147. Photodissociation of Halonaphthalenes in Solution: Comparative Photochemistry of 1-Iodo-, 1-Bromo-, and 1-Chloronaphthalenes

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Fluorescence measurements have been used to follow the build-up of photoproducts during the direct and benzophenone-sensitized irradiation of the title compounds 1-IN, 1-BrN, and 1-ClN (HN = naphthalene). Compounds 1-IN and 1-BrN react by homolytic dissociation through their lowest triplet and singlet excited states, respectively. Compound 1-ClN does *not* undergo C–Cl bond fission, except through electron transfer in the presence of an amine A,

$$^1(\text{1-ClN})^* + \text{A} \rightarrow (\text{1-ClN})^{\cdot-} + \text{A}^{\cdot+}, \text{ then } (\text{1-ClN})^{\cdot-} \rightarrow \text{N}^{\cdot} + \text{Cl}^-$$

In the absence of this electron transfer, 1-ClN reacts only through substitution and oxidation processes.

Introduction. – One of the major reaction pathways in the photochemistry of halogen-substituted organic molecules RX is the homolytic dissociation of a C–X bond to form a free radical $R^{\cdot}$ and a halogen atom $X^{\cdot}$, $RX \xrightarrow{h\nu} R^{\cdot} + X^{\cdot}$ [1]. F-Substituted molecules are exceptional in this respect because of the very high C–F bond dissociation energy (DE), but, even in the naphthalene series, the homolytic dissociation of C–Cl has been reported for chloronaphthalenes [2] as well as for bromo- and iodonaphthalenes. This is at first sight surprising in view of the dissociation energy of the aromatic C–Cl bond (94.5 kcal/mol) [3] relative to that of the first excited singlet state of 1-Cl-naphthalene (1-ClN, 89 kcal/mol), and we set out to investigate, in detail, the mechanism of this reaction. Whereas most investigations of the photoreactivity of halonaphthalenes (XN) have relied on the chromatographic separation of the photoproducts, we have used spectroscopic detection of UV absorption and, specifically, fluorescence spectra for the continuous monitoring of the build-up of photoproducts during the course of irradiation. From these experiments, it is concluded that the homolytic dissociation of C–Cl does not in fact take place in 1-ClN and that the photochemical reactivity involves only substitution and oxidation processes. Compound 1-BrN dissociates homolytically with low quantum yields only from its singlet excited state, the triplet state being unreactive in sensitization experiments.

Experimental. – *Apparatus.* Irradiations were performed on 3-ml samples in 10 × 10 mm fluorescence cells which could be transferred directly to a *Perkin-Elmer Lambda 3* UV/VIS absorption spectrophotometer or to the fluorimeter. The irradiation light from a 100-W DC high pressure Hg arc was selected through a grating monochromator. Light fluxes were measured by the anthraquinone/EtOH actinometer [4].

The sample cells were fitted with high-vacuum greaseless stopcocks and reservoirs to allow degassing by means of several cycles of the freeze-pump-thaw-shake procedure.

Fluorescence measurements were made on a conventional instrument using high-aperture grating monochromators (*Applied Photophysics f/3,4*) and a 200-W Hg/Xe arc lamp. Fluorescence quantum yields were determined by the comparison of integrated, corrected emission spectra against a *Rhodamine-B* standard.

Chemicals and Solvents. All solvents were UV-grade from *Fluka*, used as received. Compounds 1-IN, 1-BrN, and 1-ClN were purchased from *Aldrich Chemicals*; the latter was purified by fractional distillation. Benzophenone (*Fluka*) was purified by recrystallization. 1,1'-Binaphthyl (*Kodak*) was used as received. Triethylamine (*Fluka, puriss.*) was dried with P_2O_5 and purified by fractional distillation.

Results. – 1. *Photophysics of Halonaphthalenes: Detection of Photoproducts by Absorption and Fluorescence Spectrophotometry.* The halogens F, Cl, Br, and I are 'weak' substituents from the point of view of their effect on the absorption and emission spectra of aromatic molecules: they produce small red-shifts in the order of their π-electron donor character, F < Cl < Br < I. On the other hand, they have an important influence on the fluorescence efficiency of such molecules because of the internal heavy-atom effect which enhances the rate of intersystem crossing to the triplet excited state shown in *Fig. 1*.

