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The Mechanism of the Photodissociation of 1-(Chloromethyl)naphthalene in Solution**

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Abstract: The title compound (**1**) dissociates homolytically from its lowest triplet excited state as well as from its first and second singlet excited states, in competition with internal conversion. The large resonance stabilization energy of the naphthylmethyl radical is an important factor in the energy balance.

The photoinduced homolytic dissociation of the C–X bond in halogen-substituted aromatic molecules (X = Cl, Br, I, but not F) is a well-known reaction of practical importance[1]. The energy balance and the detailed mechanism of the dissociation of chloro-arenes are however still rather mysterious in many cases; the aryl–X bond dissociation energy of 94.5 kcal/mol is higher than the excited state energies of the lowest singlet and triplet states of naphthalene-type molecules for instance, and for this (and other) reasons reaction originating from upper excited state has been postulated[2].

The photoinduced dissociation of chloromethyl-naphthalenes is much more efficient than that of chloronaphthalenes in spite of the presence of an «insulating» methylene group between the aromatic π-system and the C–Cl bond. The bond dissociation energy can be expected to be close to that of aliphatic chloro-compounds, of around 81 kcal/mol for CH_3–CH_2Cl; still too high for a naphthalene-like lowest triplet state (52 kcal/mol) or even singlet state (≈ 75 kcal/mol). Again, reaction through upper excited states such as triplet σ-σ^* has been suggested.

The photophysics of haloaromatics is complicated by the heavy atom effect which is known to enhance triplet yields and to reduce the fluorescence yields and lifetimes. In this respect the chloromethyl-naphthalenes are remarkable in having excitation wavelength dependent fluorescence quantum yields: irradiation in the second absorption band ($S_0 \rightarrow S_2$) gives a much lower fluorescence yield than excitation in the $S_0 \rightarrow S_1$ band, and this has been explained in terms of enhanced intersystem crossing from S_2 to a dissociative upper triplet state of σ-σ^* type[2].

A number of difficulties arise with the mechanisms suggested so far. In the first place, chloronaphthalenes do not show such excitation wavelength dependence of the fluorescence yield, although the heavy atom effect should be even greater owing to the proximity of the Cl atom and the aromatic ring. In the second place, it is established that in molecules in which the halogen atom is separated from the aromatic system by more than one methylene group dissociation is inefficient: in the molecules of the type Cl-Ph-O-$(CH_2)_2$-Br the stronger Cl–Ph bond breaks in preference to the much weaker aliphatic C–Br bond (≈ 68 kcal/mol)[3]. This observation throws doubt on the involvement of upper σ-σ^* triplet states, since intramolecular energy transfer in such small molecules is very fast (as shown for instance in the case of a benzophenone linked to a naphthalene through a short aliphatic chain)[4]. Since energy transfer to a dissociative C–Br σ-σ^* state does not take place in competition with the rate of Cl–Ph homolytic dissociation, it appears that the dissociation process involves directly the aromatic π-π* states.

We report here the results of a detailed study of the photophysics and photochemistry of 1-(chloromethyl)naphthalene (**1**); it is concluded that molecules of this type (Ar-CH_2X) are in a class of their own, distinct from either Ar-X or Ar-$(CH_2)_nX$ species ($n > 1$) because of the aromatic free radical stabilization energy.

1. Photochemistry of 1-(chloromethyl)naphthalene

The photochemical reaction of **1** is readily followed in aerated dilute solutions through the change in the absorption spectrum. This shows good isosbestic points from which it can be concluded that the overall reaction mechanism remains unchanged throughout the irradiation (Fig. 1).

Separation of the components of the irradiated solution (in *n*-heptane solvent, aerated) by thin layer chromatography shows that the major product is 1-naphthaldehyde, formed in nearly quantitative yield from **1**, although some other very minor products are present as well (Fig. 2).

