

**CHEMISTRY OF HYDROXAMIC ACID
XII: PHOTOCHEMISTRY OF N-PHENYLBENZENECARBO-
HYDROXAMIC ACID — STUDIES ON THE MECHANISM OF
REACTION[†]**

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(Received July 1, 1986)

Summary

The quantum yield for the photodestruction of *N*-phenylbenzenecarbohydroxamic acid was determined in a number of solvents. Protonation was found to photostabilize both the hydroxamic acid and its anion. Quenching studies showed that the reaction in cyclohexane occurs from both the singlet and the triplet state, giving benzanilide as the main photoproduct. The results are discussed in the light of other recent investigations in the field.

1. Introduction

Since Lossen first synthesized oxalohydroxamic acid more than 100 years ago [1], hydroxamic acids have been found to possess many interesting properties. The rearrangement reaction of their *O*-acyl derivatives, which bears Lossen's name [2], has found synthetic applications [3, 4]. Complexes of hydroxamic acids and their *N*-substituted derivatives with metal ions are useful in colourimetric analysis [3]. Many hydroxamic acids have been found to be biologically active [3, 5] and are used as drugs and pesticides.

Recent progress in the chemistry of hydroxamic acids has been stimulated by the isolation of naturally occurring hydroxamic acids, which are active as antibiotics, antitumour agents and growth and cell-division factors [6]. Some hydroxamic acids inhibit ribonucleotide reductase, an iron-requiring enzyme, while others are powerful mutagens [7]. The discovery that many oxidants can convert hydroxamic acids into acyl aminyloxides (nitroxides), which are active acylating agents [8], has aroused interest

[†]Part XI is to be published in *Monatshefte für Chemie*.

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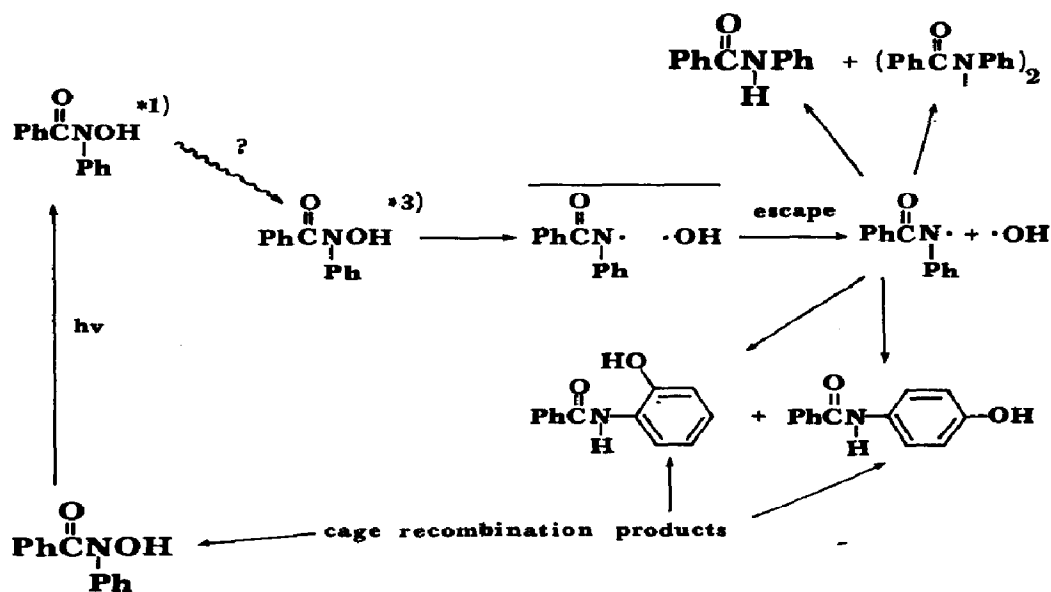
because there are strong indications that such radicals play a significant role in biological environments [9], as *N*-hydroxylation is believed to be a key step in the metabolic activation of carcinogenic amines and amides.

Acyclic hydroxamic acids have so far been considered to be photostable, and the results of recent studies have shown that they are the products of photochemical reactions. For instance, the photoirradiation of some nitrones leads to the formation of acyl aminyloxides (nitroxides) [10, 11]. The highly regiospecific and stereospecific photorearrangement of alkane-nitronate anions has been found to give hydroxamic acids in good yields [12].