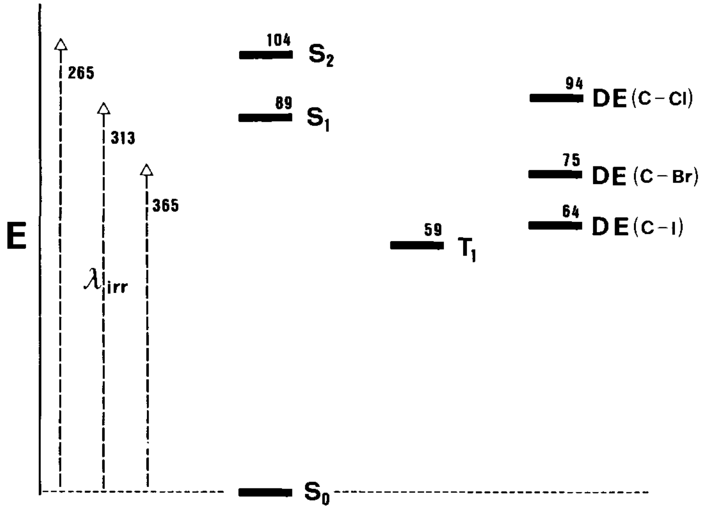

Fig. 1. *Incident wavelengths, energy levels of 1-halonaphthalenes and C–X bond dissociation energies* (DE). Values in kcal/mol.

Table. *Photophysical Data of Halonaphthalenes*

Molecule	τ_f [ns]	Φ_f	τ_p(s)[c]
NH	96.0	0.23	2.3
1-ClN	2.4	0.005[b]	0.29
2-ClN	4.2	0.01[b]	
1-BrN	0.075[a]	0.001	0.018
2-BrN	0.15[a]		
1-IN	–	–	0.002
BN	3.0	0.77	

[a] From [8]; other fluorescence data from [6].

[b] Calculated from τ_f.

[c] From [8].

Thus, 1-IN is non-fluorescent, while the fluorescence lifetimes of the other molecules in this series are increasingly longer with the lighter X-atoms. The fluorescence quantum yields increase in the same order, and the quenching action of molecular oxygen becomes increasingly important (*Table*) [5].

These properties of fluorescence efficiencies provide a convenient and accurate analytical method to follow the photochemical reaction. When naphthalene (HN) is formed from a halonaphthalene (XN), it is readily detected by its intense fluorescence in deoxygenated solutions. Likewise 1,1′-binaphthyl (BN) can be detected by its red-shifted, structureless, intense and short-lived fluorescence [6], quite distinct from that of the naphthalene derivatives (*Fig. 2*). The reaction quantum yields can be measured by comparison of the fluorescence spectra of the irradiated sample at various times with standard solutions made up of the reactant XN, HN, and BN to a constant total concentration.

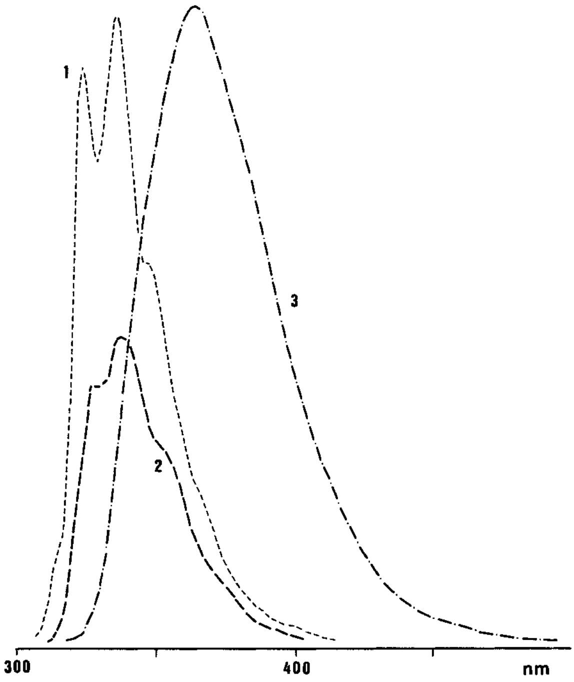

Fig. 2. *Fluorescence spectra of HN* (1), *1-ClN* (2), *and 1,1′-BN* (3) *in heptane*

