

EXCITATION ENERGY TRANSFER: PHOTOLYSIS OF SOLID STATE CLATHRATES

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Summary

Studies were made of the photochemical behaviour of crystalline clathrates formed by the complex $\text{Ni(II)(4-picoline)}_4(\text{NCS})_2$ as the "host" and by 1-bromonaphthalene (or 2-bromonaphthalene) as the "guest". The various possible photoreactions were considered in order to explain the experimental results and, in particular, to explain the large difference in dehalogenation rates for the two clathrates.

Possible mechanisms for the transfer of electronic energy from the excited host to the guest molecules are discussed and are correlated with the crystal structures of the two clathrates; a long range dipole-dipole resonance interaction mechanism, which depends on the different orientations and spatial distributions of the host and the guest components, gives a better representation of the photolytic processes observed than does a simple isotropic excitonic diffusion mechanism.

1. Introduction

The mechanism of energy transfer in organic molecules, as well as in transition metal complexes, has been extensively investigated [1, 2]. However, relatively few studies have been made on the clathrates under UV or gamma photon irradiation. The energy transfer processes in this class of solid state compounds are of interest because it is possible to choose host and guest components which possess different singlet and triplet excited states and different relative spatial distributions, thus giving "flexible" models of energy transfer. The purpose of this work is to describe the photolysis of two clathrates formed by the complex $\text{Ni(II)(4-picoline)}_4(\text{NCS})_2$, which acts as the "host", and 1-bromonaphthalene or 2-bromonaphthalene, which act as the "guests". The electronic excitation energy transfer which occurs under UV irradiation between the excited host (donor) and the unexcited guest (acceptor) was studied. These two halonaphthalenes (which

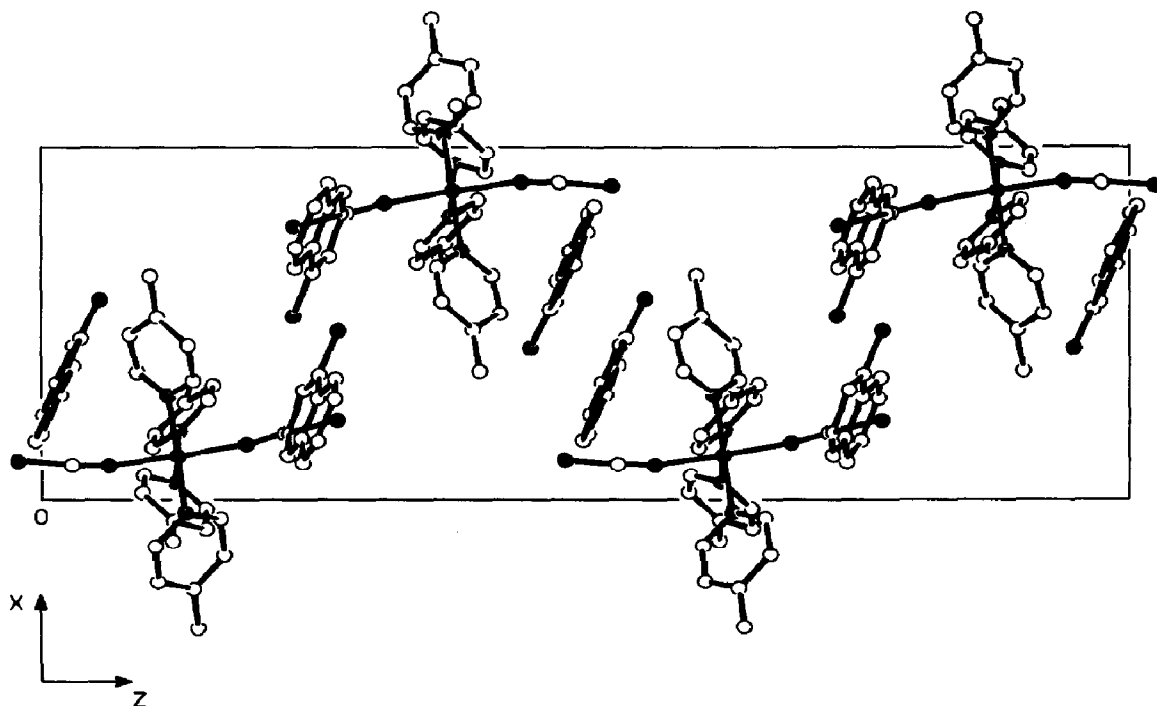


Fig. 1. The crystal structure of the 1-bromonaphthalene and $\text{Ni(II)(4-picoline)}_4(\text{NCS})_2$ clathrate.

have very similar energetic properties, luminescence lifetimes, carbon-halogen bond strengths etc.) were chosen as acceptors to emphasize the roles of the relative spatial orientation of the donor and the acceptor and the crystal structure in determining the energy transfer processes which occur during the photolysis of these clathrates.

