Photophysical and Photochemical Properties of 2,3-Dihydro-4(1 H)-quinolinones. Part II. Rates and Mechanism of Primary Processes

Sn. Bakalova
Institute of Organic Chemistry with Centre of Photochemistry,
Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

L. Biczók and T. Bérces
Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1025 Budapest,
Pusztaszeri u. 59/67, Hungary

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Dihydroquinolinones, Triplet Yields, Fluorescence Quantum Yields, Photochemical Dehydrogenation, Singlet Lifetimes

Fluorescence quantum yields, singlet lifetimes and triplet yields for 2-methyl-2,3-dihydro-4(1 H)-quinolinone and N-methyl-2,3-dihydro-4(1 H)-quinolinone were determined as a function of temperature. In non-polar solvents, an efficient non-radiative process identified as an indirect singlet → triplet transition occurring through $S_2(n,\pi^*)$ was found to depopulate the lowest $S_1(\pi,\pi^*)$ state. In polar solvents, direct singlet → triplet intersystem crossing appears to dominate.

Photochemical dehydrogenation produced the corresponding 4(1 H)-quinolinone with a yield of few times 10^{-2}. This was shown to be the only traceable reaction route.

Introduction

In a previous paper [1] we have shown that the absorption and fluorescence properties of 2,3-dihydro-4(1 H)-quinolinones strongly depend on the substituent at the nitrogen atom of the ring as well as on the solvent polarity. These observations were explained by the effect of structure and solvent polarity on the location of the two lowest singlet excited states. In this paper we deal with the influence that the experimental conditions have on the rates of the photophysical processes of the 2,3-dihydroquinolinones. The photophysical and photochemical properties of 2-methyl-2,3-dihydro-4(1 H)-quinolinone (designated here as 2 MDQ and referred to as compound **2** in Part I) and N-methyl-2,3-dihydro-4(1 H)-quinolinone (designated here as NMDQ and referred to as compound **5** in Part I) will be studied in detail.

Results

Fluorescence yield and singlet lifetime

The room temperature fluorescence yields and lifetimes of the lowest excited singlet states for 2 MDQ and NMDQ in five different solvents are presented in Table I. The solvents are arranged in order of increasing polarity as indicated by the values of the $E_T(30)$ parameter given in the second column. In this sequence, the energies of the lowest singlet 0–0 transitions (obtained from the location of the intersection of the normalized absorption and fluorescence spectra and given under heading ν_{00}) decrease. The results show that both the fluorescence quantum yields and the singlet lifetimes increase considerably with increasing solvent polarity. One can also observe that these quantities are higher for NMDQ than for 2 MDQ.

Table I. Energies of the lowest singlet transition, room temperature fluorescence quantum yields and singlet lifetimes in different deaerated solvents.

Solvent	$E_T(30)$	ν_{00} [cm^{-1}]	Q_F	$^1\tau$ [ns]
		2 MDQ		
Methylcyclohexane	31.2	26600	0.003	<0.5
Toluene	33.9	25600	0.13	4.2
Ethylacetate	38.1	25100	0.24	9.1
Acetone	42.2	24700	0.39	13.5
Acetonitrile	46.0	24500	0.42	15.4
		MNDQ		
Methylcyclohexane	31.2	25800	0.03	0.7
Ethylacetate	38.1	24300	0.31	12.8
Acetone	42.2	23900	0.40	15.1
Acetonitrile	46.0	23800	0.55	19.6

Reprint requests to Dr. Tibor Bérces.

