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Photo-Wolff Rearrangement of 2-Diazo-1,2-naphthoquinone: Stern–Volmer Analysis of the Stepwise Reaction Pathway[†]

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ABSTRACT

2-Diazo-1,2-naphthoquinone (1) and its derivatives are the photoactive components in Novolak photoresists. A femtosecond infrared study has established that the photoreaction of 1 proceeds largely by a concerted Wolff rearrangement yielding the ketene 1*H*-inden-1-ylidene-methanone (3) within 300 fs after excitation, but earlier trapping studies gave evidence for a minor reaction path via a carbene intermediate 1-oxo-2(1*H*)-naphthalenylidene (2) with a lifetime of about 10 ps. Here, we provide a quantitative assessment of the stepwise pathway by Stern–Volmer analysis of the trapping of 2 by methanol to yield 2-methoxy-1-naphthol (4). We conclude that the lifetime of the carbene 2 is at least 200 ps. Moreover, [3 + 2]cycloaddition of 2 and acetonitrile yielding 2-methylnaphth[2,1-*d*]oxazole (5) was observed. A comparison of the yields of 5 formed upon photolysis and upon thermolysis of 1 in acetonitrile provides evidence that a substantial part of the hot nascent carbene 2 formed photolytically rearranges to the ketene 3 during its vibrational relaxation (hot ground-state reaction).

INTRODUCTION

In 1944, Süs identified indenecarboxylic acid as the main product formed by irradiation of 2-diazo-1,2-naphthoquinone (**1**) in acidic aqueous solution (1). He also proposed a mechanism for the ring contraction (Wolff rearrangement via ketocarbene **2**) and designed a lithographic printing plate based on the increased solubility of those areas of a Novolak film that were exposed to light. Novolak mixtures containing **1** are still used in the fabrication of integrated circuits.

The mechanism of this reaction has been studied extensively. The product of the photo-Wolff rearrangement, ketene **3**, has been generated in rigid matrices at low temperatures and was identified by its UV (2–4) and IR (2,4,5) spectra. In aqueous solution, ketene **3** hydrolyzes through a long-lived enol intermediate, which finally ketonizes to a mixture of indenecarboxylic acids (6,7). Based on picosecond transient absorption measurements with the 5-sulfonate derivative of **1**, it was argued (4) that a short-lived α-ketocarbene intermediate **2** with a lifetime of about 20 ps precedes the formation ketene **3** (stepwise reaction, Fig. 1). However, a more recent study employing femtosecond time-resolved vibrational spectroscopy (8,9) has established that the major primary product, ketene **3**, is formed within 300 fs. The nascent ketene has an excess of vibrational energy; vibrational cooling of **3** occurs with a time constant of about 10 ps in methanol and 3 ps in water. Thus, partial formation of the ketene **3** via a short-lived carbene intermediate **2** with a lifetime on the order of 10 ps was not ruled out (8). Finally, the involvement of an oxirene intermediate was considered (10), but this was later ruled out on the basis of isotopic labeling experiments (11).

Two recent quantum dynamics calculations for the behavior of the singlet excited state of **1** (12,13) produced similar results: both the concerted Wolff rearrangement to ketene **3** and the stepwise reaction forming carbene **2** were predicted to occur on a time scale of hundreds of femtoseconds. Both studies predicted that reaction via **2** predominates. While the (partial) occurrence of a concerted rearrangement $^1\mathbf{1}^* \rightarrow \mathbf{3}$ on a subpicosecond time scale is thus well established, the amount proceeding in a stepwise fashion and the lifetime of the putative carbene **2** intermediate remain still uncertain. Michael Kasha devoted much of his recent work on the elucidation of concerted *versus* stepwise photo-induced double proton reactions (14).

