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Pyrene-Sensitized Photolysis of *N*-(1-Naphthylsulfonyl)-*N*-phenyl-*O*-(*p*-toluoyl)hydroxylamine

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The title hydroxylamine (SO_2NT) underwent singlet-sensitized photolysis in the presence of pyrene to give rearrangement and fragmentation products. SO_2NT was found to quench both pyrene-monomer and -excimer fluorescences. The presence of a sulfonyl group with a semipolar-bond character in SO_2NT was suggested to be responsible for a pronounced termolecular interaction between the pyrene excimer and SO_2NT to result in a quenching of the excimer emission. An energetic consideration of the pyrene monomer and excimer as well as the N–O bond cleavage of SO_2NT allows us to propose that not the excimer, but the monomer, activates SO_2NT to induce its sensitized decomposition. An analysis of the solvent polarity effects on both limiting the quantum yields for the appearance of the products and the quenching of pyrene fluorescence by SO_2NT demonstrated that the sensitized reaction proceeds by a singlet-exciplex mechanism in benzene, whereas an electron-transfer mechanism predominates in acetonitrile.

The photochemical and photophysical behavior of hydroxamic acids and their derivatives has recently attracted considerable attention from synthetic and mechanistic points of view.[1)] In the course of our systematic study on the excited-state behavior and reactivity of hydroxamic acid derivatives,[2)] we have found that the triplet-sensitized photolysis of *N*-(1-naphthylsulfonyl)-*N*-phenyl-*O*-(*p*-toluoyl)hydroxylamine (SO_2NT, **1**) gives 1,3- and 1,5-rearrangement products along with fragmentation products,[3)] although *N*-(1-naphthoyl)-*N*-phenyl-*O*-(*p*-toluoyl)hydroxylamine (NT) affords only fragmentation products under the same reaction conditons.[4)] The observation of toluoyloxyl-migrated products can be explained in terms of an efficient intersystem crossing of an initially-formed triplet radical pair into a singlet radical pair, the recombination of which eventually yields the rearrangement products. Internal heavy-atom-like effects of the partially-charged sulfonyl sulfur and oxygen atoms in a SO_2NT molecule were suggested to be responsible for this effective spin inversion.

A dramatic difference in the product distribution derived from the triplet sensitization of SO_2NT and NT stimulated us to compare the behavior of the pyrene-sensitized reaction of SO_2NT with that of NT in benzene, 1,2-dichloroethane, and acetonitrile. The latter sensitized reaction in nonpolar solvents has already been established to proceed through a singlet-exciplex intermediate which gives rearrangement and fragmentation products, the relative quantum yields of which are subject to pronounced solvent polarity effects.[2d)]

Results and Discussion

Pyrene-Fluorescence Quenching. Low concentrations of pyrene (less than 10^{-4} M, 1 M=1 mol dm^{-3}) could not bring about a sensitized decomposition of SO_2NT (5.0×10^{-3} M) to give measurable amounts of products with HPLC under conditions for the quantum-yield measurements. The effect of the pyrene concentration on the extent of decompositon of SO_2NT revealed that one must use relatively high concentrations of a sensitizer (greater than 10^{-3} M) in order to obtain reliable quantum yields for the reaction. Thus, pyrene-fluorescence quenching experiments were carried out under nitrogen by using the same concentration of pyrene (3.0×10^{-3} M) as that employed for fluorescence quenching by NT, for a comparison.[2d)] Pyrene at this concentration exhibits a monomer fluorescence at 395 nm and an excimer one at 470 nm at 24±1°C.

