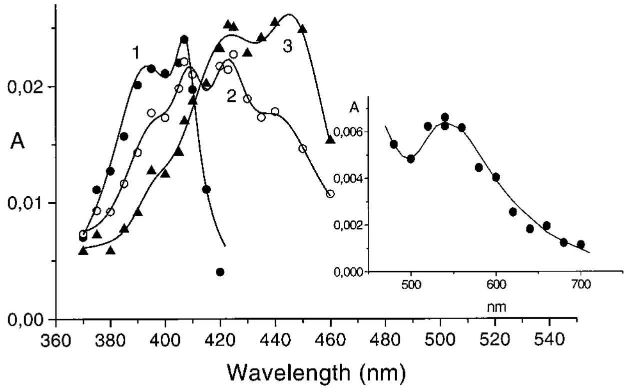
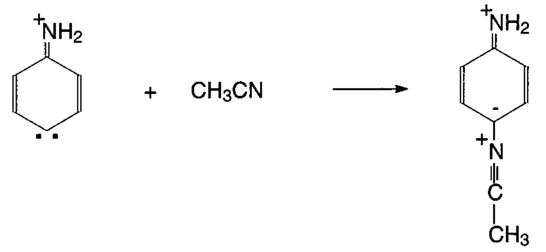


Figure 7. Transient spectra obtained in a deoxygenated solution of 4-ClA (10^{-3} M) in acetonitrile. (1) 100 ns after pulse end; (2) 1 μs after pulse end; (3) 8 μs after pulse end. *Insert*: Spectrum measured 40 μs after pulse end.

lived band with λ_{max} = 540 nm appeared; this band, shown in the insert in Figure 7, grew in with a rate of about 3×10^4 s^{-1} which was independent of the 4-ClA concentration. A similar transient was previously observed from the reaction of 4-oxocyclohexa-2,5-dienylidene with acetonitrile in 1,1,2-trichlorotrifluoroethane (but not in neat acetonitrile) and attributed to the formation of a nitrile ylide by addition to the carbene.[22] The following reaction can therefore be assumed in the case of 4-ClA:



The slow formation of the absorption assigned to the nitrile ylide had been interpreted as being due to the fact that it originates from a triplet carbene, which necessitates an intersystem crossing step; a precursor possibly responsible for this step, with maximum absorbance at 620 nm, had been identified in the study cited above.[22] In the present work, we could not detect this precursor, possibly because the transient absorbance was too low; the comparison of the band intensities around 420 and 540 nm (Figure 7) indicated that addition is of minor importance compared to H atom abstraction. This is consistent with the earlier failure to observe the nitrile ylide from 4-oxocyclohexa-2,5-dienylidene in neat acetonitrile.[22]

The photoinduced reactions of 4-ClA were finally studied in a nonpolar solvent, *n*-hexane. The transient spectrum detected in this solvent is shown in Figure 8.

The absorption spectrum obtained in this solvent had a maximum in the UV (355 nm) and a weak shoulder around 420 nm, and thus was fundamentally different from the spectra obtained in the solvents discussed earlier. The lifetime of the transient in question decreased in the presence of typical triplet quenchers such as O_2 or 2,4-hexadiene, and was therefore assigned to a triplet−triplet transition of 4-ClA. There was no indication of transient absorptions arising from photochemical reactions. The behavior of photoexcited 4-ClA in *n*-hexane is consistent with the observation of a substantial intersystem crossing quantum yield determined by energy transfer to anthracene (Table 1).

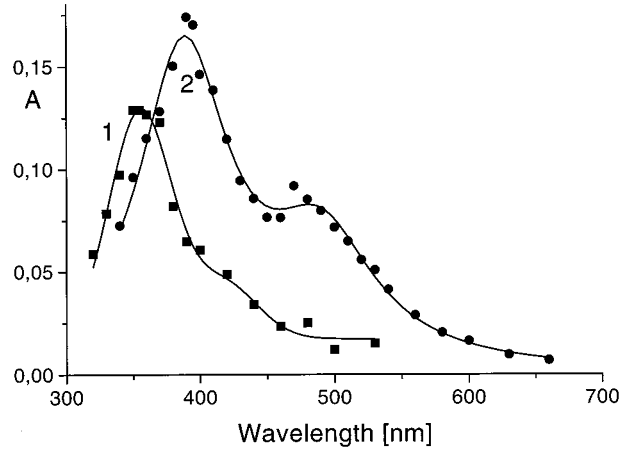


Figure 8. Transient spectra measured at pulse end in deoxygenated solutions (10^{-3} M) of 4-ClA (1) and 4-ClDMA (2) in *n*-hexane.