An attempt to trap **2** with pyridine or 2-adamantanethione failed (15). In a subsequent study of the 5-sulfonate salt of **1** in aqueous alcohols, the formation of 2-alkoxy-1-naphthols and 1,2-naphthalenediol was observed, in addition to the main indenecarboxylic acid products formed from the ketene **3**. These side products were attributed to the addition of water or alcohols to carbene **2** (4). Similar findings obtained upon preparative irradiation of **1** in methanol had been reported previously (16). We report a detailed Stern–Volmer analysis of the products formed by trapping of **2** by methanol, 2-methoxy-1-naphthol (**4**) and by acetonitrile, 2-methylnaphth[2,1-*d*]oxazole (**5**), (Fig. 2). The formation of **5** upon photolysis or pyrolysis of **1** in acetonitrile has been observed previously (17) and a similar reaction was reported for diazoacenapthenone (18).

MATERIALS AND METHODS

Instrumentation. GC–MS analysis was performed on a Hewlett–Packard GC–MS (GC: 5890 series II, 25 m SE-52 capillary column; MS: 5970A series). For NMR measurements, a 300 MHz instrument (Varian VX300) was used. Irradiation experiments were carried out with a high-pressure mercury arc lamp (Hanau St 41, 200 W) equipped with various band-pass filters. Fluorescence spectra were measured at ambient temperature (ca. 22°C) on a Spex Fluorolog (Model 111c) spectrophotometer

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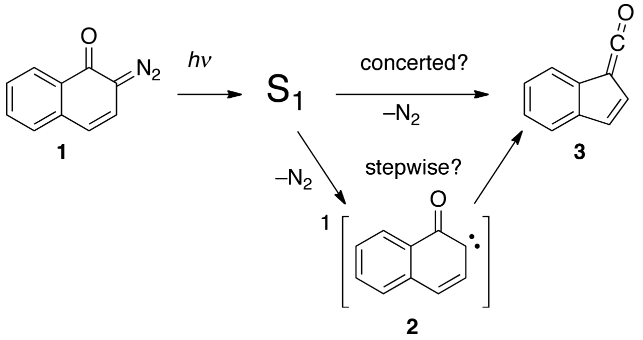

Figure 1. Concerted and stepwise pathways for the photo-Wolff rearrangement of **1**.

equipped with an EMI R928 phototube; excitation spectra were corrected by reference to a Rhodamine 6 G quantum counter. Emission spectra are uncorrected.

Synthesis of 2-methylnaphth[2,1-d]oxazole (**5**). 2-Diazo-1,2-naphthoquinone (**1**) was available from a previous study (7). 2-Methylnaphth [2,1-*d*]oxazole (**5**) was obtained by refluxing 0.9 g of **1** in acetonitrile at 80°C for 115 h. The solvent was evaporated and the residue chromatographed with methylene chloride over neutral aluminum oxide. The main fraction was distilled in vacuo (150°C) and crystallized from hexane, m.p. 38–39°C, lit. (19) 36–37°C. ^{1}H-NMR and UV–Vis spectra are in agreement with published data (20,21). ^{1}H-NMR (300 MHz, CD_3OD): δ 2.76 (s, 3H), 7.57 (t, 1H), 7.67 (t, 1H), 7.72 (d, 1H), 7.85 (d, 1H), 8.03 (d, 1H), and 8.21 ppm (d, 1H). MS: *m*/*e* 183 (M^+).

Product studies by GC–MS. Solutions of **1** (5×10^{-5} M, not degassed) in methanol or acetonitrile/methanol mixtures were irradiated with light of various wavelengths (254, 405, and 436 nm) filtered from a medium-pressure mercury arc (Hanau St.41). The reaction progress was followed by optical spectroscopy. For qualitative GC–MS analysis, approximately 50 mL of the irradiated solutions was concentrated to an end volume of ca. 200 μL. Preparative TLC was performed on silica gel (Merck, silica gel 60 F_{254}; a 1:1 mixture of hexane and ethyl acetate was used as eluent).

Actinometry. Quantum yields were determined by UV-spectrophotometric monitoring of the reaction progress using azobenzene actinometry (22,23).

RESULTS

Trapping reactions of 2

Methanol. Solutions of **1** (5×10^{-5} M) in methanol were irradiated with light of various wavelengths (254, 405 or 436 nm). The product mixture was analyzed by GC–MS. The major product, methyl indene-3-carboxylate (**6**), and a trace (1–2%) of 2-methoxy-1-naphthol (**4**), were identified using authentic samples for comparison. 1-Naphthol was detected only upon triplet sensitization of **1** with excess benzophenone.