2. *Photochemical Reactivity of 1-IN.* A solution of 1-IN (10^{-4} M) in heptane shows no detectable fluorescence; after irradiation with light of 365 nm an intense, structured fluorescence develops as shown in *Fig. 3*. This is clearly the emission of HN, as can be ascertained by its lifetime (95 ns) and the strong quenching action of O_2. The quantum yield of formation of HN is > 0.7, probably close to unity within the accuracy of such measurements. A significant observation is the *absence* of any new fluorescence which could be attributed to BN, but on further thought this is not really surprising, the primary photochemical process being the homolytic dissociation of 1-IN to iodine atom and naphthyl radical. The formation of naphthalene then implies a reaction of this radical

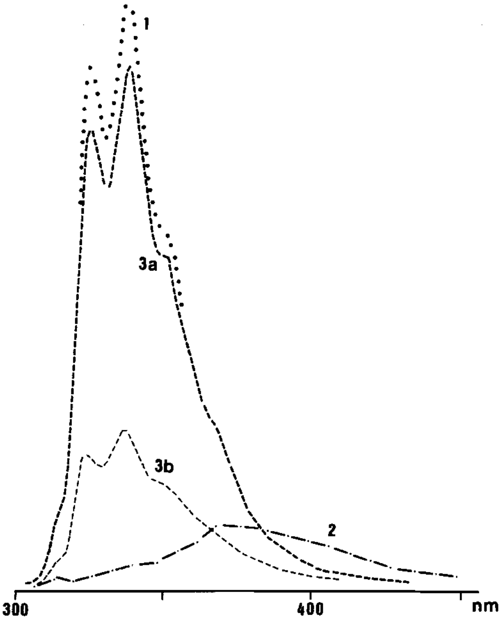

Fig. 3. *Fluorescence spectra of a sample of 1-IN in heptane (degassed) at various stages of irradiation. 1)* Fluorescence of HN standard, *2)* 1-IN before irradiation, *3a)* 1-IN after 5 h irradiation, *3b)* same sample after saturation with air.

with the solvent ZH, $N^{\cdot} + ZH \rightarrow NH + Z^{\cdot}$. In conditions of steady-state irradiation, the concentration of naphthyl radicals will then stay extremely small because of the efficient H-abstraction reaction from the solvent. The dimerization process of these radicals to form BN depends on the square of their steady-state concentration and is, therefore, insignificant.

Sensitization by Benzophenone in MeCN. When a solution of 1-IN (10^{-4}M) in MeCN with 10^{-3}M benzophenone added as a triplet sensitizer is irradiated with 365-nm light, the formation of HN is shown by the rise of its characteristic fluorescence. Benzophenone is unreactive in this solvent, and its triplet lifetime is relatively long (~ 5 µs). The triplet state T_1 of 1-IN is then formed through energy transfer, and it dissociates with unit quantum yield.

3. *Photochemical Reactivity of 1-BrN.* Irradiation of 1-BrN in different solvents yields HN. In degassed heptane, the structured fluorescence of HN develops, there being no emission attributable to BN. At the same time, the absorption spectrum shows small changes which are consistent with the overall reaction $\text{1-BrN} \xrightarrow[\text{solv.}]{h\nu} \text{NH}$, with a quantum yield of 0.03. The same reaction is observed in aerated solution, there being no detectable quenching action of O_2. In an O_2 saturated solution, the same reaction takes place, but the apparent rise in the HN fluorescence is much smaller because of the quenching action of O_2 on this long-lived fluorescence.

Sensitization by Benzophenone in MeCN. When 1-BrN (10^{-4}M) in MeCN irradiated at 365 nm in the presence of benzophenone (10^{-3} M), there is no reaction of 1-BrN. Clearly, the triplet state T_1 is of insufficient energy to allow the homolytic fission of the aromatic C–Br bond.

4. *Photochemical Reactivity of 1-ClN.* When a degassed solution of 1-Cln (10^{-4} M) in heptane is irradiated with light of 265 nm, the weak fluorescence increases very slightly but reaches apparently a stationary state as shown in *Fig. 4*. In an aerated solution in heptane the fluorescence actually *decreases* in the region of HN fluorescence but increases slightly at longer wavelengths (*Fig. 5*). The changes in both absorption and fluorescence spectra point to the formation of oxidation products.

