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CHEMISTRY OF HYDROXAMIC ACIDS XV: PHOTOCHEMISTRY OF SOME NAPHTHALENECARBOHYDROXAMIC ACIDS*

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Summary

Photochemical reactions of N-(*p*-tolyl)-2-naphthalenecarbohydroxamic acid and its N-methyl derivative were studied in polar and non-polar solvents. Quenching studies showed that the reactions occur from both the singlet and the triplet states. It is concluded that photochemical reactions of hydroxamic acids mimic the oxidation in the ground state. The relationship between the photochemical reactions of hydroxamic acids and their fluorescence behaviour is discussed.

Keywords: *photochemistry, hydroxamic acids, fluctuations in fluorescence intensity*

1. Introduction

The results of our previous studies [1-3] have revealed that aromatic acyclic hydroxamic acids have an unusual fluorescence behaviour, concluded to be a general property of this group of organic compounds [2, 3].

Our findings suggested that the compounds may undergo photochemical reactions. N-Phenylbenzenecarbohydroxamic acid, chosen for the preliminary studies on the photochemistry of hydroxamic acids, appeared to be photolabile in both neutral and basic solutions, giving benzanilide as the main product [4, 5].

The next experiments were designed to explain the mechanism of the increase and oscillation in fluorescence intensity observed during irradiation of naphthalenecarbohydroxamic acids. As "fluctuating" compounds fluoresce very weakly [2, 3], the formation of small amounts of efficiently fluorescing intermediate(s) and/or photoproduct(s) was expected to cause a significant increase in the fluorescence intensity of the irradiated solutions.

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Taking into consideration the possibility of photogeneration of nitron-like intermediates, we studied photochemistry of some α -(2-naphthyl)-nitrones and we found an increase and fluctuations in the intensity of their fluorescence, resulting from the formation of efficiently fluorescing oxaziridines [6].

In this paper we describe studies on the photochemistry of two 2-naphthalenecarbohydroxamic acids: N-(*p*-tolyl)-2-naphthalenecarbohydroxamic acid (**I**), which shows small changes in fluorescence intensity [2, 3], and its N-methyl derivative (**II**), the most fluctuating of the compounds studied.

2. Experimental details

2.1. Materials

I and **II** were synthesized as described in ref. 3. Other reagents used in this work were from E. Merck; solvents (spectroscopy grade) were from A. G. Fluka.

2.2. Apparatus

Melting points were determined on a Thomas-Hoover capillary apparatus. Elemental analyses were obtained with a Perkin-Elmer 240B analyzer. IR spectra were recorded with a Perkin-Elmer 377 spectrometer using KBr pellets. ^1H NMR spectra were run on JEOL 100 MHz and Varian 60 MHz spectrometers with Me_4Si as an internal standard. Mass spectrometry (MS) was performed using a LKB 90008 mass spectrometer. UV-VIS spectra were measured on PU-8800 and PU SP3-100 (Pye-Unicam) UV-VIS spectrometers and fluorescence spectra were run on a Perkin-Elmer 512 fluorescence spectrometer.

High performance liquid chromatography (HPLC) was performed with a PU-4000 Pye Unicam Isocratic Liquid Chromatograph equipped with a PU 4020 variable wavelength detector and a Gilson Abimed 302 HPLC chromatograph with a UV variable wavelength detector.

Irradiations were performed using quartz or Pyrex cells ($d = 1$ cm), equipped with a magnetic stirrer, using KI/I_2 or CuSO_4 filters [7] and HBO-50 mercury lamp (Carl Zeiss, Jena).

Preparative irradiations were performed with medium pressure mercury HPK 125 W or low pressure mercury Hanan St-40W lamps.

2.3. Methods

2.3.1. Preparative irradiations

A solution of a hydroxamic acid in an appropriate solvent ($c \approx (5 \times 10^{-5}) - (5 \times 10^{-4})$ M) was cooled in an ice-water bath and irradiated with an internal mercury lamp. Helium was passed through the solution during the irradiation. The photoreaction was followed by withdrawing small samples at fixed intervals without interrupting the system. The samples were analyzed by HPLC and UV-VIS methods. After the reaction was completed (about 45 min) the solvent was removed on a vacuum evaporator, and the reaction mixture was separated on a column (Silica gel 60 M, E. Merck) using a chloroform-hexane (1:1) mixture as the eluent. Compounds **IV**, **IX** and **X** were identified on the basis of the analyses described below.

Compound IV. Elemental analysis for $C_{29}H_{21}NO_3$: calculated – 80.74% C, 4.87% H, 3.25% N; found – 80.21% C, 5.05% H, 3.60% N. IR (KBr, cm^{-1}): $1740\nu_s(CO)$; $1690\nu_s(CO)$. The compound underwent thermal decomposition in the heated inlet system of the mass spectrometer; however, the peaks at m/e 171 and m/e 260 seem to support the structure of the compound. Similar problems with MS spectra of hydroxamic acids, especially their O-substituted derivatives, were reported in ref. 8.

Compound IX. Elemental analysis for $C_{12}H_9NO_2$: calculated – 72.36% C, 4.52% H, 7.04% N; found – 72.20% C, 4.00% H, 7.00% N. IR (KBr, cm^{-1}): $3100\nu_s(CH)$; $1730\nu_s(COO)$; $1680\nu_s(C=N)$; $1300\nu_{C-O}$; $940\nu_{N-O}$. MS, m/e : 199; 171; 155. 1H NMR (TMS, δ , ppm): 8.7, s (1H, aromatic), 7.8 – 8.2, m (4H, aromatic), 7.9 s (2H).

Compound X. Elemental analysis for $C_{23}H_{19}N_2O_4$: calculated – 71.32% C, 4.91% H, 7.24% N; found – 70.90% C, 5.05% H, 7.19% N. IR (KBr, cm^{-1}): $3400-3500\nu_s(OH-bonded)$, $2950 - 2930\nu_{(CH_2, CH_3)}$; $1705, 1690\nu_s(CO)$; $1480-1460\nu_{CH_2, CH_3}$; $1360\nu_{CN}$. 1H NMR (TMS, δ ppm): 8.7 – 7.8 m (7H, aromatic); 7.2 s (2H, aromatic); 7.42 s (3 H), 1.42 s (3H). The thermal instability of the compound made the interpretation of its spectrum difficult.