The discovery of oscillations in the fluorescence intensity of aromatic acyclic hydroxamic acids [13, 14] suggested that the compounds may undergo photochemical reactions.

N-Phenylbenzenecarbohydroxamic acid has been chosen for the preliminary studies on the photochemistry of hydroxamic acids. This compound was expected to be photolabile, as it has structural units of benzanilide and hydroxylamine. Benzanilide is known to undergo the Fries photorearrangement [15]. Homolytic cleavage of *N*-O bonds has been observed during photochemical reactions of diacylhydroxylamines [16] and 1-alkoxy-2-pyridones [17, 18].

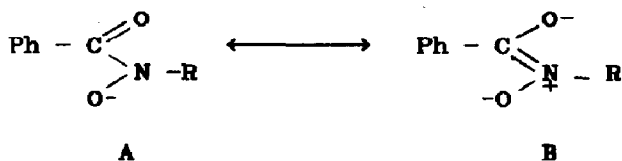
Preliminary photoirradiation experiments on *N*-phenylbenzenecarbohydroxamic acid in cyclohexane have revealed that the compound is photolabile [19]. The reaction gave benzanilide as the main photoproduct, accompanied by other compounds; their formation seemed to be consistent with the initial homolysis of the *N*-O bond as shown in Scheme 1.



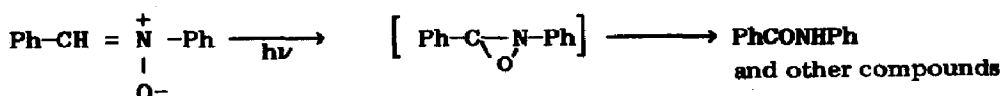
Scheme 1.

N-Phenylbenzenecarbohydroxamic acid also appeared to undergo a photochemical reaction in methanol and in a mixture (1:1 by volume) of methanol and 0.5 M NaOH(aq).

The results of ^{17}O nuclear magnetic resonance (NMR) studies [20] have suggested that the *N*-substituted benzo-hydroxamate anion has a resonance hybrid structure:

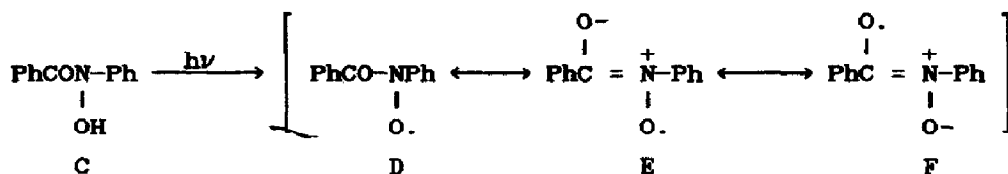


Canonical structure B resembles the nitron chromophore, which is known to undergo rearrangement via an oxaziridine intermediate [21]:



Thus, a similar reaction was expected to take place during the irradiation of *N*-phenylbenzenecarbohydroxamic acid in an alkaline medium. Studies on the quantum yield of the photodestruction of hydroxamic acid in cyclohexane, methanol and a mixture (1:1 by volume) of methanol and 0.5 M NaOH(aq) gave Φ values of 0.067, 0.007 and 0.012 respectively [22].

The results of recent electron spin resonance (ESR) measurements suggest [23] that photoirradiation of *N*-phenylbenzenecarbohydroxamic acid leads to acyl aminyloxide (nitroxide) generation



and not to the homolysis of the N—O bond, as was assumed on the basis of the results of preliminary experiments.

In this paper we shall discuss the results of our studies on the mechanism of the photochemical reaction of *N*-phenylbenzenecarbohydroxamic acid, including more detailed investigations both of the dependence of the photoreaction quantum yield on the solvent and of the nature of the excited state.

2. Experimental details

2.1. Materials

N-Phenylbenzenecarbohydroxamic acid was synthesized and purified analogously to the method described in ref. 24. *N,N*-Dibenzoyl-*N*-phenyl-

hydroxylamine was obtained according to the procedure reported in ref. 25. The melting points, ^1H NMR and IR spectra and elemental analyses of these compounds were identical with those described in the literature [25, 26].

Cyclohexane, methanol, dioxane and tetrahydrofuran (THF) (all spectroscopy grade) were from A. G. Fluka; the other reagents (all G.R. grade) were from E. Merck.