The monomer fluorescence was efficiently quenched by SO_2NT ($1.3—10\times10^{-3}$ M; excitation wavelength, $\lambda_{\rm ex}=366$ nm) following the Stern–Volmer equation: $I_0^{\rm M}/I^{\rm M}=1+K_{\rm SV}^{\rm M}[SO_2NT]$, where $I^{\rm M}$ and $I_0^{\rm M}$ refer to the monomer-fluorescence intensities at 395 nm with and without SO_2NT, respectively. From the slopes of the linear Stern–Volmer plots shown in Fig. 1, we obtained quenching constants ($K_{\rm SV}^{\rm M}$) of 230, 320, and 310 M^{-1} in benzene, 1,2-dichloroethane, and acetonitrile, respectively. A consideration of the relative excited-state energies of SO_2NT (the first singlet excitation energy, $E_{\rm S}=88$ kcal mol^{-1}; the first triplet excitation energy, $E_{\rm T}=59$ kcal mol^{-1}; 1 kcal=4.184 kJ)[3)] to pyrene ($E_{\rm S}=77$, $E_{\rm T}=48$ kcal mol^{-1})[5)] makes both singlet–singlet and triplet–triplet energy transfers from excited pyrene to SO_2NT very unlikely. Thus, observation of the efficient monomer-fluorescence quenching suggests the involvement of a nonemissive singlet exciplex in the quenching process. However, the magnitude of the free-energy change (ΔG of -13 kcal mol^{-1}) for an electron transfer from singlet pyrene to SO_2NT in acetonitrile[6)] allows us to propose that emission quenching by electron transfer occurs in preference to quenching via nonemissive singlet-exciplex formation in the polar solvent, acetonitrile.

On the other hand, the $I_0^{\rm E}/I^{\rm E}$ value for the excimer-fluorescence quenching ($\lambda_{\rm ex}=366$ nm) increases as the SO_2NT concentration increases; this upward-curving behavior is most remarkable in acetonitrile (Fig. 2). By

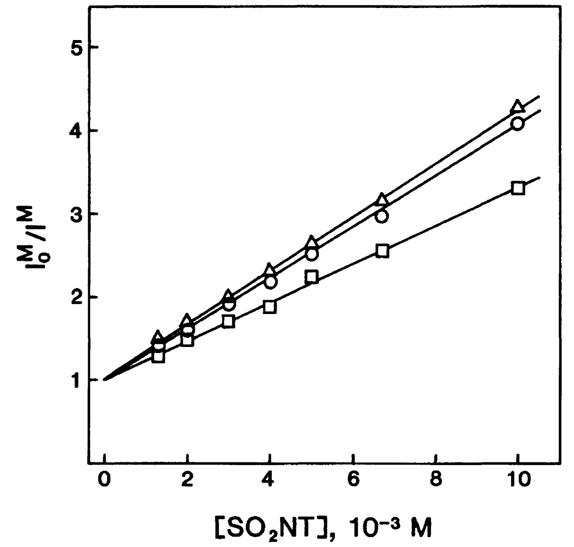


Fig. 1. Stern–Volmer plots for the monomer-fluorescence quenching of pyrene (3.0×10^{-3} M) by SO_2NT in acetonitrile (○), 1,2-dichloroethane (△), and benzene (□) under nitrogen at 24±1°C.

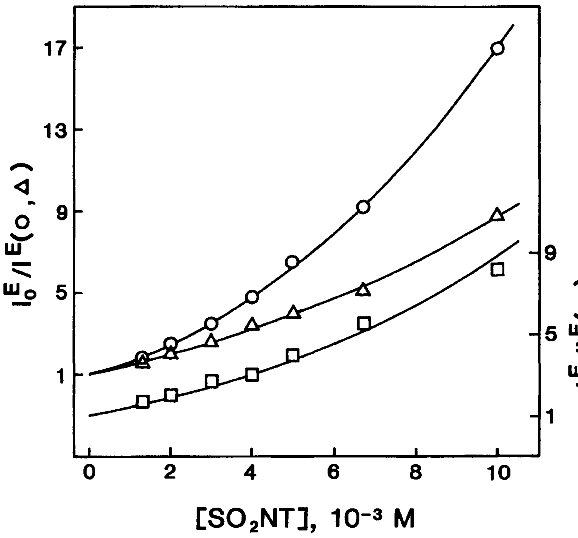


Fig. 2. Stern–Volmer plots for the excimer-fluorescence quenching of pyrene (3.0×10^{-3} M) by SO_2NT in acetonitrile (○), 1,2-dichloroethane (△), and benzene (□) under nitrogen at 24±1°C. I^E and I_0^E refer to the fluorescence intensities at 470 nm of pyrene excimer with and without SO_2NT, respectively.