Other compounds were identified on the basis of elemental analyses and MS, IR and 1H NMR spectra. Their spectral data and retention times were identical with those of the original samples.

2.3.2. Quantum yield determinations

Solutions of hydroxamic acids were irradiated in a quartz cell via a KI/I₂ filter ($\lambda \approx 254$ nm) in a Pyrex cell ($\lambda > 300$ nm) or in a Pyrex cell with a CuSO₄ filter [7].

Solutions were stirred magnetically during irradiations. All experiments were performed at room temperature. Photolyses were carried out to 30% conversion or less.

Quantum yields of the reactions were determined from the decrease in the hydroxamic acid HPLC peak. Details of the HPLC analysis have been reported elsewhere [9].

The light intensity was monitored with a potassium ferrioxalate actinometer [10].

2.3.3. Quenching studies

Samples of hydroxamic acids were prepared and analyzed as for the quantum yield determinations except that various amounts of 1,4-cyclohexadiene were added. Eight concentrations of diene in addition to the blank containing no 1,4-cyclohexadiene were used for the Stern-Volmer analysis. Repeated determinations agreed to within $\pm 10\%$.

2.3.4. Fluorescence quantum yields

Quinine bisulphate was used as a standard for fluorescence quantum yield determinations, assuming its quantum yield ϕ_F (1.0 N H₂SO₄) to be equal to 0.55 [10].

3. Results

3.1. Photochemistry of *N*-(*p*-tolyl)-2-naphthalenecarbohydroxamic acid (**I**)

N-(2-Naphthoyl)-*p*-toluidine (**III**) and an unstable compounds (**IV**) appeared to be the main products of irradiations of **I** in cyclohexane ($c = 0.2 \times 10^{-4}\text{M}$), acetonitrile ($c = 1 \times 10^{-4}\text{M}$) and methanol ($c = 1 \times 10^{-4}\text{M}$). On a prolonged irradiation, compound **IV** decomposed to **III** and to 2-naphthoic acid. It was also transformed to these products on standing in solution. Its MS and IR spectra were consistent with the structure of *N*,*O*-di(2-naphthoyl)-*N*-(*p*-tolyl)hydroxylamine. The chemical yields of the products of photoirradiation of **I** are presented in Table 1.

TABLE 1

Products of the photochemical reaction of *N*-(*p*-tolyl)-2-naphthalenecarbohydroxamic acid (**I**) ($\lambda \approx 254\text{ nm}$; conversion about 40%)

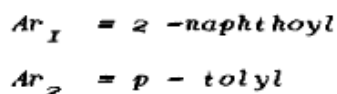
Solvent	Concentration (M)	Yield (%) of photoproduct ^a			
		<i>III</i>	<i>IV</i>	<i>V</i>	<i>VI</i>
Cyclohexane	5×10^{-5}	41	30	10	17
Acetonitrile	1×10^{-4}	52	23	2	9.5
Methanol	1×10^{-4}	62	25	2.5	10

^aChemical yields, calculated relative to the hydroxamic acid consumed.

The quantum yields of the reactions in cyclohexane, acetonitrile, tetrahydrofuran, methanol and methanol-water solutions are presented in Table 2. An increase in solvent polarity obviously favours the photostabilization of the hydroxamic acid. The present results parallel those reported for *N*-phenylbenzenecarbohydroxamic acid [5], which is found to be photostabilized by protonation. Thus, it seems reasonable to propose the mechanism of the photoreaction of compound **I** as it is shown in Scheme 1.

Benzophenone ($E_S \approx 69\text{ kcal mole}^{-1}$, $\phi_F = 0.74$, $\lambda < 385\text{ nm}$) sensitizes photodestruction of **I** ($E_S = 84\text{ kcal mole}^{-1}$, $E_T \approx 64\text{ kcal mole}^{-1}$), while 1,4-cyclohexadiene quenches it.

When a solution of the hydroxamic acid **I** in cyclohexane ($c = 1 \times 10^{-4}\text{M}$) containing benzophenone ($c = 2.2 \times 10^{-2}\text{M}$) was irradiated using a CuSO_4 filter (at $\lambda > 350\text{ nm}$, where **I** hardly absorbs), the hydroxamic acid photodestruction quantum yield was $\phi = 0.09$, while almost no reaction was observed during the identical irradiation of the solution without benzophenone (Table 2).



Compound **I** was irradiated at $\lambda \approx 254$ nm in solutions containing various amounts of 1,4-cyclohexadiene. The quantum yields of both hydroxamic acid photodestruction and photoproducts formation were determined by HPLC. A plot of ϕ_o/ϕ_q vs. $[Q]$ of the hydroxamic acid photodestruction (where ϕ_o is the quantum yield of the reaction measured in the absence of the quencher and ϕ_q is the quantum yield measured in the presence of the quencher) is shown in Fig. 1.