Acetonitrile. On irradiation of **1** in acetonitrile containing 1% of methanol, ester **6** was again the main product, indicating that the ketene intermediate **3** is efficiently trapped by the small amount of methanol. In this case, a different side product was formed, which was isolated by preparative TLC and identified as 2-methylnaphth[2,1-*d*]oxazole (**5**, Fig. 2).

Product yield of 4. Quantitative analysis of the photoproduct 2-methoxy-1-naphthol (**4**) is not straightforward, because it is a rather reactive compound. Kral *et al.* (24) reported that 2-alkoxy substituted 1-naphthols readily undergo oxidative dimerization to form diones; the dione formed from **4** has a violet color (λ_{max} = 542 nm). Irradiated solutions of **1** in methanol turned violet when they were concentrated for GC–MS analysis. ^{1}H-NMR, HPLC and GC–MS, which require relatively high concentrations, were therefore not suitable for a quantitative analysis of product **4**. We found that **4** is strongly fluorescent, whereas the major product **6** is not. A solution of **1** (4×10^{-5} M) in methanol was irradiated at 405 nm in a quartz cell until no further changes were observed in the absorption spectrum. As only compound **1** absorbs at the irradiation wavelength of 405 nm, prolonged irradiation is unproblematic. The fluorescence excitation and emission spectra of an exhaustively photolyzed solution of **1** and of an authentic sample of **4** (5×10^{-6} M) in methanol were in good agreement (Fig. 3). Slight differences in the wavelength region below 300 nm of the excitation spectrum may be attributed to the inner filter effect of absorption by **6** in the photoproduct mixture.

Thus, the fluorescence emission induced by excitation at wavelengths >300 nm provides a sensitive technique for the exclusive detection of **4** in the photoproduct mixtures without any work-up. The fluorescence spectrum of **4** depends on the solvent, λ_{max}(methanol) = 390 nm, λ_{max}(hexane) = 367 nm. The relative yield of **4**, *r*(**4**) = ϕ_4/ϕ_{dec}, was determined by calibration with solutions containing known concentrations of authentic **4** in the same solvent mixtures. The quantum yields, ϕ_4 and ϕ_{dec}, are those for the formation of **4** and the decomposition of **1**. Optically dilute solutions were used (absorbances at the excitation wavelength <0.02) to ensure that the calibration plots showed strictly linear dependence on the concentration of **4**.

In neat methanol, the yield of **4** was 15 ± 1% after exhaustive irradiation (6 min) of **1** at 405 nm (mercury arc). It decreased substantially when lower wavelengths of irradiation were used: 13 ± 1% were obtained by 351 nm excitation (XeF excimer laser), and about 8% by irradiation at either 254 nm (mercury arc) or at 248 nm (KrF excimer laser). The photoproduct **4** is not entirely stable to 248 or 254 nm irradiation; irradiation of a solution of **4** for the same period reduced its fluorescence intensity by 15%. However, this small reduction cannot account for the much lower yield of **4** obtained by 248 or 254 nm irradiation of **1**, indicating that the yield of carbene **2** is reduced to about ½ upon irradiation at short wavelengths.

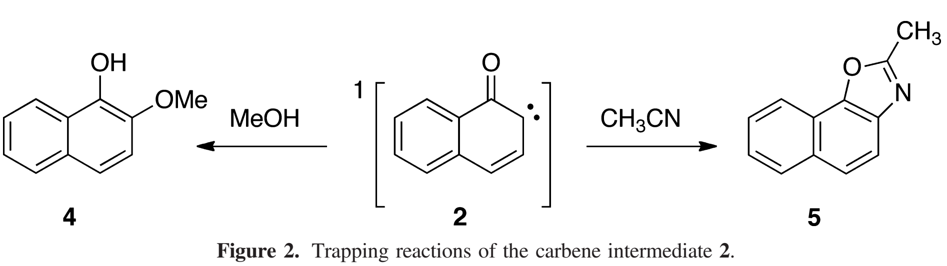

Figure 2. Trapping reactions of the carbene intermediate **2**.