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In order to obtain more information on the photophysical processes, the fluorescence yields and singlet lifetimes were investigated as a function of temperature in various solvents. The plots of the lifetimes for 2MDQ and MNDQ are given in Fig. 1 and 2, respectively. The temperature dependences of the fluorescence yields were found to be very similar to those of the lifetimes and are therefore not shown here. The major features of the observed temperature dependences can be summarized as follows: (i) Starting from the limiting low temperature values, the fluorescence quantum yields and singlet lifetimes decrease considerably with increasing temperature; (ii) The extent of the temperature dependences decreases with increasing solvent polarity; (iii) The temperature dependences of Q_F and $^1\tau$ were smaller for NMDQ than for 2MDQ. The Arrhenius plots of the $(1/^1\tau - 1/^1\tau^o)$ and $(1/Q_F - 1/Q_F^o)$ differences (where the ^{o} superscript refers to the low-temperature limiting value) gave good straight lines as shown for example in Fig. 3. The Arrhenius parameters A'_{NR} and E'_{NR} derived from such plots, together with the room temperature rate constants for the temperature independent ($k^o{}_{NR}$), the temperature dependent (k'_{NR}) and the overall (k_{NR}) non-radiative processes and for fluorescence (k_F) are summarized in Table II.

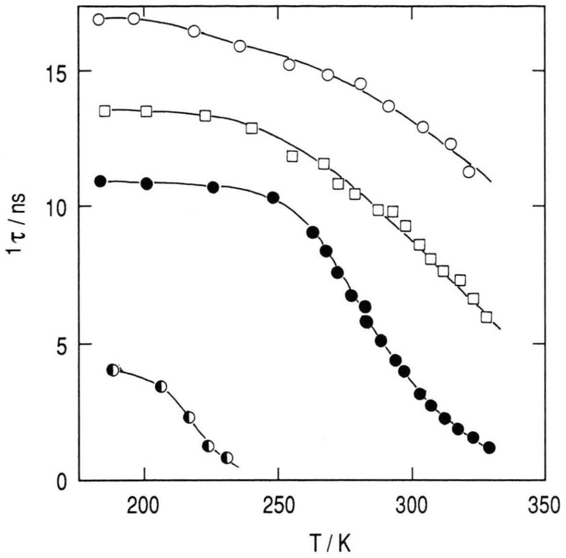


Fig. 1. Temperature dependence of the singlet lifetime of 2MDQ in deaerated acetone (○), ethylacetate (□), toluene (●) and methylcyclohexane (◐).

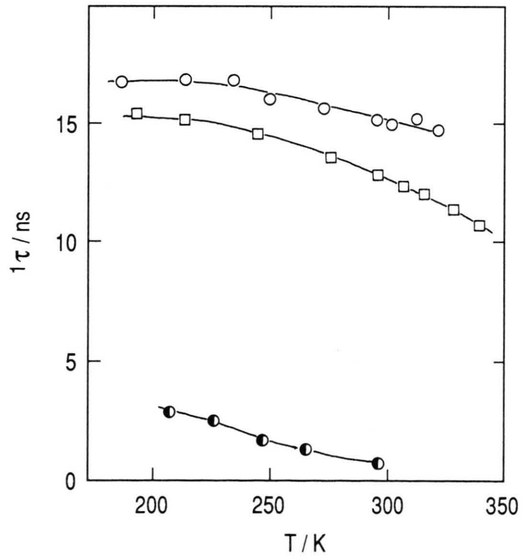


Fig. 2. Temperature dependence of the singlet lifetime of MNDQ in deaerated acetone (○), ethylacetate (□) and methylcyclohexane (◐).

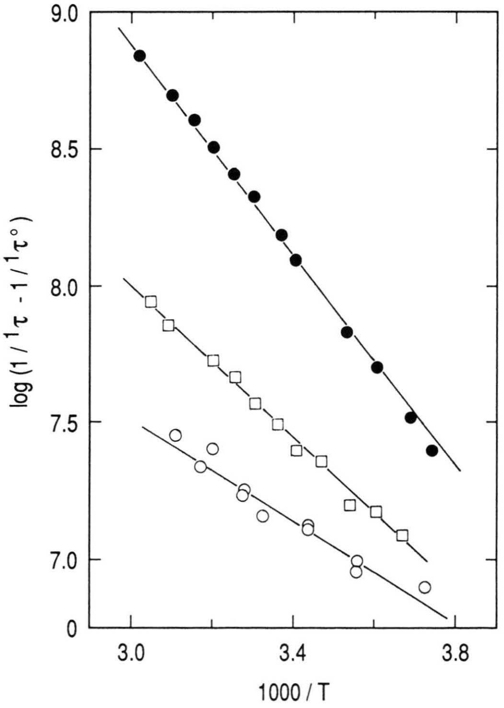


Fig. 3. Arrhenius plot for the rate coefficients of the temperature dependent non-radiative processes of 2MDQ in acetone (○), ethylacetate (□) and toluene (●).