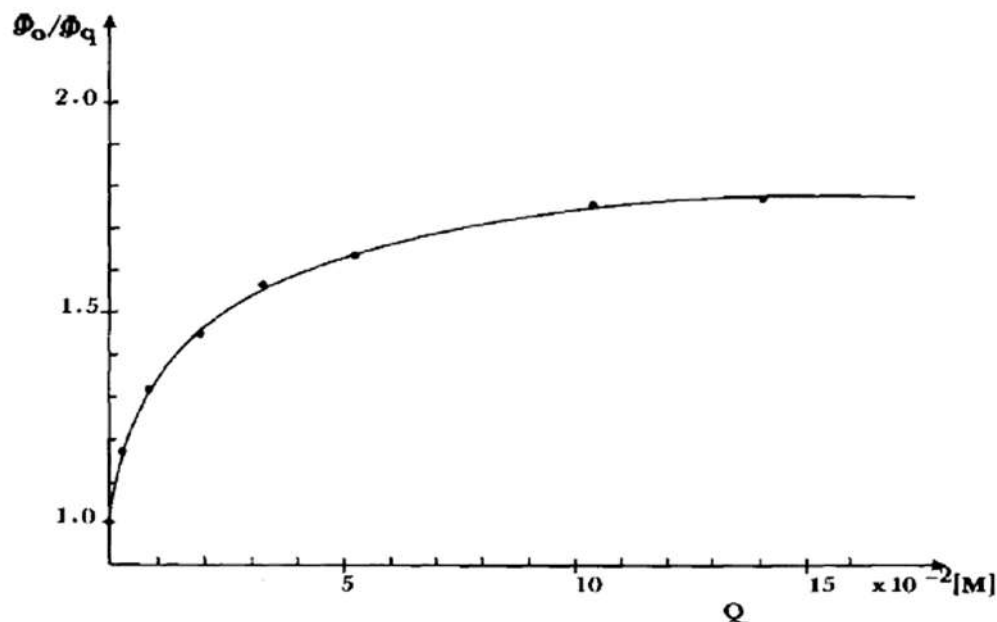


Fig. 1. Quenching of **I** photodestruction in cyclohexane by 1,4-cyclohexadiene ($c \approx 5 \times 10^{-5}$ M, after 3 min irradiation).

The observed plot is non-linear, similarly to the plot reported for the photoreaction of N-phenyl-benzenecarbohydroxamic acid [5]. We assumed that the intercept along the plateau may be considered to be equal to ϕ_o/ϕ_q for an S_1 reaction (see ref. 5 and references cited therein) and calculated the percentage of the singlet reaction, equal to $\{(\phi_o/\phi_q/(\phi_o/\phi_s)) \times 100$. Then the relative quantum yield of the triplet reaction (ϕ_o^T/ϕ_q^T) was calculated by subtracting out the amount of singlet reaction at low $[Q]$.

The slope of the linear plot of (ϕ_o^T/ϕ_q^T) vs $[Q]$ gave k for the triplet hydroxamic acid photodestruction ($k\tau = 123$ and $\tau^{-1} = 0.41 \times 10^8 \text{ s}^{-1}$ (assuming $kq = 5 \times 10^9 \text{ s}^{-1}$)).

As shown in Fig. 2, 1,4-cyclohexadiene quenches the formation of both **III** and **IV**.

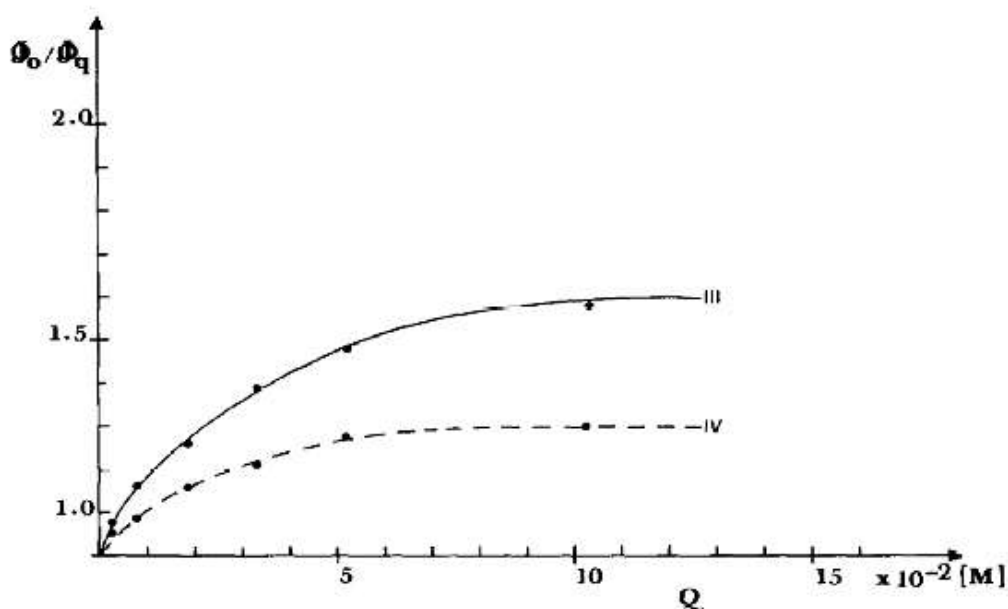


Fig. 2. Quenching of **III** and **IV** formation in cyclohexane by 1,4-cyclohexadiene ($c \approx 5 \times 10^{-5}$ M, after 3 min irradiation).

The presence of **IV** (the bimolecular reaction product (Scheme 1)) was detected even in dilute ($c \approx 5 \times 10^{-5}$ M) solution, consistent with our previous observations [3, 11] concerning the aggregation of naphthalenecarbohydroxamic acids and related molecules. Thus one might expect that **III** is formed not only in the primary photoreaction of the hydroxamic acid **I** but also in the photodestruction of **IV**. We studied the influence of the irradiation time on the ratio of photoproducts **IV/III** in the reaction mixtures after irradiation of solutions of **I** (cyclohexane, $c = 5 \times 10^{-5}$ M) containing 0.2 M 1,4-cyclohexadiene (plateau in Fig. 1) and the mixtures without the quencher. As can be seen in Table 3, **IV** is the main product of a short irradiation. On addition of diene, which quenches the photodestruction of the hydroxamic acid **I**, the ratio of the products **IV/III** is reduced.

TABLE 3

Influence of the photoirradiation time on the ratio of photoproducts (**IV/III**) of the reaction of *N*-(*p*-tolyl)-2-naphthalenecarbohydroxamic acid (**I**) in cyclohexane ($c \approx 5 \times 10^{-5}$ M)

Time (min)	Ratio IV/III	
	Without 1,4-cyclohexadiene	With 1,4-cyclohexadiene (0.2 M)
20	0.85	4.66
15	0.90	4.80
10	0.95	5.50
5	1.50	6.00
3	3.86	6.60

On a prolonged irradiation the ratio **IV/III** decreases in solutions with 1,4-cyclohexadiene and without it, but the ratio is always higher for solutions with the quencher. Thus, not only the primary photoreaction but also the secondary photoreaction involves molecules excited to the triplet state.