applying a steady-state approximation to Scheme 1, we obtain the following equations for the monomer-emission quenching and excimer-emission quenching:

$$I_0^M/I^M = 1 + K_{SV}^M[SO_2NT] \tag{1}$$

and

$$I_0^E/I^E = (1 + K_{SV}^M[SO_2NT])(1 + K_{SV}^E[SO_2NT]), \tag{2}$$

where $K_{SV}^M = k_q^M/(k_{f1} + k_{nd1} + k_{ME}[Py])$ and $K_{SV}^E = k_q^E/(k_{f2} + k_{nd2} + k_{EM})$. If K_{SV}^E is not much less than K_{SV}^M, we expect to observe upward-curving Stern–Volmer plots. This expectation is consistent with the obtained results, thus providing strong evidence for the occurrence of excimer-emission quenching by SO_2NT. Based on the observed values of K_{SV}^M and I_0^E/I^E, the K_{SV}^E values were determined to be 160±10, 110±10, and 300±10 M^{-1} in benzene, 1,2-dichloroethane, and acetonitrile, respectively. The most efficient excimer-emission quenching in acetonitrile may indicate that a charge-transfer-type termolecular interaction is responsible for this emission quenching.[9]

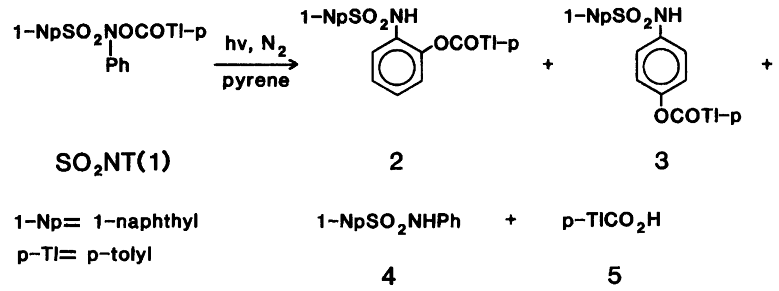
$$\begin{aligned}
Py(S_0) &\xrightarrow{h\nu} Py(S_1)\\
Py(S_1) &\xrightarrow{kf1} Py(S_0)\\
Py(S_1) &\xrightarrow{knd1} Py(S_0)\\
Py(S_1) + Py(S_0) &\xrightarrow{k_{ME}} Py{\bullet}Py(S_1)\\
Py{\bullet}Py(S_1) &\xrightarrow{kf2} 2Py(S_0)\\
Py{\bullet}Py(S_1) &\xrightarrow{knd2} 2Py(S_0)\\
Py{\bullet}Py(S_1) &\xrightarrow{k_{EM}} Py(S_1) + Py(S_0)\\
Py(S_1) + SO_2NT(S_0) &\xrightarrow[benzene]{kq^M} Py{\bullet}SO_2NT(S_1)\\
[\,Py(S_1) + SO_2NT(S_0) &\xrightarrow[CH_3CN]{kq^M} Py^{\bullet+} + SO_2NT^{\bullet-}\,]\\
Py{\bullet}SO_2NT(S_1) &\xrightarrow{kd} Py(S_0) + SO_2NT(S_0)\\
[\,Py^{\bullet+} + SO_2NT^{\bullet-} &\xrightarrow{kd} Py(S_0) + SO_2NT(S_0)\,]\\
Py{\bullet}Py(S_1) + SO_2NT(S_0) &\xrightarrow{kq^E} 2Py(S_0) + SO_2NT(S_0)
\end{aligned}$$

k: rate constant for each process Py: pyrene

Scheme 1.

In a previous study[2d] we found that both the monomer and excimer fluorescences are quenched by NT according to linear Stern-Volmer relationships, giving almost the same quenching constants (K_{SV}) in a given solvent: K_{SV} obtained from the monomer-emission quenching=70 (benzene), 62 (CH_2ClCH_2Cl), and 86 M^{-1} (CH_3CN) and K_{SV} evaluated from the excimer-emission quenching=88 (benzene), 66 (CH_2ClCH_2Cl), and 90 M^{-1} (CH_3CN). If the excimer-emission quenching by NT takes place to a negligible extent (K_{SV}^E in Eq. 2≈0), we have $I_0^E/I^E \approx I_0^M/I^M = 1 + K_{SV}^M[NT]$; thus, the result obtained for the NT-pyrene system can be explained in terms of the negligible contribution of the excimer-emission quenching to the magnitude of I_0^E/I^E. The finding that NT exclusively quenches the pyrene-monomer fluorescence, thus, provides supporting evidence for the previous assumption:[2d] only the pyrene monomer activates NT to cause its sensitized decomposition.