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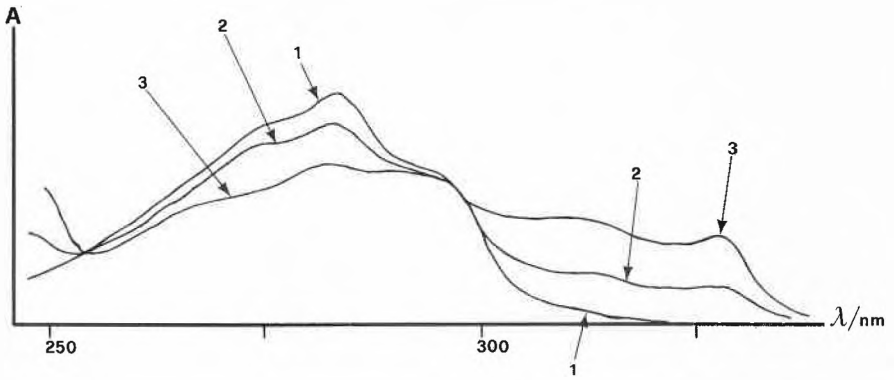


Fig. 1. Changes in the absorption spectrum of an aerated solution of 1-(chloromethyl)-naphthalene in the course of irradiation.

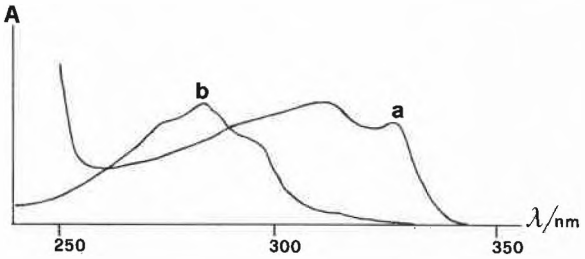


Fig. 2. Absorption spectra of the major (a) and minor (b) photoproducts following irradiation of an aerated solution of 1-(chloromethyl)naphthalene.

The quantum yield of disappearance of **1** has been measured at several wavelengths corresponding to the lines of the mercury arc; the light intensities being determined by means of an actinometer solution of anthraquinone in ethanol (degassed). The differences are probably not significant within the limits of error associated with such measurements, and it is noteworthy that the reactivity is at least as great at the longest irradiation wavelength as at the shorter ones (Table 1).

The reaction sequence can be described as the primary homolytic dissociation of **1** to produce a chlorine atom and a (1-naphthyl)methyl radical which reacts with molecular oxygen (around 10^{-3} M) to form the naphthaldehyde (Scheme 1).

If the solution is degassed the change in the absorption spectrum is different and much slower; there is no increase in absorption in the 300–330 nm region due to naphthaldehyde, but a naphthalene-like fluorescence develops in the course of irradiation. This can be explained by the formation of the naphthylmethyl dimer which must have an absorption spectrum very similar to that of **1** and a fluorescence efficiency similar to that of naphthalene itself (0.23).

Table 1. Quantum yields of disappearance of aerated solution of 1-(chloromethyl)naphthalene in *n*-heptane at various wavelengths.

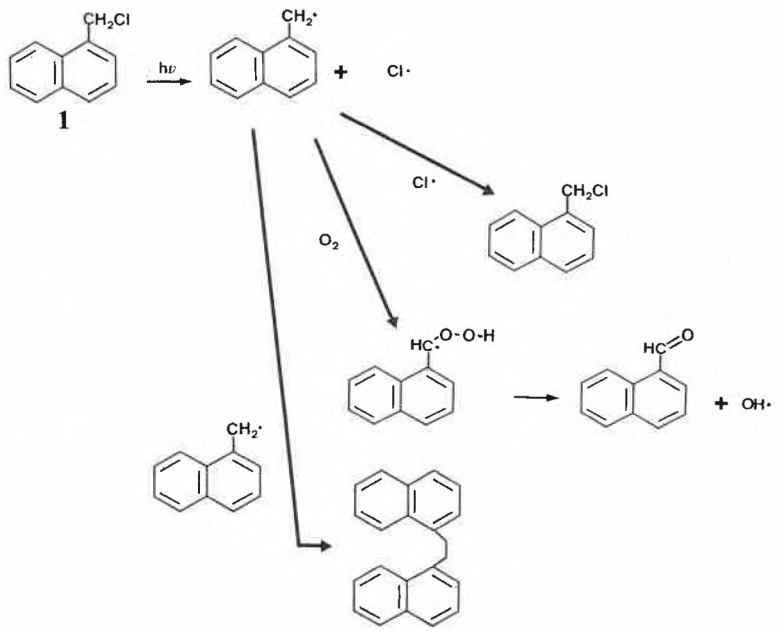
Wavelength [nm]	Photon flux [s^{-1}]	Quantum yield
313	1.1×10^{14}	0.72
296	3.7×10^{13}	0.48
265	9.0×10^{12}	0.61

The recombination of the naphthylmethyl radical with a Cl atom to reform the starting material may also reduce the observed quantum yield. It is clear that molecular oxygen acts as a radical scavenger which prevents such radical recombination processes, although it would not affect geminate recombinations in the solvent cage prior to separation and diffusion of the radicals.