We have previously [3] reported results for the gamma radiolysis of the two clathrates, and we have studied the influence of the same factors. It should be noted that the crystal structures of the 1-bromonaphthalene and 2-bromonaphthalene clathrates are quite different, which means that the relative spatial orientations of the host and guest components are different, as shown in Table 1 and Figs. 1 - 4. In Figs. 3 and 4 a host and a guest molecule for each clathrate are plotted on non-crystallographic axes, in two positions rotated by 90° about the x' axis, in order to show their spatial distributions. In Table 2 some significant distances and parameters for the host and guest molecules are listed.

2. Experimental

2.1. Materials

The methods of preparation of the $\text{Ni(II)(4-picoline)}_4(\text{NCS})_2$ complex and both clathrates have been described previously [4]. Pure spectroscopic

TABLE 1

Structural parameters of the clathrates and the nickel complex

System	Space group	Molecules per unit cell			Lattice parameters					
		Host	Guest	Guest	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
Ni(II)(4-picoline) ₄ (NCS) ₂	Tetragonal, I4 ₁ /a	8	—	—	16.76	—	22.66	—	—	—
Ni(II) complex + 1-bromonaphthalene clathrate	Monoclinic, P2 ₁ /c	4	8	—	11.88	11.82	32.79	—	—	102.0
Ni(II) complex + 2-bromonaphthalene clathrate	Triclinic, P $\bar{1}$	1	1	—	11.30	9.54	11.76	115.9	81.7	109.6

TABLE 2

Distances and interactions in the clathrates

Clathrate	Nearest-neighbour interactions							
	Host-host		Host-guest ^a		Guest-guest ^b			
Host	R (Å)	X	R (Å)	X _L	X _S	R (Å)	X _L	X _S
Ni(II)(4-picoline) ₄ (NCS) ₂	6.05	0.044	4.29	0.04	0.31	7.64	5.16	4.67
Ni(II)(4-picoline) ₄ (NCS) ₂	5.06	0.084	4.05	0.59	2.20	5.80	0.81	1.48

^a X_L is a geometric parameter calculated for the transition dipole moment through the long axis of a bromonaphthalene molecule.^b X_S is a geometric parameter calculated for the transition dipole moment through the short axis of a bromonaphthalene molecule.