2.2. Apparatus

Melting points were determined on Thomas-Hoover capillary apparatus. Elemental analyses were obtained with a Perkin-Elmer 240B analyser. IR spectra were recorded with a Perkin-Elmer 377 spectrometer using KBr pellets. ^1H NMR spectra were run on a Varian A-60 spectrometer with Me_4Si as an internal standard. UV-visible spectra were measured on a PU-8800 (Pye-Unicam) UV-visible spectrophotometer, and fluorescence and phosphorescence spectra were run on a Shimadzu RF-502 spectrofluorometer.

Irradiations were performed using a quartz or Pyrex cell ($d = 1$ cm) equipped with a magnetic stirrer, using KJ/J_2 or CuSO_4 filters [27] and an HBO-50 mercury lamp (Carl Zeiss, Jena).

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 an HPLC LKB Chromatograph equipped with an LKB 2150 HPLC pump, an LKB 2140 rapid detector, an LKB 2155 HPLC column oven and an Olivetti Personal Computer M-24.

2.3. Methods

2.3.1. Quantum yield determinations

Solutions of *N*-phenylbenzenecarbohydroxamic acid ($c = (0.6 - 2) \times 10^{-4}$ M) were irradiated in a quartz cell via a KJ/J_2 filter ($\lambda \approx 254$ nm) or in a Pyrex cell ($\lambda > 300$ nm). A Pyrex cell with a CuSO_4 filter [27] was used for irradiations of the hydroxamic acid ($c = 1 \times 10^{-4}$ M) in cyclohexane containing acetophenone ($c = 1 \times 10^{-2}$ M).

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

The light intensity was monitored with a potassium ferrioxalate actinometer [28].

A solution of FeCl_3 ($c \approx 6 \times 10^{-3}$ M) in methanol was acidified with 10% HCl and mixed (1:1) with a solution of the hydroxamic acid in an appropriate solvent. The absorbance of the resulting mixture (pH 4.5) was measured at $\lambda = 535$ nm using FeCl_3 solution-solvent (1:1) as a reference. The concentrations of the hydroxamic acid were read from a calibration curve prepared for the solutions of hydroxamic acid in the range (6×10^{-6}) - (6×10^{-4}) M. Details of the HPLC analysis will be reported elsewhere [29].

2.3.2. Examination of the concentration effect

A solution of *N*-phenylbenzenecarbohydroxamic acid ($c \approx 7.5 \times 10^{-4}$ M) in THF was irradiated with a low pressure mercury Hanan St-40W lamp under nitrogen for 30 min. The temperature was kept at about 0 °C. The reaction mixture, which contained *N*-phenylbenzenecarbohydroxamic acid, benzanilide, benzoic acid, phenylhydroxylamine and *N,O*-dibenzoyl-*N*-phenylhydroxylamine, was evaporated using a rotary evaporator and was separated on a column (Silica gel 60M, E. Merck) using a chloroform-hexane (1:1) mixture as the eluent. The spectral characteristics and HPLC retention times of the obtained compounds were identical with those of the original samples.

N,O-Dibenzoyl-*N*-phenylhydroxylamine in THF ($c \approx 5 \times 10^{-4}$ M) was irradiated as described above. 70% conversion was observed after 50 min. The products benzanilide and benzoic acid were identified by comparison with the original samples using HPLC.

2.3.3. Quenching studies

Samples of the hydroxamic acid in cyclohexane ($c = 0.8 \times 10^{-4}$ M) were prepared and analysed as for the quantum yield determinations except that they were degassed and varying amounts of 1,3-hexadiene were added. Eight concentrations of diene in addition to the blank containing no 1,3-hexadiene were used for the Stern-Volmer analysis. Repeated determinations agreed within $\pm 10\%$.

3. Results and discussion

The quantum yields of the photoreaction were calculated from the ratio of the decrease in the number of *N*-phenylbenzenecarbohydroxamic acid molecules to the number of quanta absorbed by the hydroxamic acid. The purple-coloured complex of the hydroxamic acid with Fe^{3+} (1:1, $\lambda_{\text{max}} = 535$ nm) formed the basis for the sensitive quantitative determination of the substrate concentration. The results agreed (within experimental error) with those obtained by the HPLC method, used also for the analysis of the photo-product mixtures.

The effect of the experimental conditions (*e.g.* solvent, wavelength and concentration) on the quantum yield was studied and the results are given in Table 1.