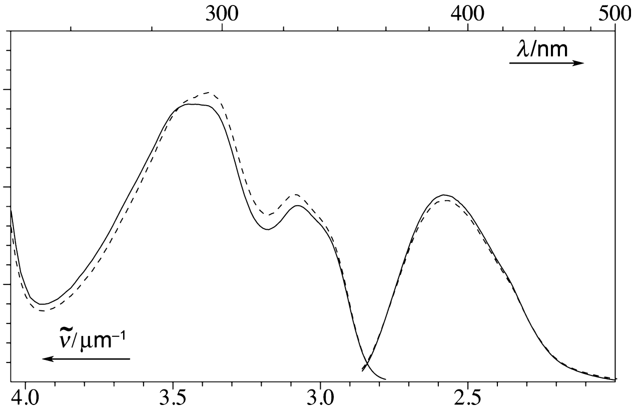

Figure 3. Fluorescence emission and excitation spectra of a 4 × 10^{-5} M solution of **1** in methanol after exhaustive irradiation at 405 nm (dotted line), and of a 5 × 10^{-6} M solution of **4** in methanol (solid line). Excitation wavelength for emission: 330 nm. Emission wavelength chosen for the excitation spectrum: 390 nm.

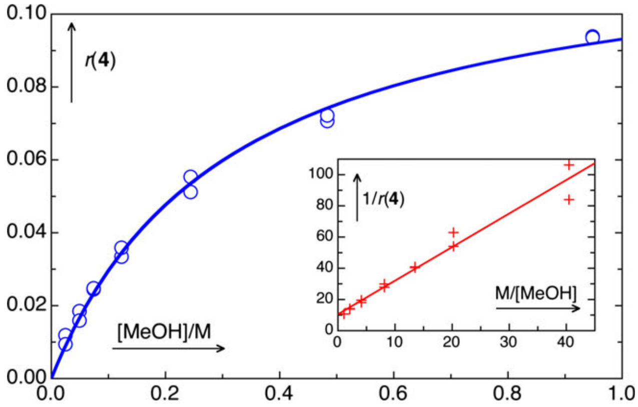

Figure 4. Relative yields of **4**, $r(\mathbf{4})$, obtained by 405 nm irradiation of **1** in hexane as a function of added methanol. The solid line represents the best fit of Eq. (1) to the experimental data. A linear regression to the same data according to Eq. (1a) is shown in the inset.

Stern–Volmer analyses; methanol in hexane. Methyl indenecarboxylate (**6**) was the only product detected by GC–MS after irradiation of **1** (5 × 10^{-5} M) in hexane containing 1% of methanol. Neither 1-naphthol nor a hexane insertion product was found. Fluorescence revealed the presence of a trace of **4**; the yield of **4** increased with increasing methanol concentration, but rapidly approached a plateau of about 12% at the highest achievable methanol concentration of 2 M. Saturation of trapping would not be expected, if the Wolff rearrangement proceeded exclusively via the trappable carbene intermediate **2**. On the contrary, related work has shown excess reactivity of singlet carbenes toward methanol at high methanol concentrations in an inert solvent (25). The relative yields of **4** determined after exhaustive photolysis of **1** at 405 nm, $r(\mathbf{4}) = \phi_4/\phi_{\mathrm{dec}}$, as a function of methanol concentration up to 1 M is shown in Fig. 4.

The observed saturation of the trapping yield implies that the reaction proceeds predominantly by a "concerted" formation of ketene **3**, which bypasses the trappable carbene **2**. The relative yield $r(\mathbf{4})$ as a function of methanol concentration is given by Eq. (1), as derived in the Appendix by analysis of the kinetic scheme shown in Fig. 5.

$$r(\mathbf{4}) = \frac{\phi_4}{\phi_{\mathrm{dec}}} = \frac{k_{\mathrm{MeOH}}[\mathrm{MeOH}]}{k_{\mathrm{MeOH}}[\mathrm{MeOH}] + k_{\mathrm{WR}}} \times \frac{\phi_2}{\phi_{\mathrm{dec}}} \qquad (1)$$

$$\frac{1}{r(\mathbf{4})} = \left(1 + \frac{k_{\mathrm{WR}}}{k_{\mathrm{MeOH}}[\mathrm{MeOH}]}\right) \times \frac{\phi_{\mathrm{dec}}}{\phi_2} \qquad (1a)$$