The S–O bond in a sulfonyl group has been suggested to have a somewhat large semipolar-bond character,[10] so that the sulfonyl sulfur and oxygen atoms in SO_2NT possess much greater positive and negative charges, respectively, compared with the amide carbonyl carbon and oxygen atoms in NT. The presence of a sulfonyl group with such a semipolar-bond character in SO_2NT,



Scheme 2.

increasing the reduction potential of NT (−1.86 V vs. SCE in CH_3CN)[2d] by 0.24 V, may be responsible for a pronounced termolecular interaction between the pyrene excimer and SO_2NT to result in substantial excimer quenching in any solvent examined.

Pyrene-Sensitized Photolysis. The pyrene (3.0×10^{-3} M)-sensitized photolysis of SO_2NT (1.3—10 $\times10^{-3}$ M) with 366-nm light under nitrogen at 26±3°C afforded the rearrangement (**2** and **3**) and fragmentation (**4** and **5**) products given in Scheme 2. The fact that only the singlet excited-state pyrene monomer activates NT to induce its decomposition allows us to assume that SO_2NT also undergoes sensitized photolysis through quenching of the pyrene-monomer fluorescence. If the quenching of the pyrene-excimer fluorescence by SO_2NT arises through a triplex intermediate, the energy of this intermediate must be much lower than that of pyrene excimer (ca. 60 kcal mol^{-1})[11] and, hence, may not be sufficient to cause an efficient cleavage of the N–O bond in a SO_2NT molecule with a bond dissociation energy of about 53 kcal mol^{-1}.[12] This consideration makes the assumption described above valid.

The sensitized reaction in 1,2-dichloroethane was not affected by 1,3-cyclohexadiene (1.0—5.0×10^{-2} M; $E_S=97$, $E_T=52.4$ kcal mol^{-1})[5] and *trans*-stilbene (1.0—5.0×10^{-2} M; E_S=94, E_T<50 kcal mol^{-1}),[5] which are known to be quenchers for the NT (E_S=90, E_T=59 kcal mol^{-1})[2b] and pyrene triplets, respectively. These findings are compatible with a singlet mechanism.

As typically demonstrated in Fig. 3, a relationship between the reciprocal of the quantum yields for the reaction ($1/\Phi$) and the reciprocal of the SO_2NT concentration ($1/[SO_2NT]$) can be approximated as being linear in the concentration range of SO_2NT examined. Similar linear plots were obtained for other solvents. Table 1 gives the limiting quantum yields (Φ_{lim}) estimated from the intercepts of linear double-reciprocal Stern–Volmer plots. An inspection of Table 1 reveals that the enhanced solvent polarity has a tendency to decrease $\Phi_{2,\text{lim}}+\Phi_{3,\text{lim}}$, accompanied by an increase in $\Phi_{5,\text{lim}}$, being consistent with a tendency observed in the sensitized photolysis of NT.[2d] However, the Φ_{lim} value for any product does not correlate with the solvent viscosity. This should be due to the very limited viscosity range of the solvents used.[2c]