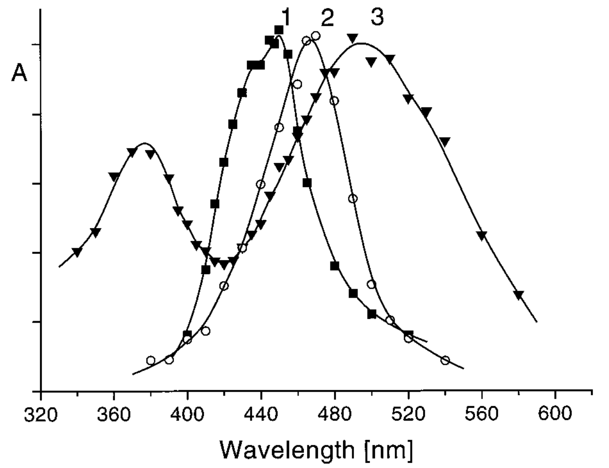


Figure 9. Laser-induced transients obtained from 4-ClDMA (10^{-4} M) in neutral aqueous solution. (1) Deoxygenated solution, pulse end; (2) deoxygenated solution, 2-propanol 0.17 M added, absorbance measured 1.6 μs after pulse end; (3) solution equilibrated with air ([O_2] = 2.5×10^{-4} M), absorbance measured 4 μs after pulse end.

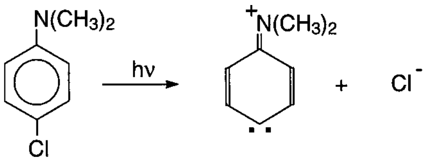
7. Transients from Photoexcited 4-Chloro-*N*,*N*-dimethylaniline. Methylation of the amino group of 4-ClA is expected to influence the photochemical behavior since prototropic equilibria at the amino nitrogen are no longer possible. In the case of the 4-chlorophenol/4-chloroanisole couple, this influence is dramatic: photoinduced dehalogenation is very efficient for both compounds in aqueous solution, but contrary to 4-chlorophenol[7] no halogen-free transients can be detected in aqueous 4-chloroanisole on the nanosecond and microsecond time scales.[26] A further major difference between these two systems is the fact that the yield of the main product of the photolysis of aqueous 4-chloroanisole, 4-hydroxyanisole, is not influenced by oxygen.[26] As mentioned above, this may be explained by assuming that formation of a carbene requires deprotonation of the carbocation produced by dehalogenation, which is impossible if the OH group is methylated; the carbocation then probably undergoes a fast reaction with H_2O to yield 4-hydroxyanisole. It was therefore of interest to see whether the same difference prevails between the photochemical mechanisms of 4-ClA and 4-ClDMA.

The transient absorption study of 4-ClDMA, carried out in aqueous solution and in the same organic solvents previously used for the study of 4-ClA, unraveled a photochemical behavior that paralleled that of 4-ClA in most respects. Figure 9 shows the spectra of the transients obtained in experimental conditions

TABLE 3: Influence of Solute Concentration, Oxygenation, and pH on Quantum Yields of Degradation of 4-ClA (ϕ_{deg})and of Chloride Formation (ϕ_{Cl^-}) in Aqueous Solutions

$C \times 10^{-3}$ M	oxygenation	pH	ϕ_{deg}	ϕ_{Cl^-}
0.2	air-equilibrated	6.5	0.66	0.29
1.0		(unbuffered)	0.67	0.43
5.2			0.89	
0.2	N_2		0.72	
0.2	O_2		0.64	0.33
1.0	N_2	6.5	0.72	0.47
1.0	O_2	(unbuffered)	0.66	
1.0		4.8	0.80	
	air-equilibrated	7.2	0.79	
		12.5	0.68	

that were analogous to those used for the 4-ClA transient spectra displayed in Figure 2. Again, a primary transient was obtained (spectrum 1, $\lambda_{max} = 450$ nm), which was replaced by secondary transients by reaction with alcohols (spectrum 2, $\lambda_{max} = 465$ nm) or O_2 (spectrum 3, $\lambda_{max} = 375$ and 490 nm). The 465 nm band could be assigned to the *N*,*N*-dimethylaniline radical cation on the basis of comparison with literature data.[27] The 450 nm band was assigned to the carbene, and the two-band spectrum 3 to the quinone oxide. In analogy to 4-ClA, the primary step can be written as