Table II. Room temperature rate constants and Arrhenius parameters for photophysical processes in different solvents[a]. (The ° and ′ superscripts refer to the low temperature limiting values and the temperature dependent values, respectively.)

Solvent	$10^{-7} \times k_F$	$10^{-7} \times k_{NR}$	$10^{-7} \times k^{\circ}_{NR}$	$10^{-7} \times k'_{NR}$	$10^{-12} \times A'_{NR}$	E'_{NR}
			2MDQ			
Methylcyclohexane	≧0.6	≧200	20	≧177	[b]	[b]
Toluene	3.1	20.7	6.1	14.6	400	8.7
Ethylacetate	2.6	8.4	4.9	3.5	1.4	6.3
Acetone	2.9	4.5	3.0	1.5	0.02	4.3
Acetonitrile	2.7	3.8	2.9	0.9	[b]	[b]
			MNDQ			
Methylcyclohexane	4.2	139	27	112	3.5	4.6
Ethylacetate	2.4	5.4	4.2	1.2	0.005	3.6
Acetone	2.6	4.0	3.3	0.7	0.0003	2.2
Acetonitrile	2.8	2.3	[b]	[b]	[b]	[b]

[a] Units are s^{-1} (for rate constants) and kcal mol^{-1} (for activation energies).
[b] Reliable values could not be determined.

Triplet state formation

A number of attempts have been made to determine the quantum yield of triplet 2MDQ formation. Various triplet quenchers (biphenyl, naphthalene, 9,10-dibromo-anthracene) were used in laser excitation systems. Using the 351 nm light from a xenon fluoride laser for excitation, no absorption due to triplet biphenyl or naphthalene could be detected. The failure to observe energy transfer is probably explained by the fact that the triplet energies of biphenyl (65.7 kcal mol^{-1} [2]) and naphthalene (60.9 kcal mol^{-1} [2]) are close to or above the energy of triplet 2MDQ (62.5 kcal mol^{-1} [1]). In case of 9,10-dibromo-anthracene (where the triplet energy is about 42 kcal mol^{-1}), a different excitation wavelength (*i.e.* the 308 nm light from a xenon chloride laser) and high 2 MDQ concentrations had to be used. Very week triplet dibromo-anthracene absorption was observed. Probably efficient 2 MDQ self quenching occurred under the conditions of these experiments.

In further work, the sensitized biacetyl phosphorescence method elaborated by Sandros [3] was applied. The triplet energy of biacetyl is sufficiently low (56.3 kcal mol^{-1} [2]), and the method has been used successfully for the determination of the triplet yields of molecules with about 100 ns triplet lifetime [4]. Very week biacetyl phosphorescence and short triplet biacetyl lifetimes were measured. With the variation of 2MDQ concentration it could be shown that 2MDQ (like other amines) quenched the biacetyl triplet very efficiently with a rate close to the diffusion controlled limit.

Since determination of the quantum yield of triplet formation by energy transfer methods was not successful, an estimation of the relative values of triplet formation efficiences was attempted. In laser flash photolysis experiments, a transient was observed by its absorption around 500 nm which was identified as the triplet state (see more details below). We have determined relative values of the heights of the 530 nm transient absorption observed by laser flash excitation of 2 MDQ at different temperatures and in different solvents. Although the strong fluorescence (especially in polar solvents) and the photochemical degradation of the compound made accurate measurements difficult, it became clear that neither the temperature nor the solvent had a significant influence on the 2MDQ triplet absorption signal: In methylcyclohexane, variation of the temperature between 293 and 200 K had no effect that exceeded the error limits. Changing the solvent from methylcyclohexane through toluene and ethylacetate to acetone had little effect; maybe a slight decrease of the triplet yields with increasing solvent polarity occurred.