The instability of **IV** made independent synthesis and quenching studies of this compound very difficult. However, HPLC analysis revealed lack of hydroxamic acid in the reaction mixtures after irradiation longer than 15 min. In order to check the influence of the quencher on the photodecomposition of **IV**, solutions containing various amounts of 1,4-cyclohexadiene were irradiated at $\lambda \approx 254$ nm for 20 min. Plots of ϕ_o/ϕ_q vs. $[Q]$ for the photodestruction of **IV** and formation of **III** are shown in Fig. 3. The slope of ϕ_o^T/ϕ_q^T vs. $[Q]$ obtained by the method described above gave $k\tau_{IV} = 145$, $k\tau_{III} = 144$ and $\tau_{IV}^{-1} \approx \tau_{III}^{-1} \approx 0.34 \times 10^8 \text{ s}^{-1}$.

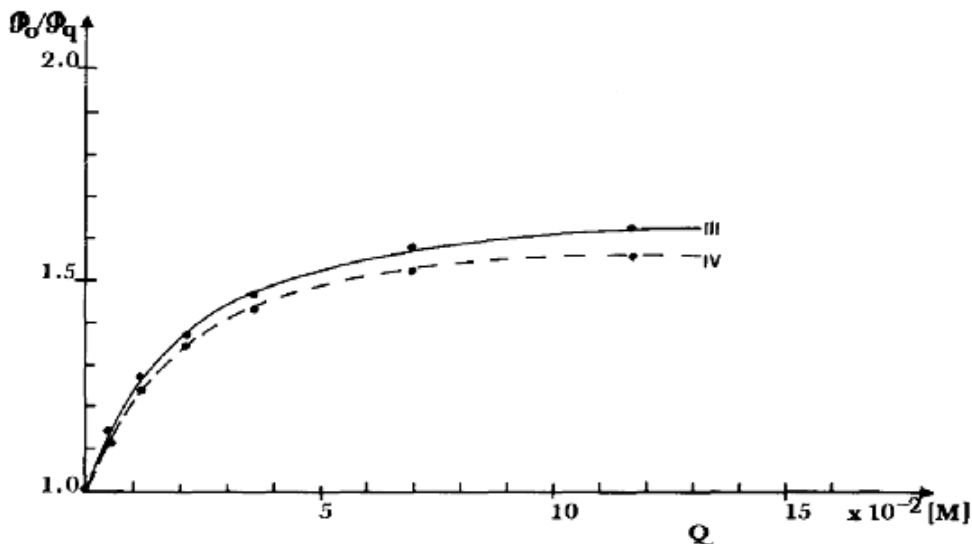
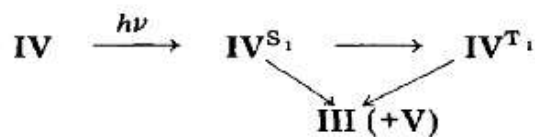


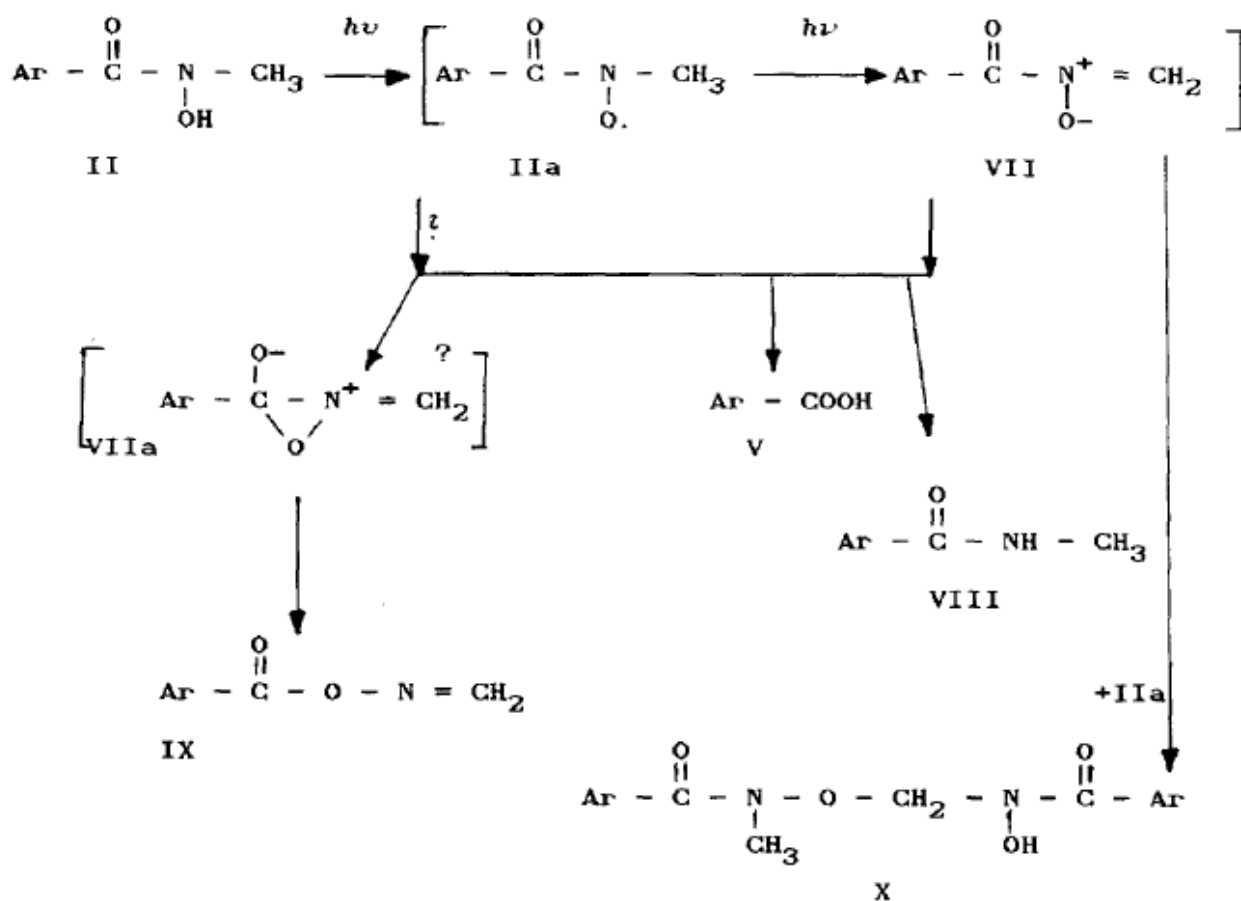
Fig. 3. Quenching of **IV** photodestruction and the formation of **III** by 1,4-cyclohexadiene (cyclohexane, $c \approx 5 \times 10^{-5}$ M, after 20 min irradiation).