The carbene structure written in this reaction should be considered as hypothetical, since the actual charge distribution in this species is not known at present. In support of this structure, it may be pointed out that the dimethylated nitrogen can accommodate a significantly higher positive charge than the dihydrogenated nitrogen; this is clearly shown, for instance, by a comparison of the computed electronic structures of the radical cations of aniline and *N*,*N*-dimethylaniline.[28]

The reactivity of the carbene obtained from 4-ClDMA was in most respects similar to that of the 4-ClA-derived carbene, described above. The most notable difference was observed in aqueous alkaline solutions: increasing the pH up to 12 did not influence the decay kinetics at 450 nm, indicating that a possible electron-transfer reaction from OH^- to the carbene is slow ($k < 5 \times 10^7$ M^{-1} s^{-1}). As noted above, this observation can be used to infer that the rapid reaction of the N-hydrogenated carbene with OH^- (see Table 2) proceeds by deprotonation. It is interesting to compare the low efficiency of the electron transfer from OH^- to the carbene with the distinctly higher one for electron transfer from the substrate molecule (reaction 4); a possible reason for this difference lies in the requirement of an intersystem crossing step in the reaction complex, which might be favored by the role of the Cl atom as a heavy atom perturber in reaction 4.

8. Product Analysis Studies. Product analysis studies were carried out upon photolysis of 4-ClA in aqueous solutions, using monochromatic excitation at $\lambda = 290$ nm, to corroborate the mechanisms deduced from the results of the transient absorption study described above. The quantum yield of photodegradation of 4-ClA, irradiated at 290 nm, was evaluated in various conditions; the results are reported in Table 3. It could be deduced that pH (in the range 4.8−12.5) and oxygenation have no significant influence on the quantum yield of photodegradation, ϕ_{deg}. On the other hand, ϕ_{deg} was significantly higher than the quantum yield of formation of Cl^- (ϕ_{Cl^-}); this holds true despite the rather high experimental uncertainty of the values of ϕ_{Cl^-} determined at low 4-ClA concentration. This was also apparent from the dependence of the amount of product on irradiation time, shown in Figure 10A: the slopes obtained at short irradiation times, from which the quantum yields were determined, were distinctly higher for the amount of degraded substrate than for the amount of produced chloride. Such a difference between the yields of degradation and product formation was not observed, however, when 4-ClA was irradiated in the presence of bromide (Figure 10B). In this experiment, 4-bromoaniline was the only product found by HPLC, and the quantum yields of degradation of 4-ClA and of formation of 4-BrA were identical.

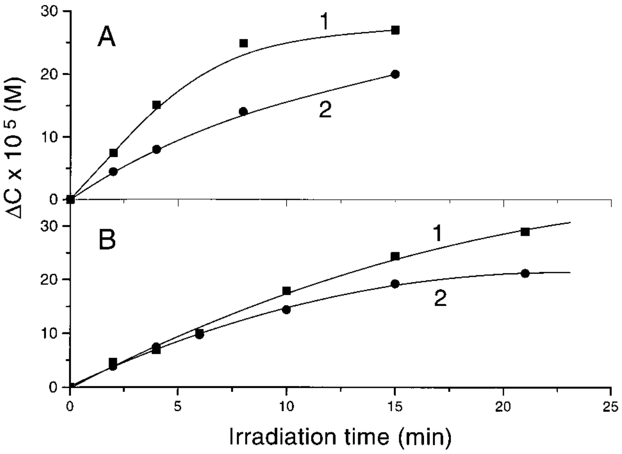


Figure 10. Dependence of substrate degradation and photoproduct formation on irradiation time in deoxygenated neutral solutions of 4-ClA. (A) [4-ClA] = 10^{-3} M, no additives. (1) Substrate degradation, (2) formation of chloride. (B) [4-ClA] = 5.9×10^{-4} M, 10^{-2} M Br^- added. (1) Substrate degradation, (2) formation of 4-bromoaniline.