Laser flash photolysis study of transients

Transient studies were made in cyclohexane solvent in order to minimize the technical problems caused by the disturbance due to the fluorescence. In Fig. 4, transient absorption spectra are presented which were obtained with different delay times in the 351 nm (22 mJ/flash) laser flash photolysis of 4×10^{-5} mol dm^{-3} 2MDQ solutions. The spectra indicate the contribution of at least two transient species: one with a maximum at 430 nm which decayed on a relatively long time scale (*i.e.* about 30 μs half-life) and another or others with absorption maxima at 480 and 530 nm and shorter decay times (*i.e.* about 10 μs life-time). The decay of the "short-lived species" (monitored by its absorption at 530 nm) and the "long-lived transient" (monitored by its absorption at 430 nm) occurred according to strict first order and roughly second order kinetics, respectively. It is to be noted, however, that the decay times given above apply only to the described experimental conditions: the lifetime of the short-lived species may change as a result of self quenching, while the half-life of the long lived transient depends strongly on the experimental conditions, as expected for the second order radical + radical processes (see below).

Transient spectra were obtained also in the laser flash photolysis of NMDQ under similar conditions as for 2MDQ. The spectra are shown in Fig. 5. Here, however, the absorption maxima related to the short-lived species (520 and 550 nm maxima) and to the long-lived transient (490 nm maximum) were redshifted, and the life-time of the former as well as the half-life of the latter were longer by about a factor of 2 than in the case of 2MDQ.

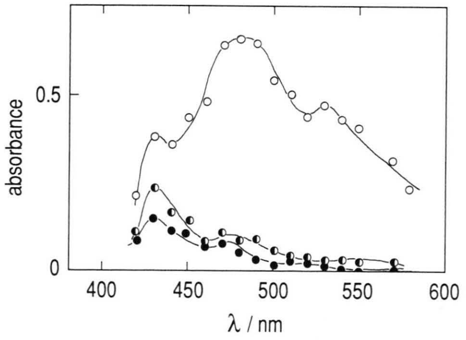


Fig. 4. Transient absorption spectra of 2MDQ photolysis in cyclohexane at 1 μs (○), 10 μs (◐) and 30 μs (●) delay, respectively.

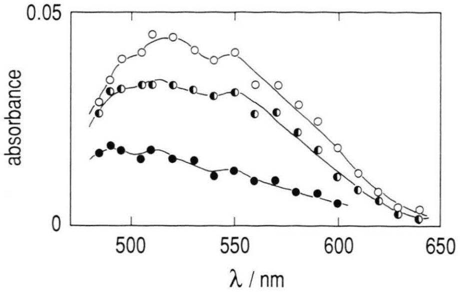


Fig. 5. Transient absorption spectra of NMDQ photolysis in cyclohexane at 5 μs (○), 10 μs (◐) and 30 μs (●) delay, respectively.

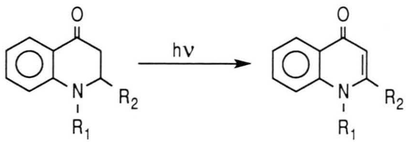
In order to identify the transients, laser flash photolysis of 2MDQ solution was carried out in the presence of small amounts of dissolved oxygen (O_2 concentration of $10^{-4}-10^{-5}$ mol dm^{-3}). Oxygen decreased the absorption (*i.e.* the concentration) of both species, however, the effect of O_2 on the life-times was different: while the life-time of the short-lived species was decreased by O_2, no effect on the decay of the other transient was obvious, at least on the time scale of our observations (*i.e.* a few times 10 μs). On this basis we identified the short-lived transient (with 480 and 530 nm absorption maxima and first order decay kinetics) as the triplet state of 2MDQ.