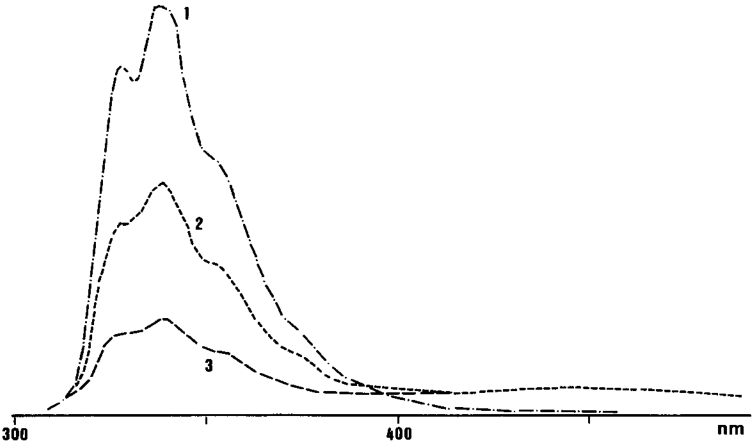

Fig. 5. *Fluorescence spectra of a sample of 1-ClN in air-saturated heptane at various stages of irradiation.* 1) Before irradiation, 2–3) up to 139 h of irradiation with 313-nm light.

Fig. 4. *Fluorescence spectra of a sample of 1-ClN in degassed heptane at various stages of irradiation. 1)* Fluorescence of HN standard, *2)* 1-ClN before irradiation, *3)* 1-ClN after 61 h of irradiation with 313 nm light.

The identity of these products was not established in the present work. 1-Naphthol can be ruled out on grounds of the absence of its typical fluorescence in the photoproducts. The spectral changes are consistent with the presence of naphthoquinones, but the weak long-wavelength fluorescence points to the presence of other oxidation products. The reaction quantum yields is however very low, 8×10^{-4} at $[O_2]$ 10^{-3}M. In O_2-saturated heptane, the spectral changes are similar, but the quantum yield is higher ($4 + 10^{-3}$). The primary photochemical process is, therefore, a bimolecular reaction of (1-ClN)* with O_2.

In degassed i-PrOH solution, the gradual development of a HN-like fluorescence is observed, with a reaction quantum yield of 10^{-3}. The photoproduct is, however, *not* HN, as shown by the effect of O_2 on its fluorescence intensity: when the irradiated solution is saturated with air, the intensity decreases be a factor of 3, and when it is saturated with

O_2, it decreases further by a factor of 2.5. This quenching effect is much smaller than that observed with HN, the long-lived fluorescence (100 ns) of which decreases in intensity by a factor of 20 from a degassed to an aerated solution. Likely photoproducts are alkoxynaphthalenes (*e.g.* 1-methoxynaphthalene has a fluorescence lifetime of 12 ns in degassed solution).

In degassed Et_2O, the reaction takes a similar course as in i-PrOH.

Effect of Oxygen. In an air-saturated i-PrOH solution, the fluorescence spectrum changes in the course of irradiation, with a stronger emission at longer wavelengths (380–480 nm), as shown in *Fig. 6*. On further irradiation, this new fluorescence decreases, the primary photo-oxidation products being themselves photoreactive.

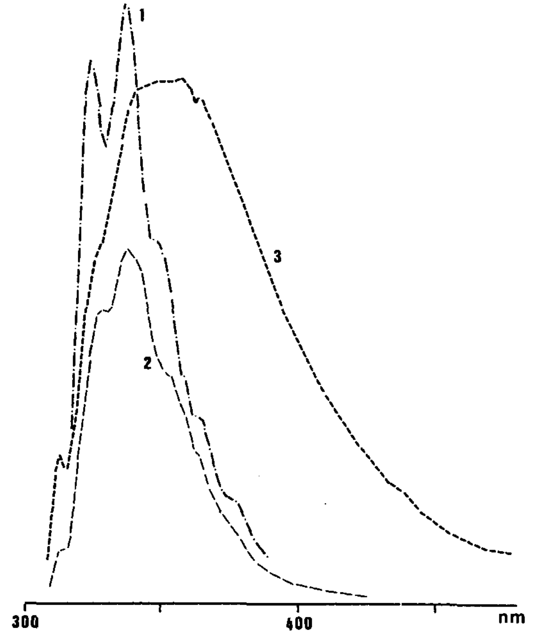

Fig. 6. *Fluorescence spectra of a sample of 1-ClN in air-saturated i-PrOH at various stages of irradiation. 1)* HN standard (at reduced amplification), *2)* 1-ClN before irradiation, *3)* 1-ClN after 64 h irradiation.