Our preliminary results [22] suggested that the quantum yield of the reaction depends on the solvent. The present systematic studies of the photoreaction quantum yield in non-polar, polar aprotic and polar protic solvents confirm that an increase in solvent polarity favours the photo-stabilization of the hydroxamic acid. As can be seen in Table 1, practically no photochemical reaction occurs in a methanol-water mixture.

An upfield shift of the ^{17}O NMR carbonyl oxygen signal in alcohol was attributed to an increased contribution of the polar valence bond resonance

TABLE 1

Quantum yield of *N*-phenylbenzenecarbohydroxamic acid photodestruction in polar and non-polar solvents

<i>Solvent</i>	<i>Quantum yield</i>
Cyclohexane	0.067 ^a , 0.001 ^b , 0.055 ^c
Cyclohexane + He	0.083 ^a
Cyclohexane + O ₂	0.059 ^a
Dioxane	0.0412 ^a
Tetrahydrofuran	0.028 ^a
Methanol	0.0073 ^a , 0.001 ^d
Methanol + He	0.0083 ^a
Methanol + O ₂	0.0059 ^a
Methanol + H ₂ O (1:1 by volume)	0.001 ^a , 0.001 ^d
Methanol (pH ≈ 13) + sodium methanolate	0.033 ^a , 0.092 ^d
Methanol-NaOH(aq) (1:1 by volume) (pH ≈ 13)	0.012 ^a , 0.069 ^d

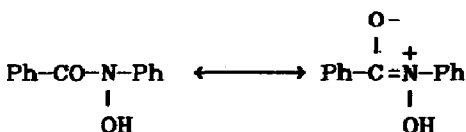
^aIn a quartz cell with a KJ/J₂ filter ($\lambda \approx 254$ nm).

^bIn a Pyrex cell with a CuSO₄ filter (without acetophenone).

^cIn a Pyrex cell with a CuSO₄ filter (with acetophenone).

^dIn a Pyrex cell ($\lambda > 300$ nm).

structure C⁺-O⁻ [20], and thus to an enhanced contribution from the canonical structure G:



The UV spectra of *N*-phenylbenzenecarbohydroxamic acid in cyclohexane-methanol varied with the composition of the solvent (Fig. 1). In order to observe the relation between the quantum yield of the hydroxamic acid photodestruction and hydrogen-bond formation, the quantum yields of the reaction in cyclohexane-methanol were plotted against the methanol concentration. As can be seen in Fig. 2, it is the protonation of the hydroxamic acid which leads to the photostability of the compound.

To all practical purposes, *N*-phenylbenzenecarbohydroxamic acid does not fluoresce. In ethylene glycol-water (9:1) glass a weak fluorescence and phosphorescence can be observed, both being typical of $n-\pi^*$ transitions. All $n-\pi^*$ reactions are known to proceed preferentially via D states [30]; primary $n-\pi^*$ photochemical processes produce radicals and the overall photoreactions mimic radical chemistry. So it seems reasonable to assume that the acyl aminyloxide (nitroxide) radical observed during ESR experiments [23] is the primary intermediate of the photochemical reaction of *N*-phenylbenzenecarbohydroxamic acid.