The comparison of the quantum yields listed in Table 3 with the transient absorption results allows several conclusions to be drawn. First, the fact that neither the pH nor the presence of O_2 influence the degradation yield is in agreement with a fast primary photolysis step. Second, the higher yields of degradation as compared to chloride formation can be explained by considering that, in the absence of added reactants, the carbene formed by dehalogenation can react with both H_2O and 4-ClA; the latter reaction consumes further substrate molecules. If O_2 is added as a reactant for the carbene, a comparable result is obtained (see Table 3), but this time the reaction of the iminoquinone oxide with 4-ClA is responsible. Addition of bromide as a reactant, however, abolishes the difference between the yields of substrate degradation and product formation (Figure 10B); in this case, the product, 4-bromoaniline, is formed by direct addition of bromide to the carbene, without involvement of further intermediates that might react with the substrate.

The quantum yield of chloride formation found in the product study at [4-ClA] = 10^{-3} M, $\phi_{Cl^-} = 0.43 \pm 0.05$, is in satisfactory agreement with the quantum yield of carbene determined by laser flash photolysis. The somewhat higher value found in the latter case may be due to the different excitation wavelengths used; at $\lambda = 266$ nm, the wavelength employed for the pulsed laser irradiations, excitation leads to highly vibrationally excited S_1 levels. A considerable effect of excitation wavelength on the quantum yield of dehalogenation has recently been found for a related system, 4-chlorosalicylate;[25] the same situation may apply to 4-ClA.

Table 4 shows the results of quantum yield measurements carried out in aqueous solutions on two further haloanilines,

TABLE 4: Quantum Yields of Degradation (ϕ_{deg}) and of Halide Formation (ϕ_{X^-}) of 4-Halogenoanilines in Air-Equilibrated Unbuffered Aqueous Solutions and in Organic Solvents

compound	solvent	concentration (M × $10^{3)}$	ϕ_{deg}	ϕ_{X^-}
4-BrA	H_2O	1.01	0.38	0.27
4-ClA		1.01	0.67	0.43
4-FA		0.70	0.80	0.50
4-ClA	CH_3CN	0.79	0.82	
4-ClA	methanol	0.86	0.69	
4-ClA	hexane	0.96	0.45	

4-fluoroaniline and 4-bromoaniline, and in organic solvents on 4-ClA. In aqueous solution, the quantum yield of phototransformation is higher with 4-FA and lower with 4-BrA, in agreement with the trend observed for the yields of carbene formation. Substantial values of ϕ_{deg} were also determined in organic solvents, including *n*-hexane. In methanol, aniline was the major photoproduct, accounting for more than 60% of substrate degradation; this is consistent with a mechanism involving the intermediate formation of the aniline radical cation, as discussed above. The products formed in acetonitrile and *n*-hexane were not identified. It is noteworthy that photodegradation also takes place in a nonpolar medium; in this case, the transient absorption results suggest a different, as yet unidentified mechanism.

An analytical study of the photoproducts of 4-ClA in neutral aqueous solution was carried out by means of various techniques as described in the Experimental Section. Broad band irradiation was used for the purpose of the identification of individual photoproducts; the range of excitation was limited to wavelengths corresponding to the S_1 state of 4-ClA. The experimental conditions were thus comparable to those used in the remainder of this work. Typical HPLC chromatograms obtained upon monochromatic excitation at $\lambda = 290$ nm are displayed in Figure 11. The upper (A) and lower (C) chromatograms are those obtained in irradiated unbuffered solutions (10^{-3} M) at 12% substrate transformation, respectively, in the presence of air (A) and in deoxygenated solution (C). Chromatogram (B) shows the effect of dark reactions on the distribution of the products shown in chromatogram (A).

The comparison between chromatograms (A) and (C) indicates that the products P_2, P_7, P_8, and P_9 result from reactions involving O_2. P_2, P_8, and P_9 are not stable at room temperature and disappear after a few hours, while P_7 increases (Figure 11B). The absorption spectra of P_8 and P_9 have maxima at 450 and 427 nm, respectively, and stronger bands in the UV range (262 and 280 nm, respectively), whereas the first absorption band of P_7 is located at 290 nm. P_1, P_5, and P_6 are the main photoproducts in deoxygenated solution; it can be noted that P_1 is favored in diluted solution ($<10^{-4}$ M) and that the formation of P_5 and P_6 increases with increasing concentration.