There is not enough information available on the other transient for an unambiguous identification of the species. The second order decay kinetics may be taken as evidence for the free radical character of the long-lived transient. In these systems, a probable source of free radical formation is the photoreduction reaction between triplet and ground state 2,3-dihydro-4(1H)-quinolinone molecules, thus the long lived transient can be tentatively identified as a carbon centered free radical with the unbonded electron in position 2 (*i.e.* in the α-position to the N-atom) and/or the appropriate ketyl radical. Although this identification appears to be the most probable one, it has to be admitted that neither kinetic nor spectroscopic observations exclude the possibility that the isomeric free radicals, for instance those with the unbonded electron in position 1 or 3 may contribute to the long-lived transient absorption.

Product formation

In Fig. 6, we present the absorption spectra of acetonitrile solutions of 2MDQ before steady-state UV irradiation with a 200 W high pressure mercury arc (Osram HBO) and at various irradiation times. The spectra clearly show that certain peaks of 2MDQ disappear (as for instance the one at 27000 cm^{-1}) as a result of irradiation, while new peaks appear which belong to the reaction products (see the structured peak with maxima at 30500, 31500 and 35000 cm^{-1}). Isobestic points can be recognized on the Figure which indicates either the formation of only one major product or if more reaction routes exist, their ratio remains unchanged. The same is true also in other solvents.

In Fig. 7 the spectra of NMDQ solution in acetonitrile are shown before and after irradiation which are in accordance with the 2MDQ results presented above. The third curve indicated in the Figure by dotted line is the spectrum of an authentic sample of N-methyl-4(1H)-quinolinone (NMQ). This perfectly agrees with the spectrum obtained with the photolyzed sample. Therefore, we can conclude that the reaction which occurs is photodehydrogenation:



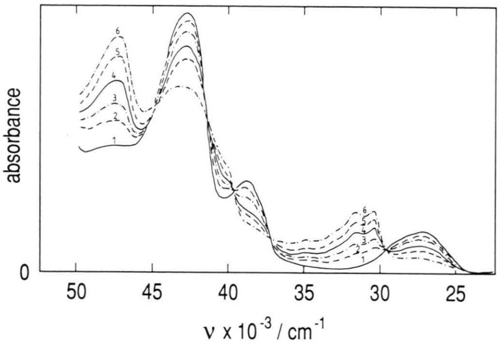


Fig. 6. Absorption spectra taken in the photolysis of 2MDQ in acetonitrile. Reaction time: 0 min (1), 15 min (2), 30 min (3), 45 min (4), 60 min (5), 120 min (6).

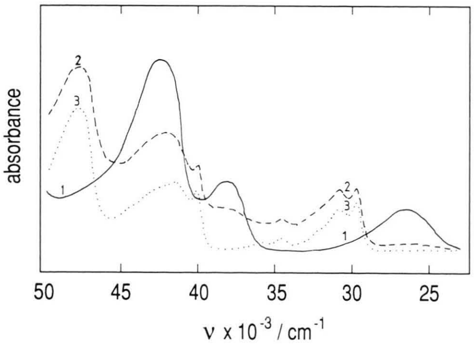


Fig. 7. Absorption spectra taken in the photolysis of NMDQ in acetonitrile before (1) and after (2) irradiation. Model compound NMQ (3).

The identification of the photochemical primary product has been carried out also by mass spectrometric analysis of a photolyzed sample ($\geqq 90\%$ conversion) of 2MDQ solution in acetonitrile. Only one major reaction product could be detected a 159 molecular weight compound corresponding to an overall formula of $C_{10}H_9NO$. This is in full agreement with the results of the spectroscopic study of product formation which showed NMQ to be the major photoproduct. Moreover, mass spectrometric analysis revealed the formation of a minor product (about 4–7% of the major one) with an overall formula of $C_{20}H_{20}N_2O_2$.