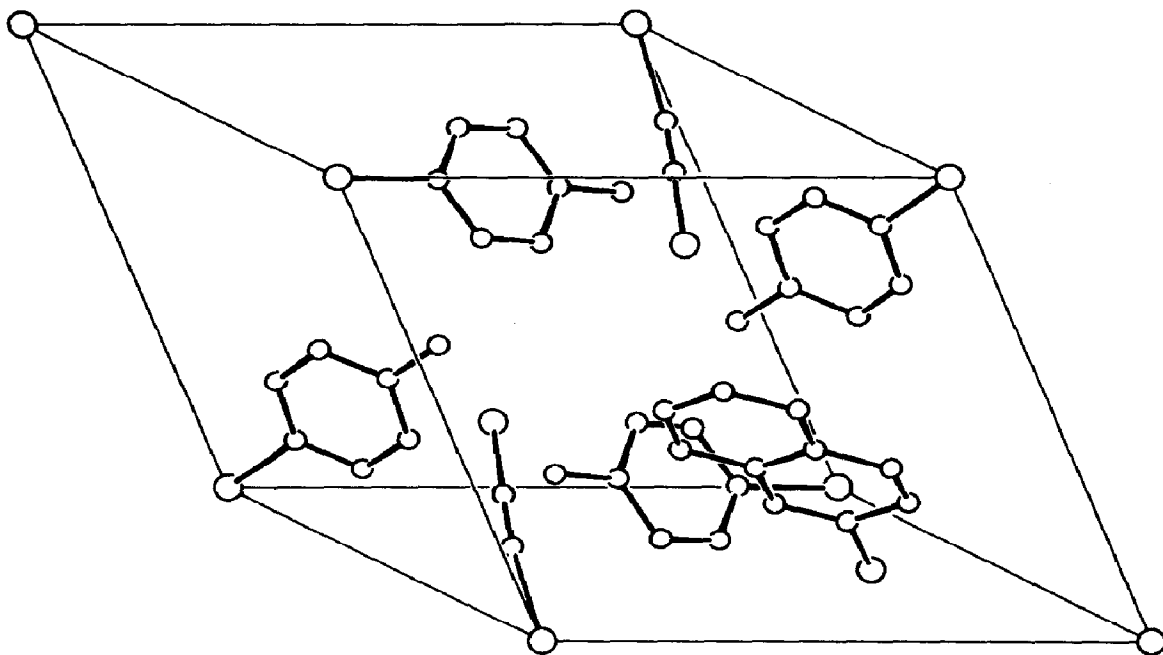


Fig. 2. The crystal structure of the 2-bromonaphthalene and $\text{Ni(II)(4-picoline)}_4(\text{NCS})_2$ clathrate.

grade 2-bromonaphthalene (solid) and 1-bromonaphthalene (liquid at room temperature) were supplied by C. Erba and Fluka A.G. respectively. The guest content, which was determined using gas chromatography, was 40 wt.% for the 1-bromonaphthalene clathrate and 0.3 wt.% for the 2-bromonaphthalene clathrate.

2.2. Irradiations

The photolysis was carried out using a PCQ-XI low pressure lamp (Ultraviolet Product, U.S.A.) formed by four irradiating loops. The incident light intensity, about 3.8×10^{14} quanta $\text{cm}^{-2} \text{s}^{-1}$, was measured with a ferrioxalate actinometer [5]. In order to avoid direct absorption by the bromonaphthalenes a filter was used to eliminate photons of energy lower than $38\,000 \text{ cm}^{-1}$. The clathrates were irradiated as thin layers of constant thickness of the powdered crystals held between two quartz plates. Some irradiations were carried out in a Dewar flask containing liquid nitrogen and equipped with an adequate quartz window. 1-Bromonaphthalene and 2-bromonaphthalene (0.1 M) were irradiated in pure spectroscopic grade cyclohexane solution in outgassed and sealed quartz tubes. All the experiments were performed under steady state irradiations. In order to calculate the quantum yield of naphthalene formed, the amount of energy transferred from the host molecule, directly excited by the photons impinging on the

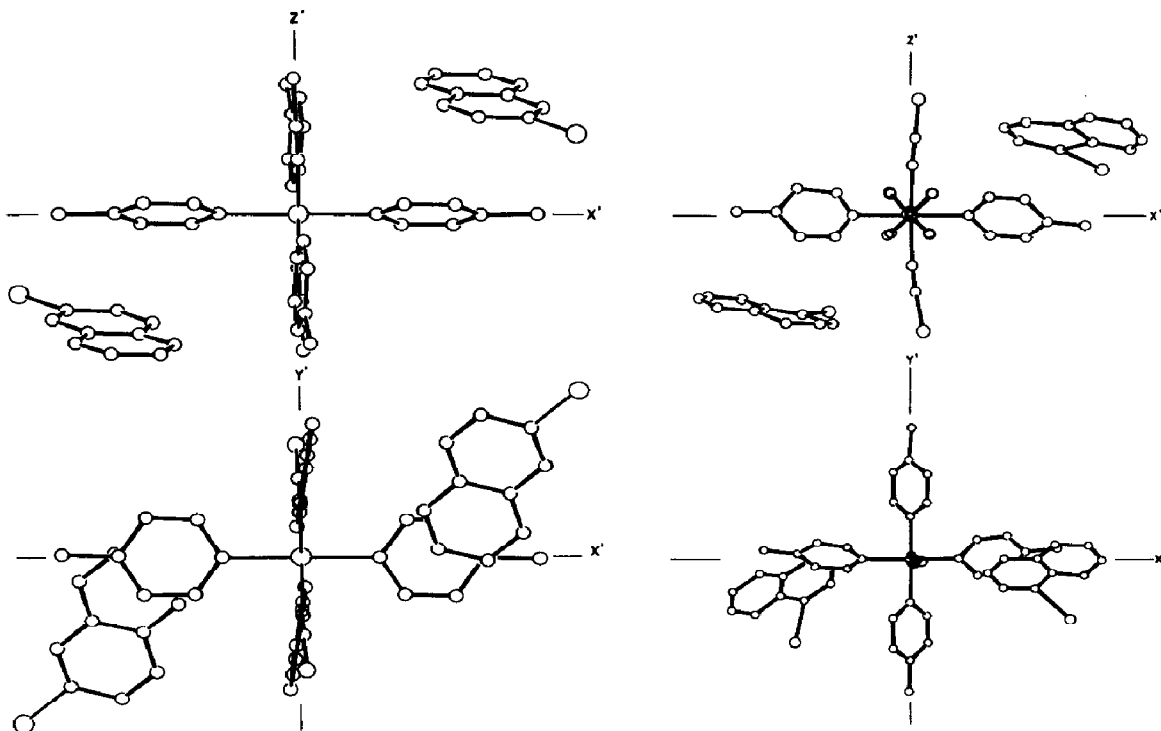


Fig. 3. The spatial orientations of the host (Ni(II) complex) and the guest (1-bromonaphthalene) molecules plotted on non-crystallographic axes.