Plots in Fig. 3 are similar to those obtained for the photodestruction of **I** (Fig. 1) and suggest that molecules of **IV** excited to both singlet and triplet states undergo the photochemical reaction:



3.2 Photochemistry of *N*-methyl-2-naphthalenecarbohydroxamic acid (**II**)

Preparative irradiations of **II** in cyclohexane ($c \approx 1 \times 10^{-4} \text{ M}$), benzene ($c \approx (1 - 6) \times 10^{-4} \text{ M}$), tetrahydrofuran ($c \approx 1 \times 10^{-4} \text{ M}$) and methanol ($c \approx 1 \times 10^{-4} \text{ M}$) resulted in the same photoproduct (**VII**), detected by HPLC. The compound appeared to be too unstable to be isolated. It decomposed quickly at room temperature to a mixture of products. After evaporation of solvents, these compounds were separated on a silica-gel column and identified on the basis of their spectral data (Scheme 2, Table 4). Similar mixtures were also obtained during prolonged irradiations of solutions of **II** (Fig. 4).



$\text{Ar} = 2\text{-naphthyl}$

Scheme 2.

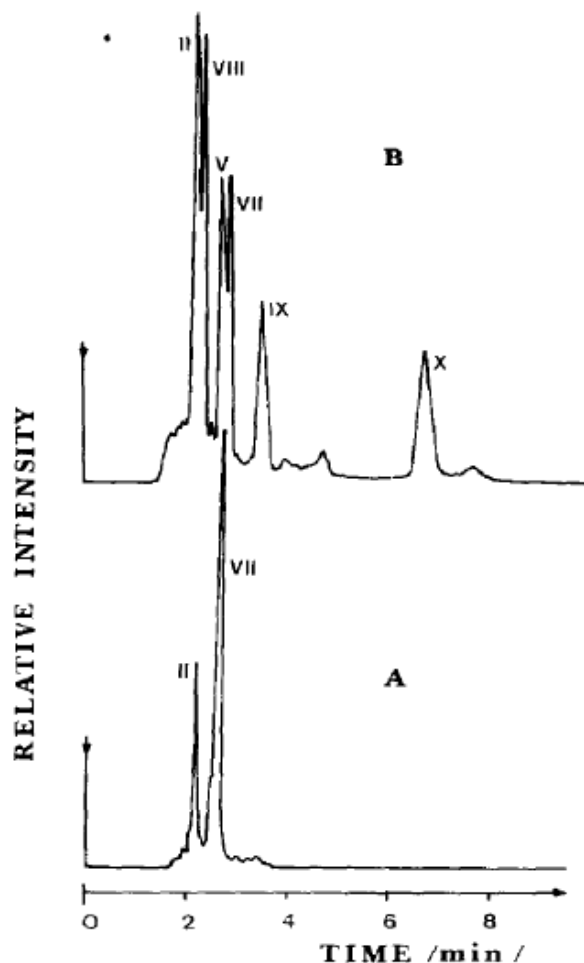


Fig. 4. HPLC chromatogram (ODS; eluent, phosphate buffer, pH 3.0/methanol 1:3 (by volume)) of the solution after a preparative irradiation of **II** in benzene ($c \approx 2 \times 10^{-4}$ M). (A) After 40 min irradiation; (B) after 90 min irradiation.

Oxidation of **II** with aqueous alkaline $K_3Fe(CN)_6$, analogously to the method reported in ref. 12, gave a compound with spectral characteristics identical with those of product **X** and different from those of the unstable N,O-di(2-naphthoyl)-N-methyl-hydroxylamine, obtained from the hydroxamic acid and 2-naphthoyl chloride by a method analogous to that described in ref. 13.

An unstable photoproduct with the same retention time (HPLC) as compound **VII** was also detected during the irradiation of benzene solutions of **II** ($c \approx 1 \times 10^{-3}$ M) in a quartz cell in a spectrofluorometer ($\lambda_{exc} = 290 \pm 10$ nm). 30 min of irradiation afforded 1.5% of the product **VII**, and after the next 2 h the amount of **VII** increased to about 7%, but traces of decomposition products were also detected.

TABLE 4

Chemical yields of the compounds obtained in the photoreaction of *N*-methyl-2-naphthalenecarbohydroxamic acid (**II**) (benzene, $c \approx 6 \times 10^{-5}$ M)

Product	Yield (%)		
	A ^a	B ^b	C ^c
II	19	19	11
VII	79	74	—
VIII	—	Trace	12.3
V	—	Trace	7.9
IX	—	Trace	22.1
X	—	—	26

The yield was determined by HPLC.

^aA = after irradiation (about 40 min).

^bB = after evaporation of the solvent under vacuum (at room temperature) dissolved in methanol, $c \approx 10^{-3}$ M.

^cC = Solution as for B, after about 24 h at room temperature.

Quantum yields of the photodestruction of **II** in non-polar and polar solvents are presented in Table 5. They are lower than those of the photoreaction of **I** (Table 2). As it has been observed for *N*-phenylbenzenecarbohydroxamic acid [5] and **I** (Table 2), protonation photostabilizes **II**, too.

