

Flash Photolysis of α -Diazonaphthoquinones in Aqueous Solution: Determination of Rates and Equilibria for Keto-Enol Tautomerization of 1-Indene-3-carboxylic Acid

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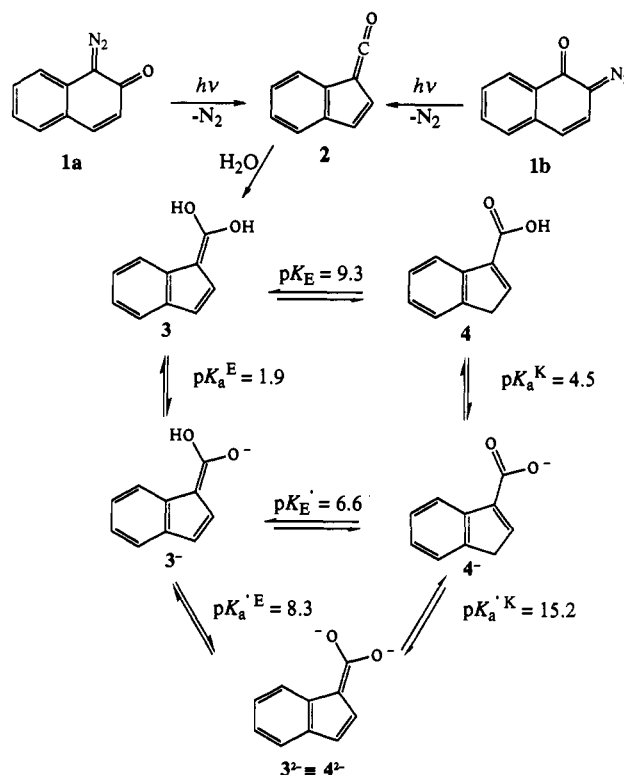
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Abstract: Flash photolysis of either 1-diazo-2(1*H*)naphthalenone (**1a**) or 2-diazo-1(2*H*)naphthalenone (**1b**) generates benzofulven-8-one (**2**). Hydrolysis of ketene **2** forms benzofulvene-8,8-diol (**3**), the enol tautomer of indene-3-carboxylic acid (**4**). pH rate profiles for the reactions **2** \rightarrow **3** and **3** \rightarrow **4** were determined in aqueous solution. Ketone **3** is catalyzed by acid and by base. Catalysis by protons saturates in strongly acidic solutions, thereby defining the first ionization constant of the enol, $pK_a^E = 1.90 \pm 0.05$, catalysis by hydroxyl ions saturates in dilute base, defining the second ionization constant, $pK_a^E = 8.3 \pm 0.2$. The first (OH) and second (CH) ionization constants of **4** were determined by spectrophotometric titration, $pK_a^K = 4.50 \pm 0.03$ and $pK_a^K = 15.2 \pm 0.2$. Two independent estimates of the enolization constants of **4** and **4**⁻, the first based on thermodynamic cycles, the second on the ratio of enolization and ketonization rates, were combined to give $pK_E = 9.3 \pm 0.3$, $pK'_E = 6.6 \pm 0.3$. Ketene **2** is formed by irradiation of 1-bromo-2-naphthol at 12 K in an argon matrix, but neither it nor its isomer 2-bromo-1-naphthol were suitable for the generation and observation of **2** and **3** by flash photolysis in aqueous solution.

Photo-Wolff rearrangement of the parent α -diazonaphthoquinones, 1-diazo-2(1*H*)naphthalenone (**1a**) or 2-diazo-1(2*H*)naphthalenone (**1b**), generates benzofulven-8-one (**2**), a ketene that hydrolyzes rapidly in water to form benzofulvene-8,8-diol (**3**), the enol of indene-3-carboxylic acid (**4**) (Scheme 1). We have determined the rate profile for the tautomerization of enol **3** in aqueous solution over the pH range from 1 to 13 by flash photolysis. These data, combined with the first and second ionization constants of **4** define all equilibria of enolization and ionization of carboxylic acid **4** in aqueous solution.