Finally, a further check of the identity of the photolysis product was made by HPLC analysis. The column was "Column Hibar" (250 × 4) with the stationary phase Lichrospher 100 RP-18, while the mobile phase was a 60:40 mixture of methanol-water used with 1 $\mathrm{cm}^3\,\mathrm{min}^{-1}$ flow rate. Comparison of the chromatogram of a photolyzed solution of NMDQ (2×10^{-4} mol dm^{-3} in acetonitrile) with that of NMQ clearly showed that photodehydrogenation occurred. Apart from the unreacted compound and the NMQ peak, only one more substance could be detected in the sample which was shown to be formed by photodestruction of the dehydrogenation product.

Photodehydrogenation was found to occur both in the presence and in the absence of air although oxygen decreased significantly the yield of product formation. Quantum yields of the photochemical reaction (Q_R) were determined for 2MDQ in deaerated solvents using the 366 nm filtered light of a high-pressure mercury arc. The results showed that the photodecomposition yields were low in all solvents, especially in the polar acetonitrile and the protic alcohol: Q_R (cyclohexane) = 0.057, Q_R (acetonitrile) = 0.024, Q_R (ethanol) = 0.012.

Discussion

Primary photophysical processes

The available fluorescence quantum yields and excited singlet lifetimes allow us to calculate the rate constants for fluorescence (k_F) and for the non-radiative processes (k_{NR}). Such data for room temperature are given in the second and third columns of Table II. They indicate that the fluorescence rate constants (k_F) are independent both of the solvent and of the substitution, while the rate constants of the non-radiative processes change with these parameters.

The k_{NR} rate constant is actually an overall quantity which consists of a temperature independent and a temperature dependent contribution. Using the limiting low-temperature lifetime, a temperature independent (k_{NR}^{o}) and a temperature dependent (k'_{NR}) non-radiative rate constant may be obtained and the appropriate Arrhenius parameters can be determined (see Table II). Both k_{NR}^{o} and k'_{NR} decrease considerably with increasing solvent polarity and at the same time a very significant change of the Arrhenius parameters can be also observed. The latter may be an indication of a change in the mechanism of the non-radiative processes.

The results presented in Table II show that in non-polar solvents very efficient deactivation processes set out from the lowest excited singlet state and these processes show strong temperature dependence. The deactivation processes, however, loose considerably in their importance with increasing solvent polarity. It would be essential to know something of the nature of the efficient non-radiative processes. We know that photochemical decomposition from the singlet excited state is insignificant (see below). Considering the practically temperature independent triplet yields and the efficient temperature dependent non-radiative singlet decay in methylcyclohexane, we assume that in non-polar and in weakly polar solvents the predominant deactivation of the $S_1(\pi,\pi^*)$ state is a thermally enhanced transition to $S_2(n,\pi^*)$ followed by a cross-over to a $T(\pi,\pi^*)$ triplet state. The assumption of such an indirect deactivation route is supported by the El-Sayed [5] and extended El-Sayed [6] rules and is in accordance with the high A-factors found in non-polar and weakly polar solvents. A similar relaxation mechanism has been suggested by Kasama *et al.* for excited acridine in water [7].

In polar solvents where the temperature dependent non-radiative processes are characterized by low A-factors and lower activation energies, probably the direct singlet → triplet transitions and fluorescence are dominating the depopulation of the lowest singlet state.

In Fig. 8, an energy diagram is given which may be taken as representative for that type of compounds as 2 MDQ in non-polar solvents. The location of the energy levels indicated has been given in accordance with the spectroscopic observations and discussion presented in Part I [1]. The lowest excited singlet state is identified as a $S_1(\pi,\pi^*)'$ state with energy of about 26600 cm^{-1} above ground level. The second singlet, a $S_2(n,\pi^*)$ state, is at 27100 cm^{-1}, while by analogy with the substituted benzaldehydes where the S−T split is known to be around 1750 cm^{-1} [8], a $T_2(n,\pi^*)$ state has been indicated at 25300 cm^{-1}. Both experimental and theoretical results [1] predict unanimously the