Reactivity in i-PrOH/Heptane. In a mixture of 1% i-PrOH in heptane (degassed), the spectral changes are similar to those observed in neat heptane, and there is no build-up of substitution products (*e.g.* alkoxynaphthalenes). This shows that the reaction is bimolecular in neat i-PrOH, and in that in the dilute mixture the lifetime of the S^1 excited state of 1-ClN is too short.

The absence of any HN-like fluorescence shows that homolytic dissociation of 1-ClN does not take place under the conditions of investigation. It is indeed clear from the photochemistry of 1-IN and 1-BrN that, if the naphthyl radical is formed, it reacts with the solvent to yield HN; the absence of fluorescence of HN implies the absence of naphthyl radicals, and this implies the absence of homolytic C—Cl dissociation.

Dissociation through Electron Transfer. In the presence of 0.1M Et_3N in degassed heptane solution, the fluorescence of 1-ClN appears structureless and greatly red-shifted

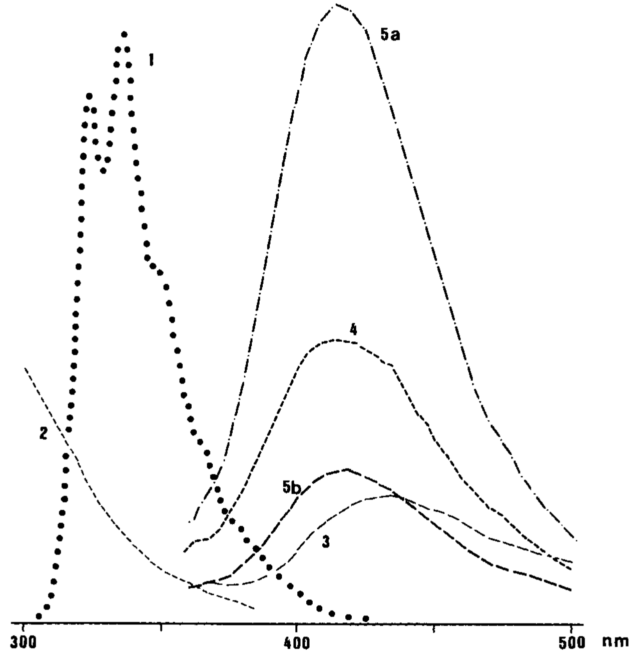

Fig. 7. *Fluorescence spectra of a sample of 1-ClN/TEA in degassed heptane solution.* *1*) Fluorescence of HN standard, *2*) fluorescence of TEA alone, *3*) 1-ClN with TEA, before irradiation, *4*) 1-ClN at TEA, after 24 h irradiation with 313-nm light, *5a*) HN standard with TEA, *5b*) sample *5a* after saturation with air.

(*Fig. 7*). This can be ascribed to an exciplex emission, characteristic of the interaction

$$^{1}(\text{1-ClN})^{*} + \text{Et}_3\text{N} + {}^{1}(\text{1-ClN}\cdot\text{Et}_3\text{N})^{*}$$

$$h\nu \swarrow \text{e.t.}$$

$$\text{1-ClN} + \text{Et}_3\text{N} \leftarrow (\text{1ClN}\cdot\text{Et}_3\text{N}) \mid (\text{1-ClN}\cdot\text{Et}_3\text{N}^{+}) \rightarrow \text{N}^{\cdot} \times \text{Cl}^{-} + \text{Et}_3\text{N}^{+}$$

Electron transfer within the exciplex produces the radical anion of 1-ClN which dissociates to Cl^- and naphthyl radical $\text{N}^{\cdot}$, this reaction providing a non-radiative decay path which competes with emission. The radical $\text{N}^{\cdot}$ reacts with the solvent (heptane) to form HN through H-atom abstraction, and then a new exciplex with a shifted emission spectrum is formed between HN and Et_3N.