TABLE 5

Quantum yields of *N*-methyl-2-naphthalenecarbohydroxamic acid (**II**) photodestruction in polar and non-polar solvents

Solvent	Quantum yield
Cyclohexane	0.021 ^a , 0.005 ^b , 0.018 ^c , 0.0079 ^d
Cyclohexane + He	0.026 ^a
Cyclohexane + O ₂	0.015 ^a
Toluene	0.023 ^a
Tetrahydrofuran	0.007 ^a
Acetonitrile	0.012 ^a , 0.003 ^d
Methanol	0.0015 ^a
Methanol-H ₂ O (1:1 by volume)	0 ^a

^aIn a quartz cell, without any filter.

^bIn a Pyrex cell with a CuSO₄ filter, without benzophenone.

^cIn a Pyrex cell with a CuSO₄ filter, with benzophenone.

^dIn a quartz cell with a KI/I₂ filter.

Quantum yields obtained from experiments conducted in solutions saturated with oxygen and those saturated with helium were different (Table 5).

1,4-cyclohexadiene was found to quench the photoreaction. The plot of ϕ_o/ϕ_q vs. $[Q]$ for the photodestruction of **II** is shown in Fig. 5. Using the procedure described above, $\tau^{-1} = 0.39 \times 10^8 \text{ s}^{-1}$ was calculated for the photodestruction of **II**.

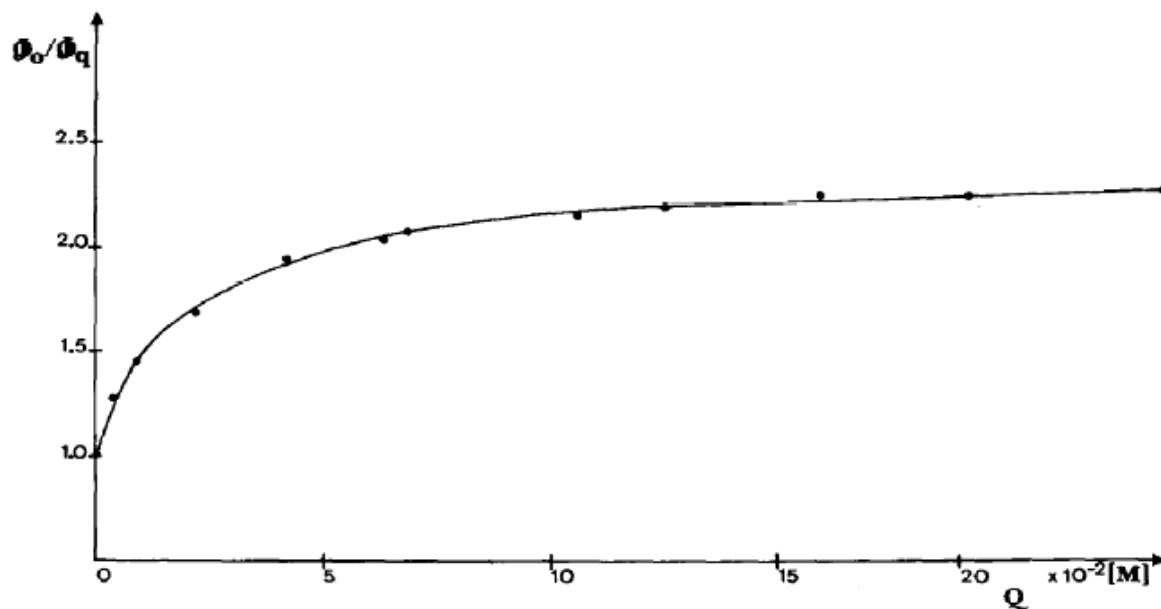
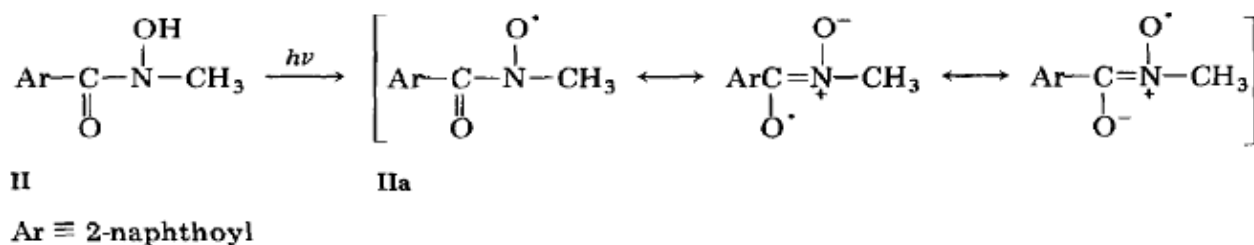


Fig. 5. Quenching of II photodestruction by 1,4-cyclohexadiene (cyclohexane, $c \approx 5 \times 10^{-5} M$).

4. Discussion

The results of our investigations suggest that the photochemical reaction of aromatic acyclic hydroxamic acids mimic the well-known oxidation reactions of these compounds in the ground state. Many oxidants have been reported to convert hydroxamic acids into acyl aminyloxides [12, 14-16]. We have found that photoirradiation of the compounds also produces such radicals. For example, an irradiation ($\lambda > 300 \text{ nm}$) of **II** (3-methylpentane, 170K) gives an ESR signal with the hyperfine pattern, α_N and g typical of acyl aminyloxides: $\alpha_N = 7.0 \text{ G}$; $\alpha_H^B = 7.9 \text{ G}$; $g = 2.0077$ [17].

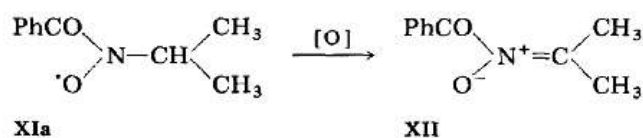


It seems reasonable to assume that acyl aminyloxides (nitroxides) are the primary intermediates of the photochemical reactions of hydroxamic acids. The quenching effect of oxygen and the reduction of the quantum yields of hydroxamic acid photodestruction (Tables 2 and 5 and ref. 5) by protic solvents support this conclusion. For example, solvation of the carbonyl group, which enhances nitrogen lone-pair delocalization, may make the photooxidation more difficult.