The homolytic dissociation of **1** can be sensitized by benzophenone ($E_T = 69$ kcal/mol) in aerated benzene solution; a relatively high concentration of **1** must be used to minimize the quenching effect of molecular oxygen on benzophenone triplets, as well as to ensure that energy transfer to **1** is at least ten times faster than the unimolecular (or pseudo-unimolecular) decay of triplet benzophenone in benzene. This decay time is of 5 μs from flash photolysis measurements, so that concentrations of **1** in excess of 10^{-3}M were used, with irradiation at 365 nm were **1** does not absorb. The quantum yield of disappearance of **1** is found to be close to unity.

Quenching of the photoinduced dissociation of **1** has been observed with very high concentrations of *cis*-piperylene ($E_T = 57$ kcal/mol). The reaction quantum yield is approximately halved with a 2 M concentration of quencher, and it can be concluded that around 50% of the reaction must originate from quenchable triplet states. Although this is most likely to be the lowest state T_1 the participation of upper triplets cannot be excluded since with such high quencher concentrations static quenching becomes a definite possibility.

Scheme 1



2. Photophysics of 1-(chloromethyl)naphthalene

The absorption spectrum of **1** is very similar to that of 1-methylnaphthalene, with the $S_0 \rightarrow S_1$ (^1L_b) transition near 320 nm and the $S_0 \rightarrow S_2$ (^1L_a) transition near 300 nm. The first transition is very weak, being symmetry-forbidden in naphthalene itself, and the natural radiative lifetime of S_1 is of the order of 100 ns. The fluorescence emission $S_1 \rightarrow S_0$ is very weak and for this reason difficult to record accurately against the background of Raman

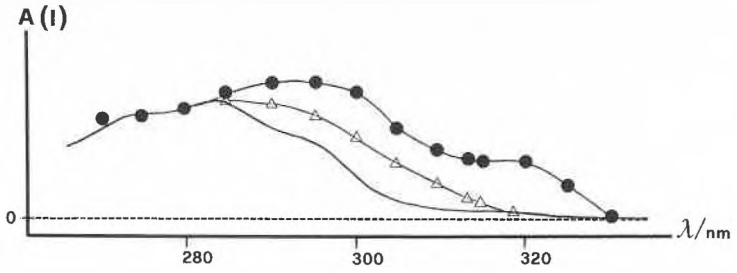


Fig. 3 Comparison of the absorption spectrum of 1-(chloromethyl)naphthalene (–) with its corrected fluorescence excitation spectrum (●) and corrected low-temperature phosphorescence excitation spectrum (△).

scattering and solvent fluorescence blank, but it is similar to that of 1-methylnaphthalene. With excitation at 265 nm in S_2 the fluorescence intensity is very much lower, the observed emission quantum yields being 1.3×10^{-2} for excitation at 313 nm and $\approx 10^{-3}$ for excitation at 265 nm. This confirms the previously reported finding that the corrected fluorescence excitation spectrum of **1** does not correspond to its absorption spectrum[2] (Fig. 3).

The phosphorescence spectrum of **1** recorded in ethanol glass at 77 K is similar to that of 1-methylnaphthalene with the 0-0 transition at 484 nm; the phosphorescence quantum yield is much higher than that of naphthalene, being 0.14 for excitation at 313 nm (measured with respect to an internal standard of benzophenone for which a phosphorescence quantum yield of 0.71 is assumed).

The corrected phosphorescence excitation spectrum of **1** follows fairly closely the absorption spectrum, unlike the room temperature fluorescence excitation spectrum; the phosphorescence quantum yields are similar for excitation at 313 and 265 nm (that is, in S_1 and S_2), although there is evidence for some enhancement of quantum yield for excitation near 300 nm.