A "dual reciprocal plot" of the data, ($1/r(\mathbf{4})$ *versus* 1/[MeOH]), was linear, in agreement with Eq. (1a). The fit parameters $k_{\mathrm{MeOH}}/k_{\mathrm{WR}} = 3.2 \pm 0.2$ M^{-1} and $\phi_2/\phi_{-\mathrm{N2}} = 0.12 \pm 0.01$ were, nevertheless, best determined by nonlinear least-squares fitting of Eq. (1) to the experimental data $r(\mathbf{4})$ to avoid distortion by the increasing experimental errors in $1/r(\mathbf{4})$ with decreasing methanol concentrations [MeOH]; the standard errors in $r(\mathbf{4})$ are constant. It is seen from Fig. 4 that the yields $r(\mathbf{4})$ are well reproduced by the fitted function. At high methanol concentration nearly all of carbene **2** is trapped by methanol. The asymptotic yield of **4** obtained from Eq. (1) for [MeOH]/M → ∞ and thus $r(\mathbf{4}) \rightarrow \phi_4/\phi_{\mathrm{dec}}$ is 12 ± 1%. Thus, the Wolff rearrangement appears to proceed mainly (88%) along a "concerted" pathway.

Methanol in dioxane. Similar results were obtained with solutions of methanol in dioxane (not shown). These solvents are miscible in all proportions. Again, **6** was the only product identified by GC–MS and **4** was the only product detected by fluorescence spectroscopy. The parameters obtained by nonlinear least-squares fitting of Eq. (1) are $k_{\mathrm{MeOH}}/k_{\mathrm{WR}} = 1.2 \pm 0.2$ M^{-1} and $\phi_2/\phi_{-\mathrm{N2}} = 0.15 \pm 0.01$ and the data are accurately reproduced by the fitted function.

Methanol in acetonitrile. In the solvent mixtures of methanol with hexane and dioxane used above, only methanol was sufficiently reactive to intercept the carbene **2** prior to its rearrangement to ketene **3**. Other solvent addition products were not detected even at very low methanol concentrations. A different situation arises in mixtures of methanol and acetonitrile, because carbene **2** is also trapped by acetonitrile (Fig. 2). Hence, the relative yield of **4** is expected to depend on the concentrations of both methanol and acetonitrile, Eq. (2).

$$r(\mathbf{4}) = \frac{\phi_4}{\phi_{\mathrm{dec}}} = \frac{k_{\mathrm{MeOH}}[\mathrm{MeOH}]}{k_{\mathrm{MeOH}}[\mathrm{MeOH}] + k_{\mathrm{MeCN}}[\mathrm{MeCN}] + k_{\mathrm{WR}}} \times \frac{\phi_2}{\phi_{\mathrm{dec}}} \qquad (2)$$

The molar concentrations of pure methanol and acetonitrile are [MeOH] = 24.6 M and [MeCN] = 18.9 M at 25°C. Excess molar volumes in mixtures of these solvents are slightly negative, but never below -0.165 cm^3 mol^{-1} (26), *i.e.*, the reduction in volume upon mixing is well below 1% in all mixtures. Ignoring these small changes of the partial molar volumes, the concentration of acetonitrile may be expressed as a linear function of the methanol concentration in acetonitrile/methanol mixtures.

$$[\mathrm{MeCN}] \cong 18.9\mathrm{M} - \frac{18.9}{24.6}[\mathrm{MeOH}] \qquad (3)$$

Combining Eqs. (2) and (3), the relative yield of **4** can be expressed as a function of methanol concentration only, Eq. (4).