Fig. 4. The spatial orientations of the host (Ni(II) complex) and the guest (2-bromonaphthalene) molecules plotted on non-crystallographic axes.

clathrate must be known. However, because of the uncertainty involved in computing this value, we report for the two clathrates the experimental percentages of naphthalene produced from the bromonaphthalenes [6]; these percentages at a dose of 1×10^{19} quanta cm^{-2} are reported in Table 3.

2.3. Analyses

The photolysis products were analysed using a Hewlett-Packard model 5700 gas-liquid chromatograph. A column 2 ft long was packed with E 301 as the stationary phase to detect naphthalene; a column 6 ft long and maintained at a higher temperature was packed with the same phase to detect higher halogenated compounds and binaphthyl.

3. Results

Naphthalene and traces of Br_2 and HBr were the only photolytic products observed for both clathrates; no higher halogenated naphthalenes

TABLE 3

Properties of the clathrates formed from 1-bromonaphthalene or 2-bromonaphthalene and Ni(II)(4-picoline)₄(NCS)₂

Compounds	E_S (cm ⁻¹)	E_T (cm ⁻¹)	D_{C-Br} (cm ⁻¹)	Guest band shift ($\gamma(C-H)$) $\Delta\bar{\nu}$ (cm ⁻¹)	Host band (Ni ²⁺) shift (${}^3A_{2g} \rightarrow {}^3T_{1g}$) $\Delta\bar{\nu}$ (cm ⁻¹)	Quantum yield ϕ	Quantity of naphthalene (%) at a dose of 1×10^{19} quanta cm ⁻²
4-Picoline	$\pi^* \leftarrow n$	$\approx 29\ 700$	—	—	—	—	—
	38 168						
	$\pi^* \leftarrow \pi$						
	39 216						
1-Bromonaphthalene	$\pi^* \leftarrow \pi$	$\sigma^* \leftarrow \pi$	24 800	—	—	0.12	2.55
	34 100 (S ₂)	$\approx 30\ 000$ (T _{dim})					
	$\pi^* \leftarrow \pi$	$\pi^* \leftarrow \pi$					
	31 300 (S ₁)	20 600 (T ₁)					
2-Bromonaphthalene	$\pi^* \leftarrow \pi$	$\sigma^* \leftarrow \pi$	24 500	—	—	0.15	1.93
	33 900 (S ₂)	$\approx 30\ 000$ (T _{dim})					
	$\pi^* \leftarrow \pi$	$\pi^* \leftarrow \pi$					
	31 100 (S ₁)	21 100 (T ₁)					
Clathrate with 1-bromonaphthalene	—	—	—	12	182	—	0.05
Clathrate with 2-bromonaphthalene	—	—	—	20	60	—	0.81

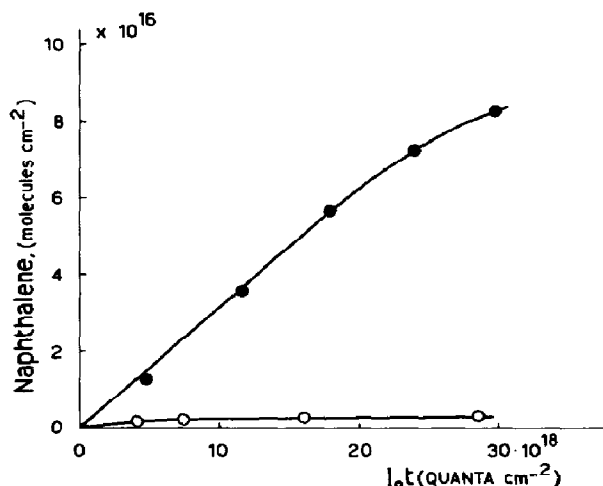


Fig. 5. The dehalogenation (naphthalene) yields *vs.* the absorbed dose I_0t : ○, 1-bromonaphthalene clathrate; ●, 2-bromonaphthalene clathrate.