The contrast between the fluorescence properties of naphthalene, chloronaphthalenes, and chloromethyl-naphthalenes is striking: the absorption spectra are very similar and fluorescence always originates from the lowest excited singlet state, S_1, but the fluorescence quantum yields and lifetimes vary by several orders of magnitude[2]:

naphthalene	95 ns
1-chloronaphthalene	2.4
2-chloronaphthalene	3.3
1-(chloromethyl)naphthalene	0.5

In addition, there is a remarkable difference in the fluorescence excitation spectra between naphthalene and chloronaphthalenes on the one hand, and chloromethyl-naphthalenes on the other hand: the former follow «*Vavilov*'s rule», that is the fluorescence quantum yield is independent of excitation wavelength; whereas the latter hardly fluoresce at all when excitation promotes the molecule to the second excited state, S_2, while fluorescence is observed with quantum yields of the order of 10^{-2} for excitation in the first absorption band (an order of magnitude higher than for $S_0 \rightarrow S_2$ excitation).

Some of these effects may be ascribed to the heavy atom effect which increases the rate of all intersystem crossings, but this is probably not a sufficient explanation for the differences between chloronaphthalenes and chloromethyl-naphthalenes which share the same heavy atom Cl. It must also be stressed that Cl is at the borderline of the definition of a «heavy» atom in photophysics, and it is difficult to understand why it should enhance intersystem crossing from the second singlet state S_2 to some dissociative triplet state in chloromethyl-naphthalenes but not in chloronaphthalenes in which the heavy atom is closer to the aromatic system.

The most likely explanation for the photophysical and photochemical properties of chloromethyl-naphthalenes is that all its excited states are to some extent dissociative, even the lowest triplet state. This results from the particularly favourable energetics of the homolytic dissociation in these molecules, owing to the stabilization energy of the naphthylmethyl radical compared to the naphthyl radical.

This resonance stabilization energy E_{res} is estimated to be around 15 kcal/mol for naphthylmethyl-type radicals[5], and taking this into account it can be concluded that homolytic dissociation is energetically allowed in the excited singlet states and only very slightly unfavorable in the lowest triplet state:

$$S_1: E(\text{C-Cl}) - E^*(S_1) - E_{res} = 80 - 91 - 15 = -34 \text{ kcal/mol}$$

$$T_1: E(\text{C-Cl}) - E^*(T_1) - E_{res} = 80 - 61 - 15 = +4 \text{ kcal/mol}$$

The low fluorescence quantum yield for excitation into the S_1 state is therefore ascribed to ultra-fast homolytic dissociation in that state, rather than to enhanced intersystem crossing. The fate of the chlorine atom and the free radical depends however on the multiplicity of the dissociative state: in the case of singlet state reactions the geminate recombination of these species may provide an energy-wasting process without observable overall photochemistry, whereas such geminate recombination is improbable when the radicals are formed in a triplet state. Although it has not been possible to measure the actual rate constant of dissociation in the S_2 excited state, this must be of the order 10^{13} s^{-1} since it competes efficiently with internal conversion.

The low fluorescence quantum yield of around 10^{-2} for excitation into S_1 compared to the fluorescence quantum yield of naphthalene is therefore attributed essentially to dissociation from this state, and to a lesser extent to the enhancement of intersystem crossing through the heavy atom effect. Fig. 4 summarizes our interpretation of these results, considering only the three relevant excited states S_1, S_2, and T_1.

These states are all π-π* states similar to those of naphthalene, and there is no need to introduce hypothetical σ-σ*

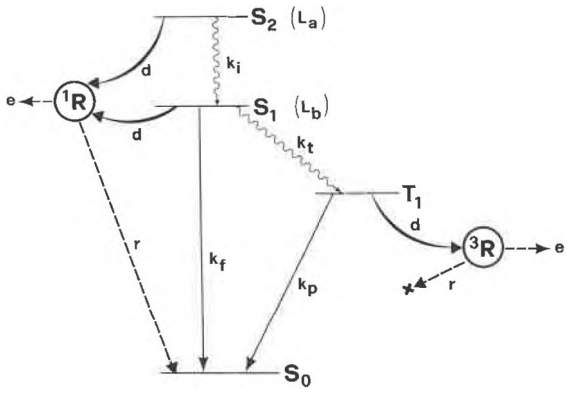


Fig. 4. Energy level diagram and deactivation pathways of 1-(chloromethyl)naphthalene. d: Homolytic dissociation $RCl \rightarrow R^{\odot} + Cl^{\odot}$; e: escape of these radicals from the solvent cage; r: geminate recombination of these radicals; ^1R: geminate radical pair formed in a singlet state; ^3R: geminate radical pair formed in a triplet state.

states for which there is no spectroscopic evidence in the wavelength region concerned in this work.