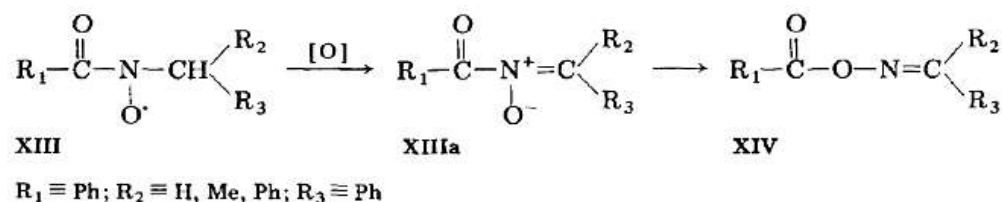
Both photoirradiation and oxidation of hydroxamic acids in the ground state lead to similar products. Oxidation of N-aryl-benzenecarbohydroxamic acids with silver oxide has been found to result in corresponding anilides and N,O-dibenzoyl-N-arylhydroxylamines [14, 15]. Similar products have been detected in the photochemical reactions of **I** (Table 1) and N-phenyl-benzenecarbohydroxamic acid [5].

Irradiation of **II** gave different products. Obviously, the substituent at the nitrogen atom influences the stability of acyl aminoxyl-oxide radical [17] and it determines the final product of the photoreaction.

It has been reported [16] that an ethereal solution of N-isopropyl-benzenecarbohydroxamic acid (**XI**) shaken with aqueous alkaline $K_3Fe(CN)_6$ initially turned green, consistent with the formation of a high concentration of acyl alkylaminyloxide **XIa**. The radical was suggested to disproportionate to give N-acyl nitrone **XII** [16], a powerful acylating agent:



In no case was such a compound isolated. However, evidence has been obtained for such structures because the O-acyloximes **XIV** were isolated [16, 18] during oxidation of hydroxamic acids **XIII** in the ground state:



The green colour of the reaction mixture was also observed at the beginning of our photoirradiation of **II** in tetrahydrofuran ($c \approx 10^{-4}\text{M}$). As described in Section 3, the photoreaction results in an unstable product, probably N-acyl nitrone **VII** (or its isomeric oxaziridine **VIIa**), which eventually undergoes intramolecular reactions or acts as an acylating agent with **IIa** (Scheme 2).

The formation of an oxaziridine-like intermediate was postulated for the photoreaction of N-phenylbenzenecarbohydroxamic acid anion [5]. No oxaziridine ring formation was observed during our investigations. However, many of these compounds, for example N-aryl-substituted oxaziridines, are not sufficiently stable to be isolated at room temperature [6, 20]. The photostabilizing effect of protic solvents (Tables 2 and 5 as well as ref. 5) may

be due to the fact that the solvation of hydroxamic acids makes free radical generation more difficult and that it also may hinder photoisomerization of nitron-like structures to the corresponding oxaziridines. Therefore oxaziridine formation during photochemical reactions of hydroxamic acids cannot be excluded.

Studies on the excited states of hydroxamic acids have revealed unusual fluorescence behaviour [1-3]. The observed fluctuations in fluorescence intensity have been found to be spatial and not temporal and have been suggested to be a general phenomenon of aromatic acyclic hydroxamic acids [3].

The fastest increase and the highest amplitudes of fluctuation were observed for non-polar solutions, and the slowest in protic solvents [2, 3].

The fluorescence intensity of solutions saturated with oxygen increased slowly (Fig. 6(B)) or did not increase at all, while the oscillations ceased.

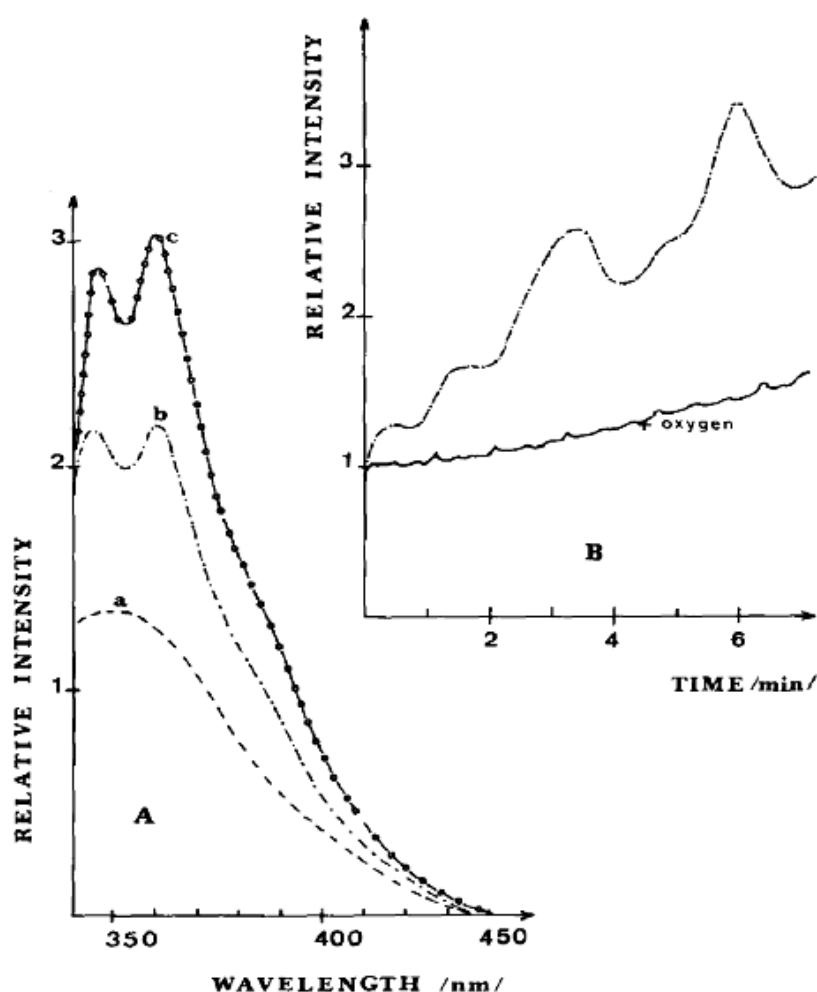


Fig. 6. (A) Changes in fluorescence spectrum of II in cyclohexane ($c \approx 5 \times 10^{-5}$ M) during irradiation in a spectrofluorometer: curve a, 0 min; curve b, 2 min; curve c, 4 min. (B) Changes in fluorescence intensity of the solution as in (A) (observed at $\lambda = 360 \pm 3$ nm) in time during irradiation in a spectrofluorometer ($\lambda_{\text{exc}} = 290 \pm 20$ nm).