P_1 and P_4 were identified as 4-aminophenol and aniline, respectively, by comparison of their HPLC retention times and UV spectra with those of authentic samples. P_2 was identified as benzoquinone imine. This compound could not be isolated, but a solution was obtained by oxidizing 4-aminophenol by ferricyanide.[29] P_5, P_6, and P_7 were isolated and identified, respectively, as 4′,5-diamino-2-chlorobiphenyl, 2,4′-diamino-5-chlorobiphenyl and 4-amino-4′-chlorodiphenylamine, on the basis of their mass and ^{1}H NMR spectra, as described in the Experimental Section. A minor peak appearing in the mass spectrum at $m/e = 219$, having similar GC retention time and similar NMR signature as P_7 was tentatively identified as 4-hydroxy-4′-chlorodiphenylamine (P_7'). Finally, the HPLC peak of product P_1 (4-aminophenol) hides a further product, P_1' which becomes more important in concentrated deoxygenated solution. Its MS analysis ($m/e = 200$) and the observation that the same product was obtained by irradiation of P_6 enable us to identify P_1' with 2,4′-diamino-5-hydroxybiphenyl.

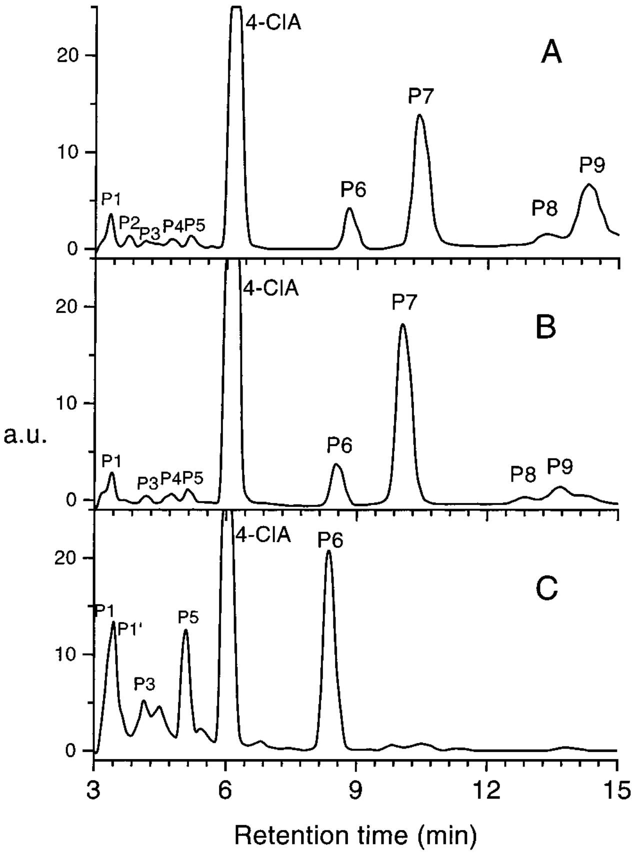
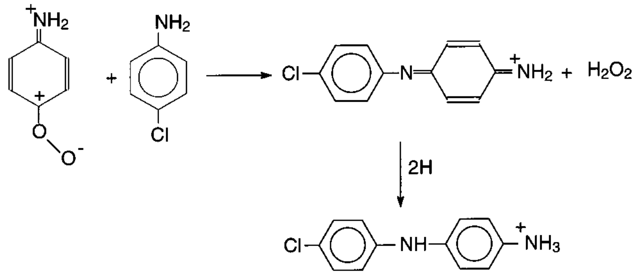


Figure 11. HPLC chromatograms obtained upon irradiation ($\lambda = 290$ nm) of 10^{-3} M 4-ClA in neutral aqueous solution (12% substrate transformation); detection wavelength 280 nm. (A) Air-equilibrated solution, immediately after irradiation; (B) same as (A), 1.5 h after irradiation; (C) deoxygenated solution, immediately after irradiation.