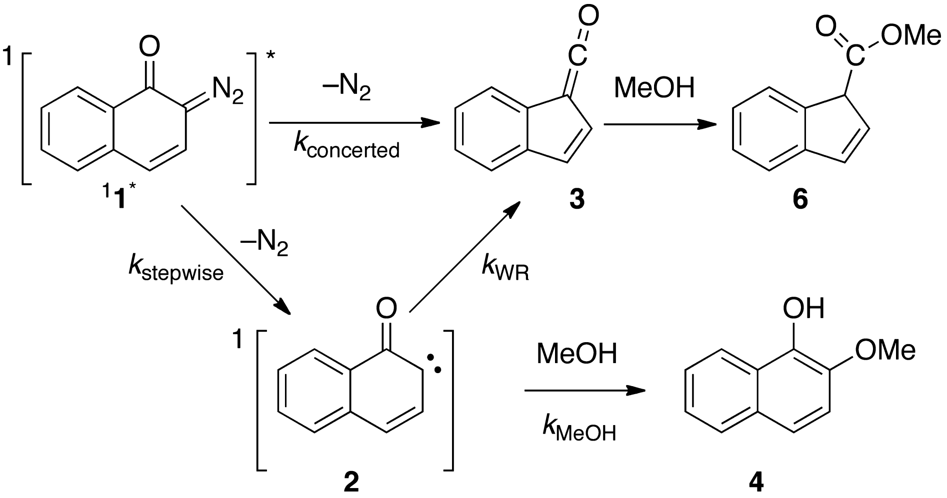

Figure 5. Kinetic scheme for the trapping reaction of **2** by methanol.

$$r(\mathbf{4}) = \frac{\phi_{\mathbf{4}}}{\phi_{\mathrm{dec}}} \cong \frac{k_{\mathrm{MeOH}}[\mathrm{MeOH}]}{\left(k_{\mathrm{MeOH}} - \frac{18.9}{24.6}k_{\mathrm{MeCN}}\right)[\mathrm{MeOH}] + k_{\mathrm{MeCN}} \times 18.9\,\mathrm{M} + k_{\mathrm{WR}}} \times \frac{\phi_{\mathbf{2}}}{\phi_{\mathrm{dec}}} \tag{4}$$

Relative yields of **4** in mixtures of methanol and acetonitrile are shown in Fig. 6. The rate constant k_{WR} was ill defined by least-squares fitting of Eq. (4). That is reasonable, as we know that essentially all of the interceptable carbene **2** is trapped in these solvent mixtures. For example, using the ratio $k_{\mathrm{MeOH}}/k_{\mathrm{WR}} = 3.2\ \mathrm{M}^{-1}$ obtained from the analysis of Eq. (1) (methanol in hexane), the ratio $k_{\mathrm{MeOH}}[\mathrm{MeOH}]/k_{\mathrm{WR}}$ for neat methanol equals about 80. Nonlinear least-squares fitting of Eq. (4) to the experimental data was thus done by neglecting the term k_{WR} relative to the other terms in the denominator, which gave an excellent fit with the two parameters $k_{\mathrm{MeOH}}/k_{\mathrm{MeCN}} = 1.7 \pm 0.1$ and $\phi_{\mathbf{2}}/\phi_{\mathrm{dec}} = 0.15 \pm 0.01$. The limiting yield of 15 ± 1% is the same as that determined for the dioxane/methanol solvent mixture above, but is reached only in neat methanol, because the competing reaction of **2** with acetonitrile is nearly as fast as that with methanol.

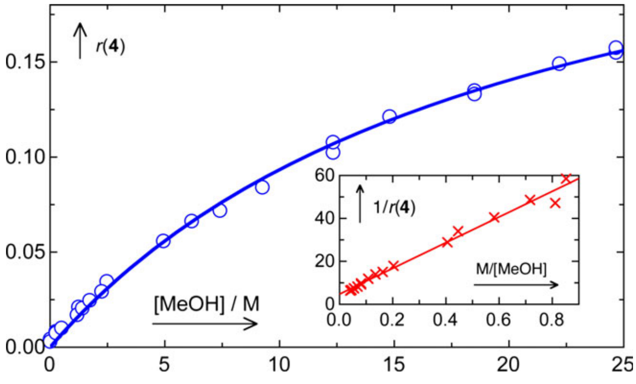

Figure 6. Relative yields of **4**, *r*(**4**), obtained by irradiation of **1** in acetonitrile/methanol mixtures. The solid line represents the best fit of Eq. (4) to the experimental data. A linear regression to the same data (down to 0.025 M methanol) using the inverse of Eq. (4) is shown in the inset. At still lower methanol concentrations the scatter becomes excessive.