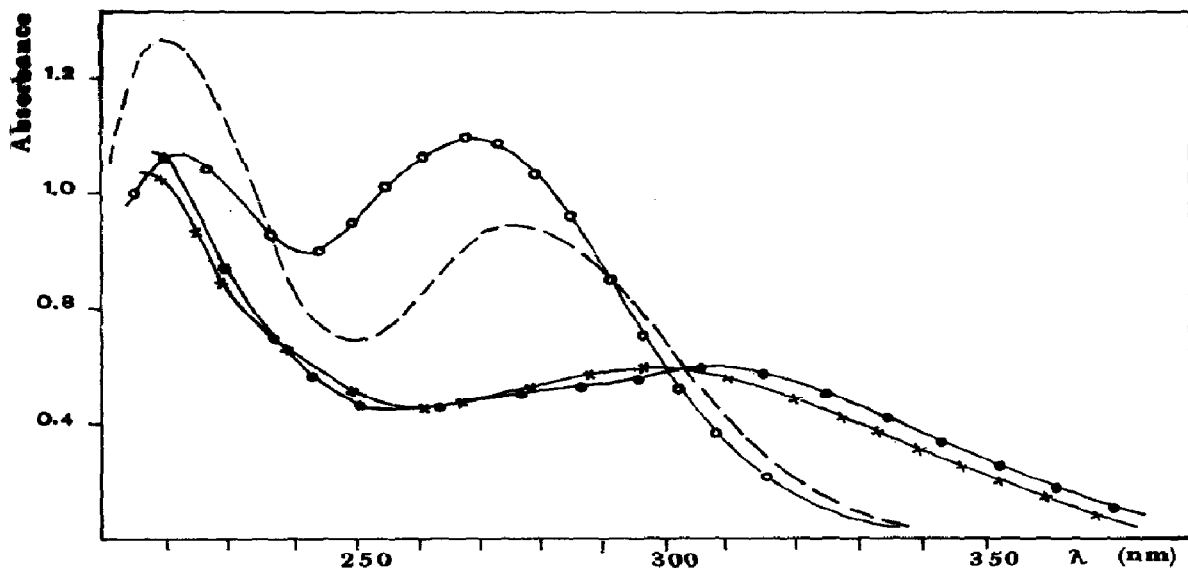


Fig. 1. UV spectra of *N*-phenylbenzenecarbohydroxamic acid ($c = 7.5 \times 10^{-5}$ M, $d = 2$ cm): ---, cyclohexane; —○—, methanol; —●—, methanol (pH \approx 13); —×—, methanol-NaOH(aq) (pH \approx 13).

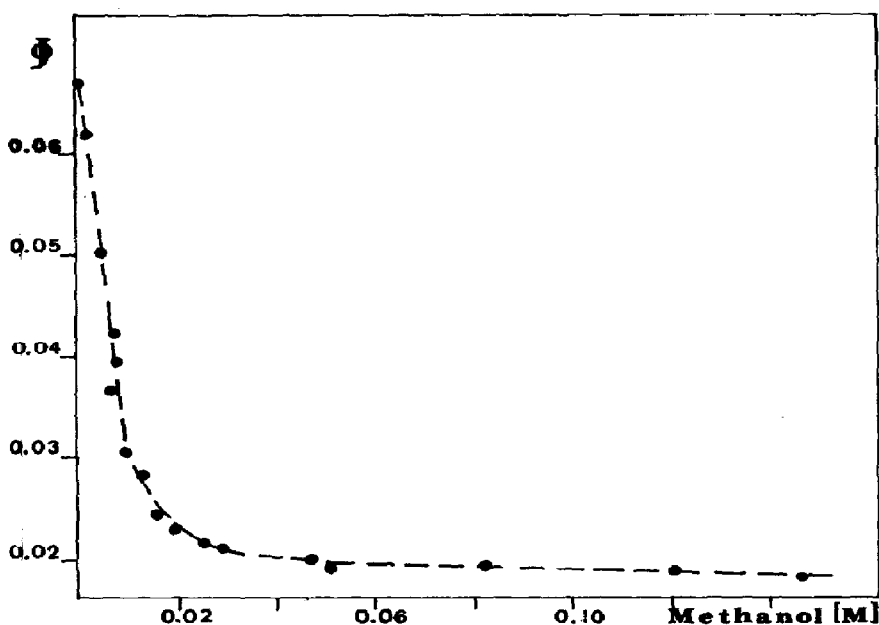


Fig. 2. Influence of methanol on the quantum yield of the *N*-phenylbenzenecarbohydroxamic acid photoreaction in cyclohexane ($\lambda \approx 254$ nm).

Any factor that increases the degree of p character of the C—N bonds in the aminyloxides (nitroxides) tends to decrease the p character and hence increase the s character of the nitrogen lone pair. As a consequence, the

overlap between the nitrogen lone pair orbital and the oxygen 2p unpaired electron orbital will decrease. Since this overlap stabilizes the aminyloxy, any decrease in the extent of the overlap will destabilize the radical and cause the strength of the OH bond to increase. For example, the O—H bond strength found for the hydrogenated precursors of the 2,2,6,6-tetramethylpiperidine-*N*-oxyl and di-*tert*-butyliminoxy radicals [31]



are 69.6 kcal mol⁻¹ and 84.3 kcal mol⁻¹ respectively.

The principal effect of the acyl group is to delocalize the nitrogen lone pair and thus concentrate spin on the nitroxide oxygen (structure E). As a result the O—H bonds of hydroxamic acids are generally stronger than those in simple hydroxylamines [32]. Thus, solvation of the carbonyl group with a protic solvent which increases the contribution of the canonical structure G (*e.g.* enhances nitrogen lone-pair delocalization) may make photo-oxidation more difficult.