Discussion. – Compound 1-IN undergoes photochemical homolytic dissociation with near unit quantum yield in solutions at room temperature, to form I-atoms and naphthyl radicals. These radicals react very rapidly with H-donor solvents to form HN and a solvent radical: $\text{N}^{\cdot} + \text{ZH} \rightarrow \text{NH} + \text{Z}^{\cdot}$.

The nature of the reactive species of 1-IN deserves attention. 1-IN is non-fluorescent in fluid solutions at room temperature, so it might be concluded that the triplet yield comes close to unity because of the heavy-atom effect. Dissociation would then take place from the lowest triplet excited state.

An entirely different explanation for these experimental observations can be suggested on the basis of an 'instantaneous' homolytic dissociation of 1-IN from the first excited singlet state S_1. If this dissociation were fast enough to compete with both fluorescence and intersystem crossing, then quenching of the fluorescence of 1-IN could be ascribed to the high dissociation rate constant of its S_1 state rather than to the enhancement of intersystem crossing to T_1. It is difficult to make a clear-cut distinction between the heavy-atom effect and the lowering of the C–X bond energy, as both follows a common trend I > Br > Cl > F. Indeed, the very low fluorescence efficiency of 1-(chloromethyl)naphthalene is clearly related to the deactivation of S_1 and even higher exited singlet states through ultra-fast homolytic dissociation, rather than to a heavy-atom effect [7]. In any case, sensitization of the dissociation of 1-IN by benzophenone clearly proves that its triplet state is intrinsically reactive, so it is to be expected that the higher energy singled excited state S_1 should in principle also lead to C–I bond dissociation.

The efficiency of the dissociation of 1-BrN is much lower, and sensitization by benzophenone fails altogether. It can be concluded that the triplet state T_1 is unreactive in view of its low energy relative to the aromatic C–Br bond energy, and that dissociation can arise only from the singlet excited state S_1. The low reaction quantum yield results from the competition of crossing over to T_1, the rate of which is greatly enhanced by the heavy-atom effect.

Turning finally to 1-ClN, the absence of HN as a photoproduct shows that homolytic dissociation *does not take place* from either S_1 or T_1. This finding is in contradiction with previous reports concerning the photoreactivity of this compound [2], but is in keeping with the relative energies of the excited states of 1-ClN and the aromatic C–Cl bond energy (*cf. Fig. 1*). Yet 1-ClN does react photochemically, albeit with low quantum yields, but the nature of the photoproducts depends on the solvent and on the presence of O_2. It was beyond the scope of this work to attempt a detailed analysis of these photoproducts under various conditions of irradiation, but it is most likely that a substitution reaction with the solvent and/or oxidation processes take place.

The Nature of the Photoreactive State. According to the absorption and luminescence spectra, the excited states of XN molecules are essentially naphthalene-like π-π^* states. The halogens are indeed weak σ-e^- acceptor and π-e^- donor substituents which have very little effect on the energy of low-lying electronic states of aromatic molecules, in contrast to their important heavy-atom effect. The results reported in this work are consistent with a homolytic dissociation in 1-IN and 1-BrN taking place from the T_1 (π-π^*) and S_1 (π-π^*) excited states, respectively.

If these states are in fact dissociative with respect to the C–X bond, the reaction can be considered as the result of crossing from the π-π^* state to some dissociative state (formally a σ-σ^* or n-σ^* state localized on CX) [8]. Further investigations will be necessary to clarify the shapes of the potential curves and the mechanism of the crossing.

Conclusions. – The photo-induced dissociation of 1-IN and 1-BrN takes place from their π-π^* excited states, T_1 for 1-IN and S_1 for 1-BrN. The final photoproduct is naphthalene, formed through H-atom abstraction by the naphthyl radical from the solvent. This process is so much faster than radical dimerization that BN is not formed as a major product.

Compound 1-ClN does not react through homolytic Ar–Cl bond fission, and this unreactivity is understandable on energetic grounds alone. Like 1-FN, 1-ClN reacts only through solvent substitution and/or oxidation processes, except in the presence of strong electron donors such as amines with which it forms the radical anion. This then dissociates with loss of Cl^-.

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