The fluorescence spectra of exhaustively irradiated ($\lambda_{\mathrm{irr}} = 405$ nm) solutions of **1** (4×10^{-5} M) in acetonitrile/methanol mixtures are shown in Fig. 7. The change of the fluorescent products from predominantly **5** ($\lambda_{\max} = 350$ nm) in acetonitrile to predominantly **4** ($\lambda_{\max} = 390$ nm) in methanol is clearly seen.

Photochemical *versus* thermal deazotization of 1 in acetonitrile

The relative yield of **5**, $r(\mathbf{5}) = \phi_{\mathbf{5}}/\phi_{\mathrm{dec}}$, was determined by measurement of the fluorescence intensities that were calibrated using solutions of known concentrations of **5**. Thermal decomposition of **1** by refluxing an acetonitrile solution at 80°C gave $r(\mathbf{5}) = 23\%$. A solution heated to 190°C in an autoclave gave $r(\mathbf{5}) = 18\%$. Exhaustive irradiation of a solution of **1** at 405 nm gave $r(\mathbf{5}) = 7.6\%$ in acetonitrile and $r(\mathbf{5}) = 5.3\%$ in acetonitrile-d_3.

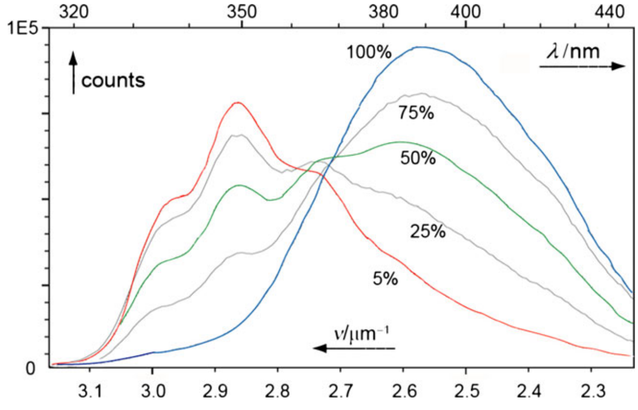

Figure 7. Uncorrected fluorescence spectra of the photoproducts of **1** in methanol (vol-% shown)–acetonitrile mixtures. Excitation: 260 nm.

Quantum yield of the photoreaction of 1

Quantum yields of decomposition of **1**, ϕ_{dec}, were measured by several groups; values reported range from 0.14 to 0.79 (4,27,28). The most recent value, measured by photolysis of **1** in methanol at 405 nm, is 0.54 (4). It has been reported that the quantum yield of photoconversion of quinonediazides (aromatic 1,2-diazoketones) depends on the wavelength of irradiation (27,28). We have measured $\phi_{\mathrm{dec}}(\mathbf{1})$ at various wavelengths of irradiation: $\phi_{\mathrm{dec}}(254\ \mathrm{nm}) = 0.38 \pm 0.04$, $\phi_{\mathrm{dec}}(313\ \mathrm{nm}) = 0.52 \pm 0.04$, $\phi_{\mathrm{dec}}(365\ \mathrm{nm}) = 0.62 \pm 0.04$, $\phi_{\mathrm{dec}}(405\ \mathrm{nm}) = 0.38 \pm 0.03$. The quoted standard errors do not include possible systematic errors of our measurements. The differences between the values obtained at different excitation wavelengths may, therefore, not be significant.