It has been concluded on the basis of ¹⁷O NMR studies that an unexpectedly large charge delocalization must take place on deprotonation of the *N*-substituted hydroxamic acid, to give a species which can be represented by resonance structure B. Independent support of this conclusion is provided by the large bathochromic shift observed in the UV spectra of the ions of *N*-arylhydroxamic acids [33]. It has been suggested that structure B makes a major contribution to the anion of *N*-phenylbenzenecarbohydroxamic acid [20, 22] because of the close similarity of its absorption (Fig. 1) to that of *C,N*-diphenylnitronone [34].

It can be seen in Table 1 that the results of our present examinations show the quantum yield of the *N*-phenylbenzenecarbohydroxamic acid anion photoreaction to be wavelength dependent, and that the highest quantum yield is for the anion in methanol irradiated at $\lambda > 300$ nm. As was observed previously for the neutral molecule, the quantum yield of anion photodestruction is reduced in the presence of water. The resemblance of the UV spectrum of the anion to that of nitronone led us to the conclusion that it must be the nitronone-like chromophore which is responsible for the formation of the photoproducts. Therefore oxaziridine formation should be considered. Oxaziridines have been postulated to be intermediates in a number of photoreactions, for example the photodecomposition of oximes leading to Beckmann rearrangements [35].

No oxaziridine ring formation was observed during our experiments. However, this was to be expected, because *N*-aryl-substituted oxaziridines are not sufficiently stable to be isolated at room temperature. For example, the IR spectrum of α -*N*-diphenyloxaziridine has been recorded only at 77 K [36]. In this study we have observed that solvation with water leads to a decrease in the quantum yield of the photoreaction of the hydroxamic acid anion. Thus it has not been excluded that the reaction may occur via oxa-

ziridine formation. The solvation of the neutral *N*-phenylbenzenecarbohydroxamic acid molecule with a protic solvent which enhances the contribution of the nitron-like structure may photostabilize the compound, making the formation of oxaziridine difficult.

Benzanilide appeared to be the main product of the irradiation of *N*-phenylbenzenecarbohydroxamic acid in dilute solutions in all the solvents used. For example, it amounts to 80% of the photoproducts after irradiation in cyclohexane ($c \approx 7 \times 10^{-5}$ M), 73% in THF ($c \approx 7.5 \times 10^{-5}$ M) and 70% in methanol ($c \approx 1 \times 10^{-4}$ M, pH > 13) (see Table 2).

Small amounts of benzoic acid and nitrosobenzene were also formed. On prolonged irradiation benzanilide underwent the Fries photorearrangement, this being fast in cyclohexane and slow in alcohol, as reported in ref. 15.

Photoirradiation of more concentrated solutions ($c \geq 5 \times 10^{-4}$ M) resulted in the formation of a new photoproduct which had the IR spectrum typical of an *N,O*-diacylhydroxylamine ($\nu_{s(\text{CO})} = 1760 \text{ cm}^{-1}$, $\nu_{s(\text{CN})} = 1685 \text{ cm}^{-1}$) and the same retention time (HPLC) as *N,O*-dibenzoyl-*N*-phenylhydroxylamine. The compound was photolabile and decomposed to benzanilide and benzoic acid on prolonged irradiation. It was also transformed to these products on standing in solution. Photolysis of independently prepared *N,O*-dibenzoyl-*N*-phenylhydroxylamine in THF afforded benzanilide and benzoic acid. The same products were detected by HPLC after the solution had been kept in the dark for 2 days.

Oxidation of *N*-arylcarbohydroxamic acids with silver oxide has been reported to give the corresponding aryl nitroso compounds, *N,O*-dibenzoyl-*N*-phenylhydroxylamines, aryl nitro compounds and amides [26]. It seems to be reasonable to assume that *N,O*-dibenzoyl-*N*-phenylhydroxylamine formed during the photoirradiation of concentrated solutions of *N*-phenyl-