or binaphthyl were detected. As shown in Fig. 5, the naphthalene yield for the 2-bromonaphthalene clathrate was always much larger than that for the 1-bromonaphthalene clathrate. For experiments carried out at 77 K the same very small yield (about 0.1% at the maximum dose of 3×10^{19} quanta cm^{-2}) of naphthalene was observed for both clathrates. The yield of naphthalene obtained from direct irradiation of 1-bromonaphthalene or 2-bromonaphthalene in cyclohexane was higher than that observed in the solid state clathrate. The percentages of naphthalene formed under the various conditions are reported in Table 3; the quantum yields of naphthalene formed from the bromonaphthalenes in solution are also shown.

4. Discussion

4.1. Ground state host-host and host-guest interactions

Host-host and host-guest interactions in the ground state have been described previously [4]. These interactions have been correlated with the crystal structures of the clathrates, with the site symmetries of the host and the guest components, and with the relative spatial orientations of the 4-picoline rings of the host complex and the aromatic rings of the guests. Some shifts which were observed in the vibrational and visible spectra of these clathrates are reported in Table 3.

4.2. Radiolysis of the clathrates

The radiolysis of the 1-bromonaphthalene and 2-bromonaphthalene clathrates has been reported previously [3]. Naphthalene and traces of Br_2 and HBr were the final radiolytic products. A possible mechanism of energy

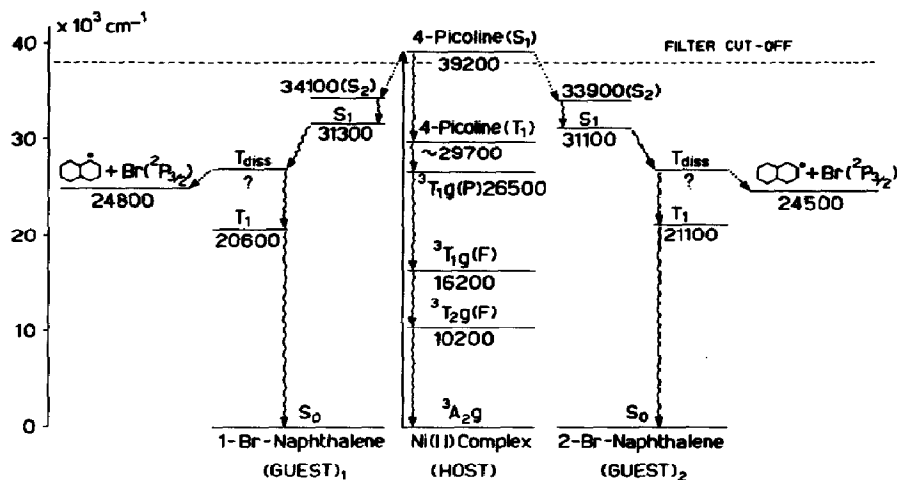


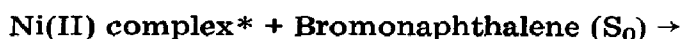
Fig. 6. A diagram of energy transfer from the host (Ni(II) complex) to guest₁ (1-bromonaphthalene) and to guest₂ (2-bromonaphthalene).

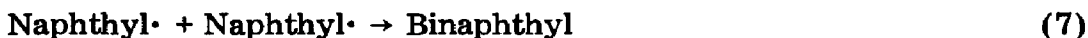
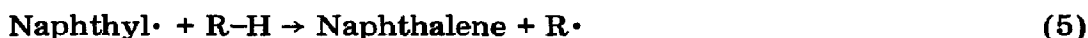
transfer from the Ni(II) complex to the halogenated guest molecules has been suggested; this mechanism takes into account the larger naphthalene yield obtained for the 2-bromonaphthalene clathrate compared with the yield observed in the irradiation of the 1-bromonaphthalene clathrate.

4.3. Photolysis of the clathrates

There have been many intensive investigations [7, 8] of the photolysis in solution of bromonaphthalenes. The major photolytic products observed are naphthalene, binaphthyl and traces of Br₂ and HBr. Higher halogenated products such as bromobinaphthyls or dibromonaphthalenes do not appear to be generated in detectable quantities. Because of the limited space available within the clathrates where the primary naphthyl and bromine radicals are formed, only some of these previously reported solution processes may take place. Also the formation of binaphthyl, dihalonaphthalenes and halobinaphthyls can be reasonably excluded and, in fact, these products have not been observed in either radiolytic or photolytic experiments.