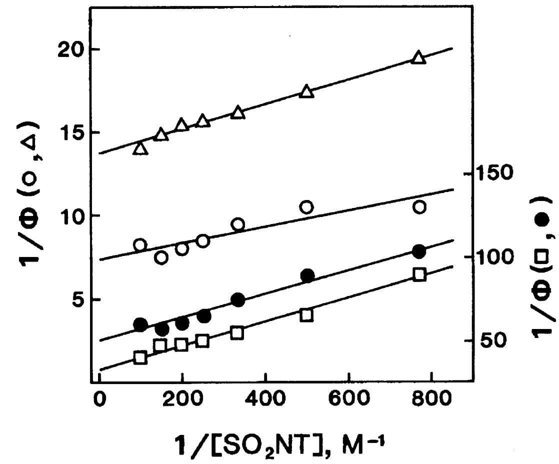


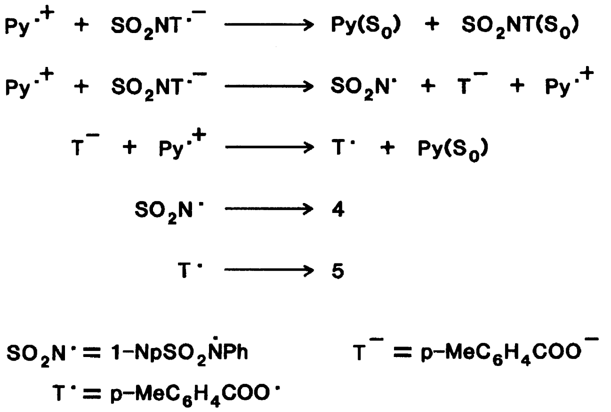
Fig. 3. Stern–Volmer plots of $1/\Phi_{-SO_2NT}$ (○), $1/\Phi_2$ (□), $1/\Phi_3$ (●), and $1/\Phi_5$ (△) versus $1/[SO_2NT]$ for the pyrene (3.0×10^{-3} M)-sensitized photolysis of SO_2NT with 366-nm light in benzene under nitrogen at 26±3°C.

Table 1. Limiting Quantum Yields (Φ_{lim}) for the Pyrene-Sensitized Photolysis of SO_2NT with 366-nm Light under Nitrogen at 26±3°C

Solvent	Φ_{lim}				
(ε,[a] η[b])	Φ_{-SO_2NT}	Φ_2	Φ_3	Φ_4	Φ_5
Benzene	0.14	0.03	0.02	—[c]	0.07
(2.274, 0.562)		(0.03)[d]	(0.02)[d]	(0.07)[d]	(0.04)[d]
CH_2ClCH_2Cl	0.11	0.01	0.01	0.02	0.08
(10.37, 0.730)		(0.03)[d]	(0.01)[d]	(0.07)[d]	(0.06)[d]
CH_3CN	0.14	<0.01	<0.01	0.03	0.14
(35.94, 0.326)		(<0.01)[d]	(<0.01)[d]	(0.01)[d]	(0.15)[d]
CH_2ClCH_2Cl[e]	0.10	0.03	0.03	0.01	0.05

a) Dielectric constant at 25 °C (see Ref. 13). b) Viscosity in centipoise (cP, 1 cP=10^{-3} Pa s) at 30 °C (see Ref. 13). c) Could not be determined because of overlapping with the HPLC peak of benzene. d) Φ_{lim} for the appearance of the corresponding products derived from the pyrene-sensitized photolysis of NT (see Ref. 2d). e) Direct photolysis with 313-nm light (see Ref. 3).

The previous finding,[3] that the independently-generated SO_2NT radical anion decomposes to exclusively afford **4** and **5**, provides supporting evidence for the predominant operation of an electron-transfer mechanism in acetonitrile (Scheme 3), as has already been suggested based on a thermodynamic consideration of

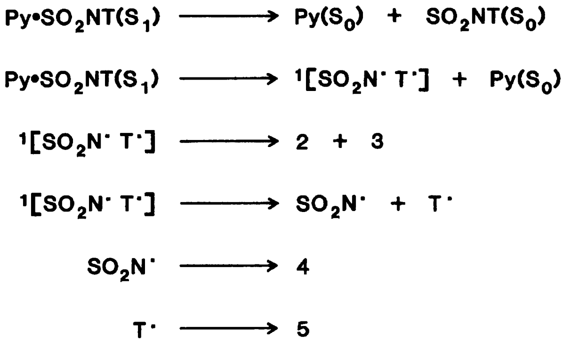


Scheme 3.

the quenching of the pyrene-monomer fluorescence by SO$_2$NT in this polar solvent. In competition with deactivation by back electron transfer from the SO$_2$NT radical anion SO$_2$NT$^{\bullet-}$ to the pyrene radical cation Py$^{\bullet+}$ (Scheme 3), SO$_2$NT$^{\bullet-}$ may readily decompose to afford the sulfonamidyl radical (1-NpSO$_2\dot{\mathrm{N}}$Ph) and *p*-methyl benzoate (*p*-MeC$_6$H$_4$COO$^-$), which is oxidized by Py$^{\bullet+}$ to give the toluoyloxyl radical (*p*-MeC$_6$H$_4$COO$^\bullet$) and pyrene. The amidyl and toluoyloxyl radicals, thus formed, abstract hydrogen atoms from solvent molecules to produce **4** and **5**.