α -Diazonaphthoquinones are important positive photoresists (Novolak, AZ) used in microlithography.¹ The mechanism of the photochemical ring contraction of α -diazonaphthoquinones and α -diazonaphthoquinones was first described in 1944 by Süss who identified carboxylic acids of cyclopentadiene and indene, respectively, as the products formed in acidic aqueous solution.² The ketenes formed initially by Wolff-rearrangement have since been trapped in rigid matrices at low temperature and characterized by their UV and IR spectra.^{3,4} Time-resolved studies of α -diazonaphthoquinones have at first led to contradictory interpretations.⁵ Two first-order processes are observed on the microsecond time scale by transient absorbance spectroscopy in acidic aqueous solution. The currently accepted identification of these reactions as ketene hydrolysis and enediol ketonization was put forward in a study of 2-diazo-1(2*H*)naphthalenone-5-sulfonic acid⁷ and of parent 1,2-benzoquinone diazide.⁸ The same sequence of reactions provided a convincing assignment of the

Scheme 1



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transient intermediates observed by Barra et al. upon flash photolysis of sulfonated α -diazonaphthoquinones.⁹ A detailed study of acid catalysis, isotope effects, and structure-reactivity relationships, reported in the recent paper by Andraos et al.,⁶ firmly establishes the assignment of these transients. However,

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the present work leads us to question our earlier interpretation⁸ of the transient absorbance changes observed by flash photolysis of 2-bromophenol in aqueous base.

Results

Continuous Irradiation. Irradiation of **1b** in acidic aqueous solution with a high-pressure mercury arc ($\lambda > 365$ nm) gave indene-3-carboxylic acid (**4**) as the only isolable product (80% yield), in agreement with previous work.¹⁰ Irradiation ($\lambda > 365$ nm) of **1b** in 0.03 N NaOH induced a prominent color change from yellow to blue (λ_{\max} 580 nm). In the presence of 2% methanol as a cosolvent, 1-naphthol was obtained as a major product (20%) that was identified by ¹H and ¹³C NMR, GC, and MS data and confirmed by co-injection of the photolysis mixture with a sample of authentic 1-naphthol. Only a trace of naphthol was detected when **1b** was irradiated in the absence of methanol as a cosolvent. The formation of 1-naphthol has been noted previously¹¹ and was tentatively ascribed to a ketocarbene intermediate undergoing hydrogen atom abstraction. This appears unlikely in view of the picosecond transient kinetics reported below, but further work will be required to clarify this issue. Along with 1-naphthol, a highly colored solid material^{12b,12-14} (mp > 170 °C) was obtained which was not identified. Polymeric substances may be responsible for the broad alkyl resonances observed in the ¹H NMR spectra and for the poor balance of integratable signals. By carrying out the irradiation of **1b** (>365 nm) in nitrogen-purged, dilute aqueous NaOH solutions (0.001 M) at lower temperature, it was possible to isolate **4** as the major product (40%). Irradiation, neutralization, and workup of the reaction were all carried out at 5 °C. 1-Naphthol was obtained as a side product (14%) in the presence of 2% methanol as a cosolvent.

The low yield of **3** in aqueous base is not surprising, since authentic **4** is unstable to aqueous base in the presence of light or of diazoquinones. The UV spectrum of a dilute solution of **4** in 0.1 M NaOH remained unchanged for 10 min in the dark, but the solution turned violet in daylight and **4** was largely decomposed within an hour. Addition of **1b** (1×10^{-4} M) to a solution of **4** (2×10^{-4} M) in 0.1 N NaOH induced rapid coloration in the dark. Complex absorbance changes throughout the visible spectrum were observed on a time scale of minutes immediately after mixing. Similar observations have been reported previously.¹⁴ Irradiation of 1-bromo-2-naphthol or 2-bromo-1-naphthol in basic solution also gave complex blue-violet mixtures. Trace amounts of 1-naphthol were again found.