Taking into account the energy levels of the excited host and the guest molecules, the following series of reactions can be used to rationalize the observed photolytic products. Reactions (7), (8) and (11) refer to processes that are highly improbable inside the clathrate cages [3].





Reactions (2) - (4) and the energy diagram of Fig. 6 show the involved excited states of the bromonaphthalene molecules. Dzvonik *et al.* [9] have suggested that the excited S_2 states formed initially are largely confined to the aromatic carbon atoms. These S_2 (π, π^*) delocalized states then decay to S_1 (π, π^*) states, and there is fast intersystem crossing (ISC) to the triplet manifold with the formation of dissociative and localized triplet states (π, σ^*). The population of the σ^* orbitals, localized on the C-Br bonds, generates triplet naphthyl and bromine radicals as shown in reaction (4). It should be noted that the S_1 singlet states are polarized through the long molecular axes and that the triplet dissociative T_{diss} states are assumed [10] to maintain this polarization. Consequently the excitation is polarized so that 2-bromonaphthalene C-Br dissociation is favoured over 1-bromonaphthalene C-Br dissociation. If the photophysical and photochemical processes reported previously [9] are valid for isolated bromonaphthalene molecules, they should also be valid when the bromonaphthalenes are guests inside a specific clathrate cage. The bromonaphthalenes interact with the neighbouring host components only by rather weak van der Waals forces [11], as shown by the vibrational shifts reported in Table 3.

When the triplet naphthyl and bromine radicals have been formed, the reactions of the bromine atoms must be studied in order to assess the ratio of dehalogenation (to form naphthalene) to recombination (to form the parent bromonaphthalene guest molecule). The bromine atoms may either diffuse up to the crystal surface, yielding Br_2 or HBr, or recombine according to reaction (6). Some irradiations were carried out at 77 K when there is almost no bromine diffusion; under these conditions the same small yield of naphthalene was observed for both clathrates, *i.e.* the recombination reaction (6) dominates over reaction (5) at 77 K to the same extent for both clathrates. It should be noted that, in solution where the physical state of

the pure compounds and their orientation play no role, 1-bromonaphthalene and 2-bromonaphthalene photolyses give approximately the same yield of naphthalene. Consequently, in order to explain the rather large yield difference in dehalogenation at room temperature for the two clathrates, the density and spatial distributions of the host and guest components should strongly influence the nature of the photolysis products. Using the crystallographic data given in Table 1, the number N_{g1} of 1-bromonaphthalene molecules per cubic centimetre of clathrate is 1.7×10^{21} and the number N_{g2} of 2-bromonaphthalene molecules per cubic centimetre of clathrate is 0.8×10^{21} , *i.e.* $N_{g2} < N_{g1}$. When the actual packing of the irradiated clathrates (see Section 2.2) is considered, the number of 2-bromonaphthalene molecules per unit volume of clathrate is even smaller, *i.e.* $N_{g2} \ll N_{g1}$.

Provided that the same steady state population of excited guest molecules is formed by the energy transfer reaction (1) for both clathrates, *i.e.* $N_{g1}^* \approx N_{g2}^*$, then it is reasonable to assume that, because of the poor packing in the 2-bromonaphthalene clathrate, the probability of reaction (6), *i.e.* recombination of the parent guest, should be significantly greater than the probability of reaction (5), *i.e.* dehalogenation of the guest, for the 1-bromonaphthalene clathrate. This was observed experimentally.

However, in order to fulfil the condition $N_{g1}^* \approx N_{g2}^*$ taking into account the fact that $N_{g2} \ll N_{g1}$, it is necessary to assume that the energy transfer rate from the host to the guest component is much larger for the 2-bromonaphthalene clathrate than for the 1-bromonaphthalene clathrate regardless of the mechanism of transfer. Two mechanisms can be invoked for a crystalline clathrate layer: a dipole-dipole resonance interaction and an isotropic excitonic diffusion transfer.