On the other hand, the quantum yield of each product for direct photolysis (Table 1), proceeding through the singlet excited state (radical-pair mechanism),[3] agrees with the corresponding Φ_{lim} in benzene within the experimental error; thus, a singlet-exciplex mechanism predominates in the nonpolar solvent, benzene (Scheme 4). This conclusion is also substantiated by the finding that the pyrene-monomer emission is quenched by SO$_2$NT to a considerable extent in this nonpolar solvent. Competing with deactivation of the singlet exciplex Py·SO$_2$NT(S$_1$) (Scheme 4), this intermediate undergoes decomposition to result in the formation of the singlet geminate-radical pair ^{1}[1-NpSO$_2\dot{\mathrm{N}}$Ph *p*-MeC$_6$H$_4$COO$^\bullet$] and pyrene. The recombination of this radical pair eventually yields **2** and **3**, while the "out-of-cage" reaction of 1-NpSO$_2\dot{\mathrm{N}}$Ph and *p*-MeC$_6$H$_4$COO$^\bullet$ leads to **4** and **5**. The formation of negligible amounts of toluene suggests that hydrogen abstraction of *p*-MeC$_6$H$_4$COO$^\bullet$ occurs in preference to its decarboxylation under our reaction conditions. In 1,2-dichloroethane both of these two mechanisms may operate to afford products **2**—**5** in limiting quantum yields (shown in Table 1).

The Φ_{lim} value of each product (Table 1) is not much different between the SO$_2$NT-pyrene and NT-pyrene systems in a given solvent, implying a small difference in reactivity between the Py·SO$_2$NT(S$_1$) and Py·NT(S$_1$) intermediates in benzene, or between the Py$^{\bullet+}$/SO$_2$NT$^{\bullet-}$ and Py$^{\bullet+}$/NT$^{\bullet-}$ intermediates in acetonitrile, although a comparison of the $K_{\mathrm{SV}}^{\mathrm{M}}$ values for SO$_2$NT with those for NT reveals that SO$_2$NT has a stronger tendency to form a singlet exciplex in a nonpolar solvent or a radical ion pair in a polar solvent than does NT.



Scheme 4.

Experimental

General Methods An analysis of the photoproducts other than toluene was performed on a Hitachi Model 638-50 high-performance liquid chromatograph (HPLC) equipped with a 2.6×500-mm ODS (Hitachi gel #3050) column or on a Shimadzu Model LC-6A HPLC equipped with a 4.6×250-mm ODS (Zorbax) column. Accurate concentrations of the starting material and the products were determined by the use of linear calibration curves for each compound, made under the same analytical conditions (mobile phase, CH$_3$CN : H$_2$O=62 : 38 v/v; detection wavelength=230 or 240 nm). The quantification of toluene was carried out on a Shimadzu Model GC-8AP gas chromatograph using a 3.0×3000-mm glass column packed with 10% Silicone SE-30 on Uniport B (60/80 mesh, Gasukuro Kogyo). Fluorescence spectra were measured under nitrogen with a Shimadzu Model RF-5000 spectrofluorimeter at room temperature (24±1°C).

Materials and Solvents. *N*-(1-Naphthylsulfonyl)-*N*-phenyl-*O*-(*p*-toluoyl)hydroxylamine (SO$_2$NT), *N*-[*o*-(*p*-toluoyloxy)phenyl]-1-naphthalenesulfonamide, *N*-[*p*-(*p*-toluoyloxy)phenyl]-1-naphthalenesulfonamide, and 1-naphthalenesulfonanilide were prepared and purified according to the method employed in our previous study.[3] Pyrene, *p*-toluic acid, toluene, *trans*-stilbene, and 1,3-cyclohexadiene were purified according to the previously described procedures.[2b,2d] The solvents used in this study were of spectroscopic grade (benzene and 1,2-dichloroethane) or purified by means of the standard method (acetonitrile).[13]

Quantum Yields. The quantum yields for the sensitized reaction were determined under nitrogen at low conversions (4—10%) of the starting SO$_2$NT by using a potassium tris(oxalato)ferrate(III) actinometer,[14] and are the average of more than five determinations. The same filter combination as used before[2d] was utilized for isolating 366-nm light from a 450 W high-pressure Hg lamp.

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