The quantum yield for consumption of **1b** in aqueous HCl (0.05 M) by 365-nm irradiation, $\phi_d = 0.34 \pm 0.03$, was determined spectrophotometrically using azobenzene actinometry.¹⁵ Analysis of the spectral changes in aqueous NaOH (0.001 M) gave $\phi_d \approx 0.42 \pm 0.11$; the formation of (unidentified) colored material was taken into account. An increase in the quantum yield of disappearance in basic solution may be attributed to consumption of **1b** by the photoproduct **4** to form the colored products.

Studies of 1,2- and 2,1-Bromonaphthol as Potential Precursors of 2. 2-Bromophenol is known to give cyclopentadienecarboxylic acids upon irradiation in aqueous base.¹⁶ We sought to establish whether **2** is similarly formed by irradiation of 1-bromo-2-naphthol. The IR spectrum of matrix-isolated benzofulven-8-one (**2**) is known from the work of Bell and Dunkin, who prepared

and identified this ketene by irradiation of two precursors, diazonaphthoquinone **1a** in a nitrogen matrix and diazoindene in a nitrogen matrix doped with CO.^{3a} Matrix isolation was done by slow evaporation at ca. 40 °C in the vacuum shroud and codeposition with an ca. 500-fold excess of argon on a CsI window that was kept at 25 K. The matrix was then cooled to 12 K and irradiated with 308-nm pulses (ca. 10 mJ/cm²) from an excimer laser at 10 Hz. The formation of ketene **2** was seen by the appearance of a strong new peak at 2149 cm⁻¹ which reached its maximum intensity after 9 min of irradiation. By that time, most of the peaks reported by Dunkin for **2** were detectable in the IR spectrum: 2149 (s), 1515 (w), 1456 (m), 1337 (w), 1189 (w), 1078 (w), 1040 (w), 781 (w), 759 (m), 739 (w), 712 (w), and 508 cm⁻¹ (w). The bands were slightly shifted relative to those reported by Dunkin, usually to higher frequency by a few wavenumbers. Additional absorptions at 3365 (s), 3210 (s), 1775 (m), 1750 (s), 1712 (m), 1687 (s), 1288 (m) and 963 (m) cm⁻¹ could not be assigned. Side reactions presumably arise from homolytic cleavage of the C-Br bond, but elimination of HBr from 1-bromo-2-naphthol to form the ketene **2** by Wolff-rearrangement is clearly a major reaction under these conditions. However, flash photolysis (*vide infra*) indicates that photoinduced bromide elimination yielding **2** by Wolff-rearrangement appears to be at best a minor side reaction of the bromonaphthols in aqueous base.

Dissociation Constants of Indene-3-carboxylic Acid (4). The dissociation constants of **4** were measured by spectrophotometric titration. Factor analysis of a series of ca. 20 spectra taken at different pH, each defined by 50 absorbance readings, gave two significant eigenvectors. Their weight in each spectrum was used to determine the ionization ratios that were fitted to a titration curve.¹⁷ Deprotonation of the carboxylic acid function gives rise to a hypsochromic shift of the first absorption band from λ_{\max} (log ϵ) = 263 nm (3.55) to 255 nm (3.73).¹⁸ Titration was carried out by addition of 0.1 M HCl to a solution of **4** (10^{-4} M) in 0.1 M aqueous sodium acetate and gave $pK_a^K = 4.50 \pm 0.03$.¹⁹ Strong base of up to 6 M NaOH was needed to induce carbon deprotonation of **4**⁻, and the dianion **4**²⁻ \equiv **3**²⁻ was very sensitive to oxidation. Titration was thus carried out under argon gas by the addition of a 10 M solution of NaOH to a 10^{-4} M solution of indenecarboxylic acid in 0.1 M aqueous NaOH at 25 °C. A strong bathochromic shift of the first absorption band indicated the formation of enol dianion **4**²⁻, λ_{\max} (log ϵ) = 343 nm (3.7).¹⁸ The logarithms of the spectrophotometric ionization ratios [**4**⁻]/[**4**²⁻] were directly proportional to the H₂ scale²⁰ with essentially unit slope. Fitting¹⁷ of the data to a titration curve based on the H₂ scale gave $pK_a^{K^0} = 15.64 \pm 0.05$. The basicity function H₂ is designed to provide an estimate of the thermodynamic dissociation constant in pure water. The concentration quotient for the second ionization at 0.1 M ionic strength, which is of interest here, was estimated from $pK_a^{K^0}$ with activity coefficients recommended by Bates,²¹ which gave $pK_a^K = 15.2 \pm 0.2$; the increased error margin for the latter value makes allowance for systematic errors that are likely to arise from the procedure described above.