Among the species described above, several are easily assignable to products expected from the carbene reactions deduced from the transient absorption study. This applies in particular to the products found in deoxygenated solution, 4-aminophenol (P_1), 2,4′-diamino-5-chlorobiphenyl (P_6), and the isomer of the latter, P_5, which are easily understood as arising from the reactions of the carbene with water on one hand, and with 4-ClA on the other. The product P_1' very probably arises from a secondary photolysis step involving 2,4′-diamino-5-chlorobiphenyl. All these reactions are in full analogy to those earlier observed in the study of the photolysis of 4-chlorophenol.[7]

The situation is more complex in the presence of oxygen. The detection of benzoquinone imine is again parallel to that of *p*-benzoquinone in the photolysis of 4-chlorophenol,[7] but contrary to the latter it is not the only product in oxygenated solution, and probably not even a major one. This is in agreement with the observation that the iminoquinone oxide formed by addition of O_2 to the carbene was found in turn to react with 4-ClA, and this latter reaction does not have a counterpart in the 4-chlorophenol system. Comparison of the HPLC chromatograms A and B in Figure 11 suggests that P_8 and P_9 are precursors to P_7, 4-amino-4′-chlorodiphenylamine. It should be noted that P_8 and P_9 cannot arise from a reaction of benzoquinone imine with 4-ClA, because they were not detected in a solution of the former prepared by oxidizing 4-aminophenol with ferricyanide. If the assignment of P_7 as an end product of the reaction of the iminoquinone oxide with 4-ClA is correct, the following reaction sequence can be tentatively put forward:



Based on stoichiometry, the overall reaction leads to formation of 4-amino-4′-chlorodiphenylamine (P_7) and molecular oxygen. The product analysis makes it obvious, however, that this reaction does not occur in one step. We postulate as a first step a reaction involving formation of 4-chlorophenyl-*N*-quinone diimine; the formation of H_2O_2 is in analogy to the previously described reaction of *p*-benzoquinone *O*-oxide with H_2O.[7] In the same way, the minor product P_7' may be envisaged to involve the intermediate formation of 4-chlorophenyl-*N*-quinone monoimine. It must be stressed, however, that the proposed pathways are hypothetical.

Conclusions

The study of the photochemistry of 4-chloroaniline in aqueous solutions and in some organic solvents (aliphatic alcohols, acetonitrile, *n*-hexane) has confirmed the previously postulated mechanism,[6] whereby the initial photolytic step in polar solvents consists of heterolytic dehalogenation. In this respect, the photochemistry of 4-ClA is analogous to that of the previously studied 4-halogenophenols.[7−12] As we have shown in this work, this analogy also holds for the species that can be detected by transient absorption spectroscopy, and to many aspects of the photolytically triggered reaction mechanism. In particular, the first species that can be detected on a nanosecond time scale has been assigned to a carbene, 4-iminocyclohexa-2,5-dienylidene. The absorption spectrum and kinetic behavior of this previously unknown species have been studied, and found to be comparable in most respects to those of its parent originating from 4-halophenols, 4-oxocyclohexa-2,5-dienylidene. The reaction behavior of 4-iminocyclohexa-2,5-dienylidene is consistent with the assumption that it has a triplet ground state: it adds O_2 and bromide with nearly diffusion-controlled rates, and abstracts an hydrogen atom from aliphatic alcohols. These reactions have been fully corroborated by the results of an analytical study of the photoproducts.

The studied transients and products did reveal, however, a number of features that distinguish the photochemistry of 4-chloroaniline from that of 4-chlorophenol. Some of these can be traced to the fact that, contrary to the oxo group, the imino group can be protonated. This entails a significant difference between these two systems inasmuch as the carbocation that is first produced by dehalogenation from neutral 4-ClA is tautomeric with the protonated carbene, while in the case of 4-chlorophenol formation of the carbene requires deprotonation of the carbocation. For this reason, photolysis of 4-chlorophenol yielded transients that were detectable on the nanosecond time scale in polar protic solvents only, but not in acetonitrile, whereas in the case of 4-ClA these transients could be observed in all polar solvents studied. In a nonpolar environment, both systems yielded only a triplet−triplet absorption but no major transients corresponding to photochemical reactions.

A further interesting result was obtained in the study of 4-chloro-*N*,*N*-dimethylaniline, the photochemistry of which was found to proceed by a mechanism that is largely analogous to that of 4-ClA, whereas 4-chlorophenol and 4-chloroanisole in this respect are different from each other. Again, this may be explained by the ability of the imino nitrogen to accommodate a positive charge. Finally, new aspects of the reaction mechanism were discovered in the product analysis of oxygenated solutions and traced to a specific reaction of the iminoquinone oxide, which results from addition of O_2 to the carbene, with 4-chloroaniline.

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