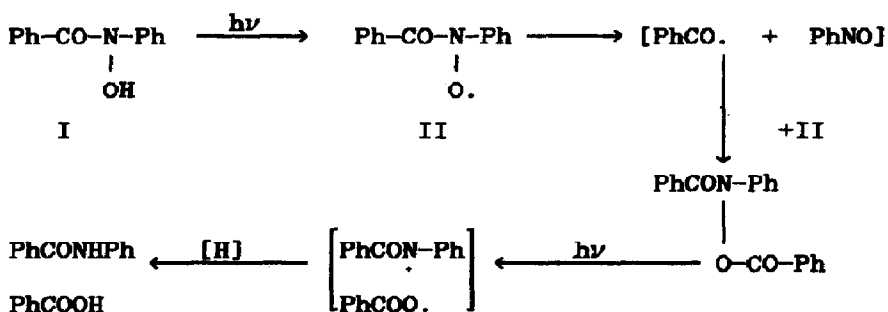
TABLE 2

Products of the photochemical reaction of *N*-phenylbenzenecarbohydroxamic acid ($\lambda \approx 254 \text{ nm}$; conversion, about 30%)

Solvent	Concentration (M)	Yield (%) of photoproduct ^a			
		Benzanilide	Benzoic acid	Nitrosobenzene	<i>N,O</i> -Dibenzoyl- <i>N</i> -phenylhydroxylamine
Cyclohexane	7×10^{-5}	80	10	9	Not detected
	6.5×10^{-4}	34	2	15	40
Tetrahydrofuran	7.5×10^{-5}	73	15	12	Not detected
	7.5×10^{-4}	35	4	17	42
Methanol (pH > 13)	1×10^{-4}	70	5	9	12
	6×10^{-4}	45	7	15	26

^aChemical yields, calculated in relation to the hydroxamic acid consumed.

benzenecarbohydroxamic acid arises in a similar way, by an intermolecular electrophilic acylation reaction (Scheme 2).



Scheme 2.

4. Nature of the excited state

Photosensitization and quenching processes which involve energy transfer of the type $D^* + A \rightarrow D + A^*$ are often used to control photochemical sequences and to study reaction mechanisms [30]. Triplet-triplet energy transfer may be used to populate indirectly A^* states or to quench D^* states.

The energies of the singlet (S_1) and triplet (T_1) states of *N*-phenylbenzenecarbohydroxamic acid are $E_S = 107 \text{ kcal mol}^{-1}$ and $E_T = 66 \text{ kcal mol}^{-1}$ respectively.

Acetophenone was chosen as the triplet photosensitizer. This compound has a high triplet energy ($E_T = 72 \text{ kcal mol}^{-1}$ [27]) (and thus the energy transfer was exothermic), a long triplet lifetime ($\tau_T \approx 100 \mu\text{s}$) and a fast rate of intersystem crossing relative to the other deactivation processes of S_1 ($\Phi_{ST} = 1.0$), and it absorbs in a region of the spectrum (up to about 364 nm) where the hydroxamic acid does not absorb significantly.

When a solution of *N*-phenylbenzenecarbohydroxamic acid ($c = 1 \times 10^{-4} \text{ M}$) in cyclohexane containing acetophenone ($c = 2.2 \times 10^{-2} \text{ M}$) was irradiated using a CuSO_4 filter, the hydroxamic acid photodestruction quantum yield was found to be only slightly lower than that of the photoreaction in cyclohexane at $\lambda = 254 \text{ nm}$ without a sensitizer (Table 1). No photoreaction was observed during the irradiation of hydroxamic acid in cyclohexane ($c = 1 \times 10^{-4} \text{ M}$) with the CuSO_4 filter when acetophenone was absent.

It is clear that the exciting light was absorbed by acetophenone and its triplet excitation energy passed on to the *N*-phenylbenzenecarbohydroxamic acid.

Oxygen was also found to have an effect on the quantum yield of hydroxamic acid photodestruction: there was a 28% difference in quantum yield between an experiment conducted in oxygen-saturated solution and one carried out with helium (Table 1). This result indicates that the triplet excited state of the hydroxamic acid may be quenched by oxygen.

1,3-Dienes have been found to quench T_1 ($n-\pi^*$) of alkanones [30] with rate constants approaching those for diffusion ($k_q = 10^9 - 10^{10} \text{ s}^{-1}$).

We have found that 1,3-hexadiene quenches the photochemical reaction of *N*-phenylbenzenecarbohydroxamic acid. The compound was irradiated at 254 nm in solutions containing various amounts of 1,3-hexadiene in cyclohexane. The quantum yields of both hydroxamic acid photodestruction and benzanilide formation were determined by HPLC. A plot of Φ_0/Φ_q vs. $[Q]$ (where Φ_0 is the quantum yield of the reaction measured in the absence of the quencher 1,3-hexadiene and Φ_q is the quantum yield measured in the presence of the quencher) is shown in Fig. 3.