DISCUSSION

The work of Wolpert *et al.* (8) has established that the photo-Wolff rearrangement of 2-diazo-1,2-naphthoquinone (**1**) to the ketene **3** is largely complete within 300 fs. Nevertheless, the side product 2-methoxy-1-naphthol (**4**) is formed in methanol, which indicates that a trappable carbene intermediate **2** is formed as well (stepwise pathway, Fig. 1). The trapping of carbene **2** by methanol and acetonitrile (Fig. 2) indicates that it reacts in its singlet state, which is presumably its ground state. The ratios of the rate constants of trapping by methanol and of Wolff rearrangement of **2**, $k_{\mathrm{MeOH}}/k_{\mathrm{WR}}$, were determined as 3.2 ± 0.2, 1.2 ± 0.2 and $1.7 \pm 0.1\ \mathrm{M}^{-1}$ in mixtures of methanol with hexane, dioxane and acetonitrile, respectively. Bimolecular rate constants for OH insertion by singlet carbenes are generally close to the diffusion-controlled limit (29–33), *i.e.*, around $k_{\mathrm{MeOH}} \approx 5 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. Assuming an upper limit of $k_{\mathrm{MeOH}} < 1 \times 10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, these values indicate that the rate constant k_{WR} for Wolff rearrangement of the trappable carbene **2** is less than $5 \times 10^9\ \mathrm{s}^{-1}$. Thus, the lifetime of **2** must be at least 200 ps, more likely around 500 ps. This range lies well above the value proposed by Vleggaar *et al.* (4), $\tau_{\mathbf{2}} = 20$ ps. Because the relative yield of **2** is less than 15% and the lifetime of **2** exceeds 200 ps, the stepwise reaction may well have escaped detection in the experiments of Wolpert *et al.* (8), whose measurements extended only up to 50 ps after pulsed excitation.

The carbonyl carbene **2** is born with a huge excess energy upon nitrogen elimination from the singlet excited state of **1**. It may well be that Wolff rearrangement of hot **2** competes with its vibrational cooling, as was proposed for related carbenes by Platz and co-workers (34,35). Evidence for this hypothesis is provided by the relative yields of oxazole **5** in acetonitrile under different reaction conditions: thermal deazotization gives nearly three times as much **5** as the photochemical reaction. Moreover, the yield of **5** obtained upon irradiation of **1** in acetonitrile-d_3 is about 30% lower than in acetonitrile-h_3. The solvent with C–H bonds is a better acceptor for the excess vibrational energy of nascent **2** than that having C–D bonds only. This may explain the apparent discrepancy with quantum dynamical calculations (12,13), which predicted that the stepwise reaction via **2** predominates over the concerted Wolff rearrangement, while we find that the relative yields of trappable **2** are only 8–15% depending on the solvent.

Acknowledgement—This work was supported by the Swiss National Science Foundation.

APPENDIX

The quantum yields of decomposition of **1** and of formation of the interceptable carbene **2** may be expressed (36) in terms of the rate constants $k_{\mathrm{concerted}}$, k_{stepwise} and k_{nr} for the concerted, stepwise and nonradiative decay of the excited singlet state of **1**, $^1\mathbf{1}^*$, (Fig. 5): $\phi_{\mathrm{dec}} = (k_{\mathrm{concerted}} + k_{\mathrm{stepwise}})/(k_{\mathrm{concerted}} + k_{\mathrm{stepwise}} + k_{\mathrm{nr}})$ and $\phi_{\mathbf{2}} = (k_{\mathrm{stepwise}})/(k_{\mathrm{concerted}} + k_{\mathrm{stepwise}} + k_{\mathrm{nr}})$. Hence, $\phi_{\mathbf{2}}/\phi_{\mathrm{dec}} = k_{\mathrm{stepwise}}/(k_{\mathrm{concerted}} + k_{\mathrm{stepwise}})$.

Similarly, the quantum yield for the formation of **4** by trapping of carbene **2** is given by $\phi_{\mathbf{4}} = \phi_{\mathbf{2}} \times k_{\mathrm{MeOH}}[\mathrm{MeOH}]/(k_{\mathrm{MeOH}}[\mathrm{MeOH}] + k_{\mathrm{WR}})$, where k_{MeOH} and k_{WR} are the rate constants for the trapping of **2** by methanol and its reaction by Wolff rearrangement. Hence, the ratio $r(\mathbf{4}) = \phi_{\mathbf{4}}/\phi_{\mathrm{dec}}$ is given by Eq. (2).

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