4.3.1. Dipole-dipole mechanism

It is known that long range coulombic dipole-dipole energy transfers with allowed diffusion of donor excitation depend on the relative spatial orientation of the donor-acceptor pairs. In this case [12] the rate of electronic energy transfer from an excited donor (which may be a host or a guest molecule) to an acceptor (host or guest molecule) is given by

$$k_{et} = k_{d-d} = \frac{1}{\tau_0} \frac{R_0^6}{R^6} = \frac{\chi^2 \alpha}{\tau_0 R^6} \quad (1)$$

where $\alpha = 8.8 \times 10^{-25} \eta_D n^{-4} J(\bar{\nu})$. η_D is the donor emission quantum yield, τ_0 is the luminescence lifetime of the donor, $J(\bar{\nu})$ is the Förster overlap integral, R is the donor-to-acceptor distance, R_0 is the critical Förster distance and χ is a dimensionless geometric parameter determined by the spatial reciprocal orientation of the donor and acceptor transition dipole moments (μ_D and μ_A respectively). The parameter χ is a function of the angle θ between the vectors μ_D and μ_A , of the angle θ_A between the vector μ_A and R and of the angle θ_D between μ_D and R , *i.e.*

$$\chi^2 = (\cos \theta - 3 \cos \theta_D \cos \theta_A)^2 \quad (2)$$

The rate constants k_{et1} and k_{et2} for energy transfer (where the subscripts 1 and 2 refer to the 1-bromonaphthalene and 2-bromonaphthalene clathrate respectively) are then given by

$$\frac{k_{et1}}{k_{et2}} = \frac{R_2^6 \chi_1^2}{R_1^6 \chi_2^2} \quad (3)$$

where the rate constants k_{et1} and k_{et2} refer to all possible host-host, host-guest and guest-guest interactions, and the other parameters of eqn. (1) are assumed to be almost the same in both clathrates. The distances R and the geometric parameters χ , calculated to a first approximation for the nearest-neighbour donor-acceptor pairs, are reported in Table 2. These values can be used to determine whether the excitation transfer occurs in a single step from the donor (host molecule) to the acceptor (guest molecule) or by means of a multistep transfer through many host-host interactions before being trapped by a guest molecule.

For the 1-bromonaphthalene clathrate the ratio q_1 of the rate constants for energy transfer is

$$\begin{aligned} q_1 &= \frac{k_{et}(\text{host} \rightarrow \text{host})_1}{k_{et}(\text{host} \rightarrow \text{guest})_1} \\ &= \frac{R^6(\text{host} \rightarrow \text{guest})_1 \chi^2(\text{host} \rightarrow \text{host})_1}{R^6(\text{host} \rightarrow \text{host})_1 \chi^2(\text{host} \rightarrow \text{guest})_1} \end{aligned}$$

and has an approximate value of 0.16.

For the 2-bromonaphthalene clathrate the ratio q_2 of the rate constants is

$$\begin{aligned} q_2 &= \frac{k_{et}(\text{host} \rightarrow \text{host})_2}{k_{et}(\text{host} \rightarrow \text{guest})_2} \\ &= \frac{R^6(\text{host} \rightarrow \text{guest})_2 \chi^2(\text{host} \rightarrow \text{host})_2}{R^6(\text{host} \rightarrow \text{host})_2 \chi^2(\text{host} \rightarrow \text{guest})_2} \end{aligned}$$

and has an approximate value of 0.005.

Consequently, for the 1-bromonaphthalene clathrate a q_1 value of 1/6 indicates a negligible amount of multistep transfer; for the 2-bromonaphthalene clathrate a q_2 value of 1/188 indicates that only single steps of excitation transfer occur from the host to the guest molecules.

Analogously, the rate of energy transfer from a host molecule to a 2-bromonaphthalene molecule is approximately 10 - 20 times faster than that from a host to a 1-bromonaphthalene molecule, depending on whether the halonaphthalenes are excited to their S_1 singlet or S_2 singlet states respectively. These calculations confirm the experimental results, *i.e.* the larger yield of naphthalene for the 2-bromonaphthalene clathrate.

4.3.2. Diffusion mechanism

From experimental values observed for the two clathrates it is possible to estimate some significant rate constants; in particular, the rate constant k_m for excitonic migration by host-to-host hopping can be estimated [13] from the non-inherent certainty principle:

$$k_m = \Delta\bar{\nu}/h \quad (4)$$

where $\Delta\bar{\nu}$ is the intermolecular interaction energy and h is the Planck constant. Taking the values given in Table 3 for a specific host absorption band shift $\Delta\bar{\nu}$, the rate constants $k_{m1} \approx 5.5 \times 10^{12} \text{ s}^{-1}$ and $k_{m2} \approx 1.8 \times 10^{12} \text{ s}^{-1}$ are obtained. These values are comparable with that for pure crystalline anthracene [14] (approximately $10^{12} - 10^{13} \text{ s}^{-1}$); this value is larger by about a factor of ten because anthracene has an "ordered" crystal structure whereas the clathrate lattice is "disordered".