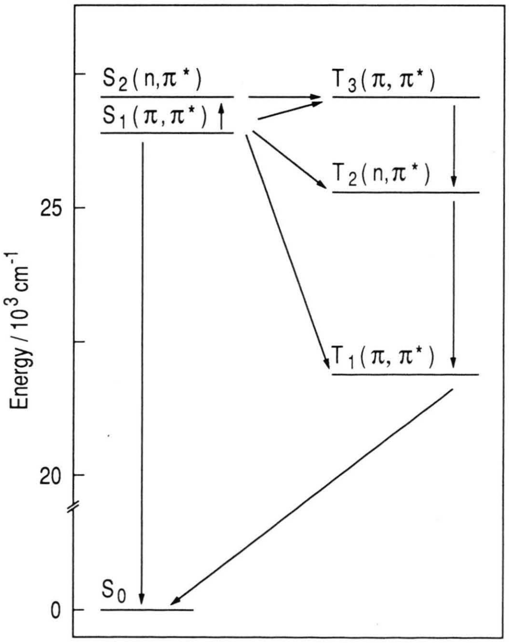


Fig. 8. Energy diagram of 2 MDQ in non-polar solvent.

location of the lowest $T_1(\pi,\pi^*)$ triplet level at 21 900 cm^{-1}. Finally, the energy of the $T_3(\pi,\pi^*)$ triplet level has been assumed to be similar to the $S_2(n,\pi^*)$ level on the ground that very efficient thermally enhanced singlet → triplet transition occurs presumably with the participation of the $S_2(n,\pi^*)$ state.

Both the indirect and the direct singlet → triplet transitions are indicated on the energy diagram. Although the S_1-S_2 and S_1-T_3 energy gaps are roughly the same as seen on the diagram, the considerably larger A-factor expected for the indirect route makes this process the dominant transition in non-polar and weakly polar solvents. If this is the case, then the experimental activation energy of about 3000 cm^{-1} obtained for the temperature dependent non-radiative processes could be identified with the value of the S_1-S_2 energy gap (*i.e.* the energy gap given in the diagram should be increased somewhat).

In polar solvents, the (π,π^*) states are shifted to lower energies. Due to the increased S_1-S_2 gap, the indirect $S_1(\pi,\pi^*) \rightarrow S_2(n,\pi^*) \rightarrow T_3(\pi,\pi^*)$ transition becomes insignificant and the processes which depopulate the $S_1(\pi,\pi^*)$ state are probably the $S_1 \rightarrow S_0$ fluorescence and maybe also internal conversion, the temperature independent $S_1 \rightarrow T_1$ and the temperature dependent $S_1 \rightarrow T_3$ transitions. The experimental activation energy of about 1500 cm^{-1} can be considered as a measure of the $S_1 \rightarrow T_3$ energy gap in polar solvents.

The scheme of photophysical processes of excited NMDQ seems to be very similar to that of 2MDQ. The difference that one notices is the slower rate for the temperature dependent component of the non-radiative singlet decay of NMDQ in all solvents. This may be due to the increased S_1-S_2 energy gap in case of NMDQ compared to 2MDQ which makes the indirect $S_1(\pi,\pi^*) \rightarrow S_2(n,\pi^*) \rightarrow T_3(\pi,\pi^*)$ transition less important even in non-polar solvents. This conclusion receives some support by the lower A-factors and activation energies as well as by the narrower A-factor range observed in case of the temperature dependent non-radiative singlet decay processes of NMDQ.

Photochemical dehydrogenation

In the discussion above we have assumed that photochemical decomposition from the excited singlet state plays no significant role in the non-radiative depopulation of singlet 2,3-dihydro-4(1 H)-quinolinones. Moreover, determination of the overall quantum yields for the photochemical reaction indicated that triplet decomposition is not a significant primary process either.