When a Stern-Volmer treatment, *e.g.* a plot of Φ_0/Φ_q vs. $[Q]$, of quenching data gives a linear curve, the slope is equal to $k_q\tau$ where k_q is the rate constant for quenching of the triplet state of the reacting compound by quencher and τ is the triplet lifetime in the absence of quencher. If the k_q are known the τ^{-1} can be calculated.

However, the plot for *N*-phenylbenzenecarbohydroxamic acid destruction is non-linear. Figure 3 shows that above a concentration of 0.2 M 1,3-hexadiene there is little or no further quenching. The observed plot, with curvature at low $[Q]$ and a plateau at high $[Q]$, reflects the situation in which both S_1 and T_1 undergo the same reaction [37]. Thus it can be concluded that the main photoproduct is formed from both the S_1 and the T_1 state

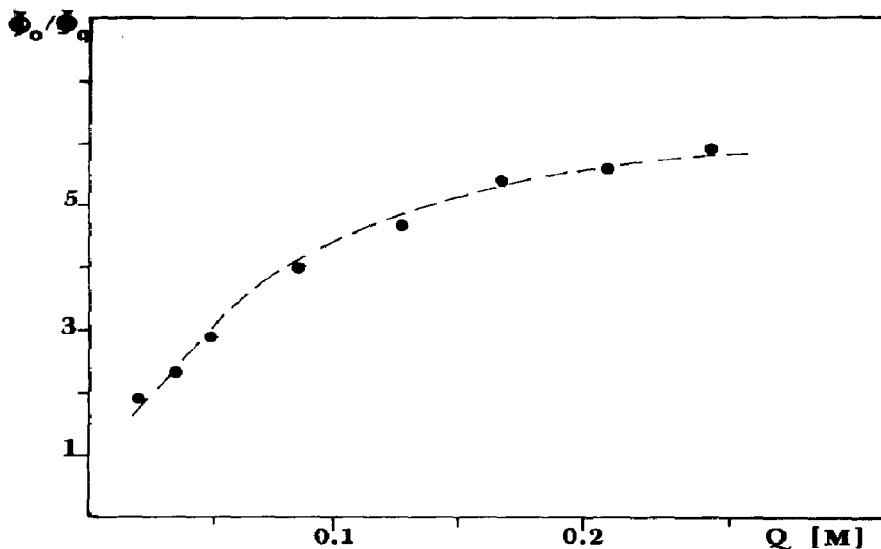
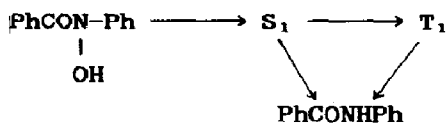


Fig. 3. Quenching of the photoreaction of *N*-phenylbenzenecarbohydroxamic acid in cyclohexane by 1,3-hexadiene.

We assume that at high concentrations of diene all the triplets are selectively quenched and that none of the singlets is quenched. In this case the value of Φ_o/Φ_q does not vary with $[Q]$ at high concentrations of $[Q]$. On the contrary, at low concentrations of $[Q]$, both S_1 and T_1 react but T_1 is quenched. Thus, the intercept along the plateau may be considered to be equal to Φ_o/Φ_s for an S_1 reaction [37].

The percentage of singlet reaction may be calculated since it is equal to $\{(\Phi_o/\Phi_q)/(\Phi_o/\Phi_s)\} \times 100$. We calculated Φ_o^T/Φ_q^T , i.e. the relative quantum yield for the triplet reaction, 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. $[Q]$ for low $[Q]$ gives k for the triplet hydroxamic acid photodestruction ($k\tau = 12.5$ and $\tau^{-1} = 4 \times 10^8$ s⁻¹ (assuming $k_q = 5 \times 10^9$ s⁻¹)). The slope of Φ_o^T/Φ_q^T vs. $[Q]$ obtained for benzanilide formation was the same within experimental error.

Acknowledgments

This work was supported by the Polish Academy of Science. E.L.-K. is indebted to Professor H. Iwamura for his interest and advice during preliminary experiments carried out when she stayed in Japan in 1981. We appreciate the help of Professor S. Schneider, who kindly offered some chemicals necessary for this work.

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