It is also possible to estimate the migration coefficient of excitation D [15] from elementary diffusion theory:

$$k_m \approx 6D/R^2 \quad (5)$$

where R is the root mean square displacement of the excitation during the time $1/k_m$. Taking values for the mean intermolecular distances for the host-host pairs in the two clathrates from Table 2, migration coefficient values $D_1 \approx 3.9 \times 10^{-3}$ and $D_2 \approx 7.7 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ are obtained; in pure crystalline anthracene the singlet excitation migration coefficient has a value of $1.5 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ [2]. From these coefficients it is possible to deduce a rough estimate of the mean distance \bar{l} that excitation will travel through host molecules during the dissociation lifetime of a guest molecule:

$$\bar{l} = (6D\tau_{\text{diss}})^{1/2} \quad (6)$$

where τ_{diss} is the dissociation lifetime of an isolated bromonaphthalene molecule and has been estimated by Dzvonik *et al.* [9] to be about 10^{-10} s . The values obtained, $\bar{l}_1 \approx 153 \text{ \AA}$ and $\bar{l}_2 \approx 68 \text{ \AA}$, confirm the shorter mean distance (about five crystal unit cell distances) that excitation travels in the 2-bromonaphthalene clathrate during the dissociation lifetime of a guest.

However, if the trapping probability of the electronic excitation in the guests is dependent only on the diffusion of the singlet excitons in the host lattice and assuming an isotropic diffusion, then the trapping rate constant k_{trap} (in molecules per second) is given by [16, 17]

$$k_{\text{trap}} \approx 4\pi DR_0 N_g \quad (7)$$

where R_0 is the trapping radius of the guest molecule (comparable with the Förster critical distance) and N_g is the density of guest molecules. It can be seen from eqn. (7) that the trapping rate constant k_{trap} is linearly dependent

on the guest densities which are $N_{g1} = 1.7 \times 10^{21}$ molecules cm^{-3} for 1-bromonaphthalene and $N_{g2} = 0.8 \times 10^{21}$ molecules cm^{-3} for 2-bromonaphthalene. Then $k_{\text{trap}1}/k_{\text{trap}2}$ is approximately 10.7 and 1-bromonaphthalene guest dissociation should be favoured regardless of the orientation of the transition dipole moments μ_D and μ_A . The experimental results suggest a different mechanism — dipole-dipole long range energy transfer.

5. Conclusions

The aim of this work was to study the clathrates as models of energy transfer in the solid state. The following conclusions can be drawn from the results obtained for the photolysis of the clathrates.

(1) Taking into account the photon wavelengths compared with the unit cell dimensions, irradiation by UV photons results in the excitation of large clathrate "domains".

(2) This excitation is directly absorbed by the host (Ni(II) complex molecules) since the energy of the impinging photons is filtered to avoid any direct guest absorption.

(3) According to the energy diagram shown in Fig. 6, the excited host molecules can transfer the excitation intermolecularly to other host or guest molecules, and intramolecularly to energetically suitable levels of the central nickel ions.

It should be noted that intramolecular excitation energy transfer has been observed in many crystalline lanthanide chelates, where the major constituent of the lattice is organic [18], and the subsequent radiative deactivation of the lanthanide ions occurs with luminescence. Unfortunately, the Ni(II) complex we employed as host in the clathrates presents no radiative deactivation of the Ni^{2+} ions; however, the fraction of energy transferred intramolecularly will be the same in the two clathrates and will not affect the intermolecular energy transfer process.

(4) The intermolecular energy transfer occurs according to the diagram given in Fig. 6 where the energy levels of the various singlet and triplet states of the host and guest components are shown. The final dissociation of the excited guests occurs from the triplet manifold and the energetics involved rule out back transfer from the excited guest to the host molecules. The reactions which follow the formation of naphthyl and bromine radicals in the lattice sites of the clathrates are restricted to dehalogenation and recombination processes.

(5) In particular, dehalogenation and recombination processes for both clathrates seem to be strongly dependent on the relative actual densities of the two guest molecules; it has been shown that, in order to explain the experimental results, the energy transfer from the host to the guest molecules must be faster for the 2-bromonaphthalene clathrate. This suggests a long range dipole-dipole mechanism of energy transfer rather than an excitonic diffusion mechanism depending only on the distance between the

two species and the excitonic diffusion coefficients. Estimates of the rate constants for migration from the excited hosts to other host molecules and of the trapping rate constants are reported and show that a dipole-dipole single-step energy transfer is favoured over an excitonic host-guest diffusion mechanism.

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