By using three different analytical techniques (MS, HPLC and UV spectroscopy), we have shown that the chemical reaction which occurs in the studied systems is photochemical dehydrogenation leading to 4(1 H)-quinolinones. The dehydrogenation products may be formed by two basically different mechanism, *i.e.* either by disproportionation of the appropriate free radicals or by direct H_2 elimination from the electronically excited 2,3-dihydro-4(1 H)-quinolinone molecules.

(i) Radical disproportionation route: Analogous disproportionation reactions leading to the formation of dehydrogenation products have been previously suggested, for instance by Malkin and Kuzmin [9]. In the investigation described in this paper, the observation of a "long-lived transient" which decayed approximately according to second order kinetics appears to be in favour of the free radical origin of the observed dehydrogenation product. Moreover, in the photolysis of 2MDQ the detection of a minor product with a formula of $C_{20}H_{20}N_2O_2$ (which may be formed by free radical dimerization) proves that free radicals play some role in the chemistry of the studied system. However, on the basis of the radical disproportionation mechanism of product formation it is hard to understand why only one major reaction product is formed. The reduced form (as for instance a major compound with an alcoholic structure) that one expects to be formed beside NMQ in the disproportionation reaction could not be detected by the three analytical methods applied.

One does not expect significant free radical formation to occur by photoreduction involving singlet excited 2,3-dihydro-4(1 H)-quinolinone molecules, nevertheless, photodehydrogenation was observed in non-deaerated samples saturated with O_2 where triplet state was quenched. One could assume that under these conditions, free radicals were formed in a different way, for instance by N−H bond fission in the singlet state, and these radicals could give the dehydrogenation product. This is, however, certainly not the case since 4(1 H)-quinolinone product is formed not only from 2MDQ but also from NMDQ where no N–H bond splitting can occur.

(ii) Molecular H_2 elimination route: Analogous H_2 elimination processes are known from the literature: Thus, intramolecular dehydrogenation has been suggested to be the dominant photodecomposition reaction of thio-chromanones [10] which are the thioanalogues of the compounds studied in this work. Molecular elimination can explain the following findings made in this work:

- Formation of only one major product, the appropriate 4(1 H)-quinolinone molecule.
- The production of the dehydrogenation products from 2MNDQ and NMDQ both from the singlet and the triplet excited states.

Considering this, we suggest that the dominating route in the photodecomposition of the 2,3-dihydro-4(1 H)-quinolinones is probably molecular H_2 elimination. However, for a better understanding of the decomposition mechanism further investigations would be required.

Experimental

The 2,3-dihydro-quinolinones were synthesized by standard procedures [1, 11, 12] and were purified by recristallization or by preparative thin-layer chromatography. Toluene was purified as described in the literature [13]; all other solvents were of spectroscopic grade and were used as received.

Spectroscopic and photophysical measurements were carried out in 1 × 1 cm quartz cuvettes and the samples were carefully degassed before use by several freeze-pump-thaw cycles.

The room temperature fluorescence quantum yields were determined relative to quinine bisulphate in 1 N H_2SO_4 media ($Q_F = 0.546$ [14]) on a Perkin-Elmer MPF 44 spectrofluorimeter. The temperature dependence of fluorescence quantum yield was measured by a home-built spectrofluorimeter equipped with a Princeton Applied Research 1140 A/B photon-counting system.

The fluorescence decays were recorded by time-correlated single photon counting technique with an Applied Photophysics SP-3 instrument. The decay curves were analyzed by non-linear least-squares reconvolution method.

In the laser flash photolysis studies of transients, the 351 nm light from an EMG 101 type excimer laser with xenon fluoride gas filling was used for excitation. Decay of transient absorption was recorded with a Datalab DL 905 transient recorder.

Product quantum yields were determined in cylindrical quartz cells with degassed samples. Steady state irradiation was carried out with a parallel light beam of 366 nm wavelength. Details of the filter system and the intensity measurements were described in ref. [15]. The product quantum yields were obtained as the ratio of the rate of product formation (measured by absorption spectroscopy) to the rate of light absorption.

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