Saturation with nitrogen accelerated the increase in emission intensity and enhanced the oscillations [3]. The disturbing effect of oxygen on the fluctuations in fluorescence intensity of naphthalenecarbohydroxamic acids has been suggested to be due to a free radical mechanism and/or a process involving molecules excited to the T_1 state.

The results of our present investigations on the photochemistry of hydroxamic acids confirm this hypothesis. Quenching studies have revealed that molecules excited to the T_1 state undergo photochemical reactions. Free radicals of acyl aminoxyloxides (nitroxides) are suggested to be primary intermediates of the photoreactions. Protic solvents, which obviously prevent fluctuations of fluorescence, photostabilize the compounds (Tables 2 and 5).

The results of systematic investigations of naphthalenecarbohydroxamic acids and related amides and anilides [2, 3] have shown that “fluctuating” compounds fluorescence very weakly, while fluorescence quantum yields (ϕ_F) of some compounds containing the NH group are very high. Thus, the formation of small amounts of efficiently fluorescing photoproduct(s) might cause the observed fluorescence behaviour of the irradiated solutions.

In the case of the compounds containing-aryl substituents, the fluorescence quantum yields are not high [3]. Thus, the difference between the quantum yields of **I** and its photoproducts (and/or intermediates) is not large and the observed changes in fluorescence intensity are not spectacular.

II appeared to be the most fluctuating of the studied compounds. On irradiation in a spectrofluorometer, the fluorescence of solutions of in non-polar and polar protic solvents increased with fluctuations and the fluorescence spectra changed in shape (Fig. 6). As shown in refs. 2 and 3, the energies of the S_1 states of hydroxamic acids and their possible photoproducts are similar. This, it is difficult to identify photogenerated species on the basis of the S_1 level. Our present studies of the photochemistry of hydroxamic acids have revealed that the N-methyl-amide of 2-naphthoic acid (**VIII**) is the one of the final products of the irradiation of **II**. Thus, the formation of this efficiently fluorescing compound ($\phi_F \approx 10^{-1}$ [3]) may be responsible for the observed fluorescence behaviour.

However, the quantum yields of the photochemical reactions of **II** are very low (Table 5) and the amide **VIII** is not the primary photoproduct. Only one, unstable primary product was detected (HPLC) during the first 30 min of irradiation of **II** in the spectrofluorometer.

As can be seen in Fig. 7, the fluorescence spectrum of a species generated during irradiation of a solution of **II** in the spectrofluorometer is shifted bathochromically compared with that of **VIII**. The fluorescence spectrum of the mixture of photoproducts after a preparative irradiation of **I** (contaminated with **VII** accompanied by other compounds) also shows a bathochromic shift. The spectra resemble that of α -(2-naphthyl)-N-methyl-nitrone rather than that of the amide **VIII** (Fig. 7).

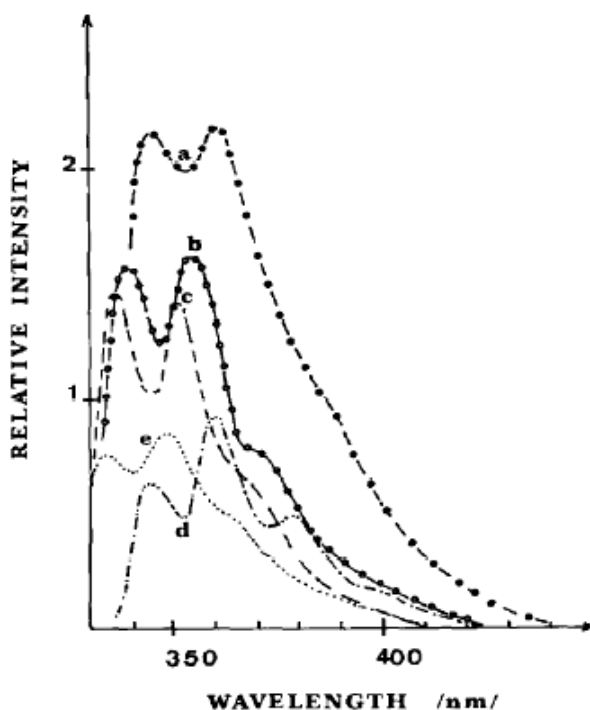


Fig. 7. Fluorescence spectra (cyclohexane, $c \approx 10^{-5}$ M) of the compounds: curve a, **II** after about 2 min of irradiation in a spectrofluorometer; curve b, photoproducts after a preparative irradiation of **II** in benzene; curve c, *N*-methyl amide of 2-naphthoic acid (**VIII**); curve d, α -(2-naphthyl)-*N*-methylnitrone; curve e, oxaziridine, isomeric to α -(2-naphthyl)-*N*-methylnitrone.

Thus, it seems reasonable to assume that the observed fluorescence behaviour is connected with the formation of the intermediate **VII**. Studies on the fluorescence and photochemistry of α -(2-naphthyl)-methylnitrone [6] have shown that the fluorescence quantum yield of this compound is not high. However, the fluorescence intensity has been found to increase with fluctuations during irradiation in a spectrofluorometer, and it was concluded that this resulted from the formation of the corresponding efficiently emitting oxaziridine. It was reported in refs. 3 and 6 that changes in the structure of naphthalenecarbohydroxamic acids, related amides and nitrones influence the fluorescence quantum yields ϕ_F significantly. Thus, ϕ_F of **VII** may be higher than that of α -(2-naphthyl)-*N*-methyl-nitrone. One could also expect that it photoisomerizes easily to its oxaziridine isomer.

Generation of nitrone- and oxaziridine-like intermediates may therefore be one of the reasons for the unusual fluorescence behaviour of compound **II** and other hydroxamic acids.

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