Excitation at long wavelength (into S_1) results in approximately 50% homolytic dissociation and 50% intersystem crossing, the fluorescence quantum yield of 1% being neglected. All the triplets dissociate and the radicals separate from the cage and react (e.g. with oxygen), but the majority ($\approx$ 35%) of the singlets form radicals which recombine prior to separation to reform the starting material.

Excitation at short wavelength (into S_2) results in very efficient dissociation (90%) in competition with internal conversion to S_1. The triplet yield is therefore low (some 5%) and the geminate recombination of the radicals formed through S_2 reduces the observed overall reaction quantum yield.

The fact that the phosphorescence quantum yield observed in a low temperature rigid matrix is the same for excitation into S_1 and S_2 seems to imply a temperature dependence of the dissociation rate constant, but this has not been investigated in this work. It is unlikely that the dissociation process itself could be suppressed simply by the rigidity of the matrix, since many examples are known of solid state dissociations[6]. The geminate recombination would undoubtedly become very important, but this would then provide an energy-wasting path and would be expected to decrease greatly the phosphorescence quantum yield when excitation promotes the molecule to the S_2 state.

Conclusions:

The photophysical and photochemical properties of 1-(chloromethyl)-naphthalene are quite distinct from those of chloronaphthalene on the one hand and of naphthalenes substituted with a chlorine atom on more remote aliphatic groups on the other hand. When the halogen atom is part of the first saturated group linked to an aromatic system, the stabilization energy of the free radical formed by homolytic dissociation is exceptionally large, whereas it is much smaller for the radicals derived from ArX and $Ar(CH_2)_nX$ ($n > 1$) molecules (Ar = aryl).

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Noch vor nicht allzu langer Zeit wurde viel in die Entwicklung analytischer Methoden investiert, um Giftstoffe zu erkennen und nachzuweisen. Im Zentrum der industriellen Interessen standen Substanzen wie Chlor, Blausäure und Phosgen, die als Ausgangsstoffe wichtiger Synthesen und oft auch in grossen Mengen gebraucht wurden. Die dazu notwendige Überwachung war für den Analytiker bereits recht anspruchsvoll. Noch schwieriger ist die heutige Situation, wo es darauf ankommt, carcinogene, mutagene und teratogene Stoffe zu überwachen. Dabei werden Anforderungen bezüglich der Nachweisgrenzen gestellt, die an die Grenzen des Technologiestands der Alltagsanalytik stossen.

Auch zogen die arbeitsmedizinischen Massnahmen die Aufmerksamkeit der Behörden auf sich. Diese bemühten sich, ein Verfügungsrecht in der Kontrolle der Schadstoffe zu erlangen und Richtlinien festzulegen. So entstanden in den USA die *Occupational Safety and Health Administration* (OSHA), ein Zweig des «Department of Labor», und das *National Institute of Occupational Safety and Health* (NIOSH), die solche arbeitshygienischen Aufgaben wahrnahmen. In Amerika wurde der Begriff «Threshold Limit Value-Time Weighted Average» (TLV-TWA) geschaffen. In der Schweiz und in der Bundesrepublik Deutschland wurden in Analogie dazu die sogenannten *MAK-Werte* eingeführt. Damit bezeichnet man die höchstzulässige Schadstoff-Konzentration (maximale Arbeitsplatz-Konzentration), die bei einer Arbeitszeit von 8 bis 9 Stunden täglich und bis zu 45 Stunden pro Woche von der stark überwiegenden Mehrzahl der Gesunden, am Arbeitsplatz Beschäftigten, ohne gesundheitliche Gefährdung ertragen werden kann. Als Schadstoffe bezeichnet man giftige Gase, Dämpfe oder Schwebstoffe (Stäube).

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