Flash Photolysis. Flash photolysis of either of the α -diazonaphthoquinones **1a** or **1b** in aqueous HCl with a 25-ns laser pulse resulted in an immediate strong bleaching centered at the

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(18) Due to the limited solubility of **4** in aqueous acid, the absolute extinction coefficient of **4** was determined with dilute aqueous NaOH (0.001 M). The extinctions of **4** and **4**²⁻ were then calculated from the factor analysis data for the titrations.

(19) All equilibrium constants are concentration quotients determined at ionic strength $I = 0.1$ M and 25 °C in aqueous solution, unless noted otherwise.

(20) The H₂ scale was defined for the deprotonation of indole carboxylates in concentrated hydroxide solutions: Yagil, G. *J. Phys. Chem.* **1967**, *71*, 1034.

(21) Activity coefficients ($I = 0.1$ M) $\gamma(4^{2-}) \approx \gamma(\text{CO}_3^{2-}) = 0.36$, $\gamma(3^-) \approx \gamma(\text{PhCO}_2^-) = 0.80$, $\gamma(\text{H}^+) = 0.83$; Bates, R. B. *Determination of pH. Theory and Practice*, Wiley: New York, 1973, p 49.

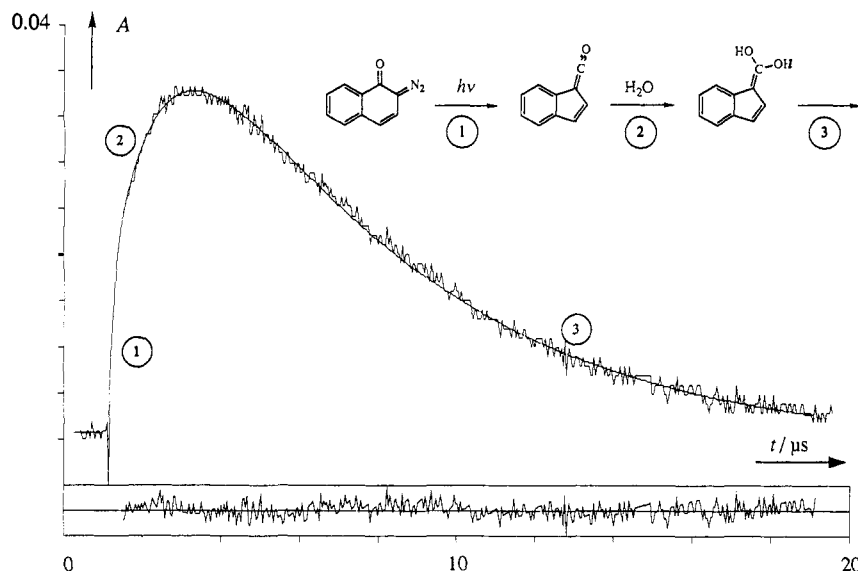


Figure 1. Transient waveform observed at 335 nm by nanosecond flash photolysis of 10^{-4} M **1b** in 0.1 N HCl. The continuous line is the least squares fit of a biexponential function to the time-resolved formation and decay of **3**. The bottom trace shows the residuals.

absorbance maxima of the diazoquinones (388 nm for **1a**, 400 nm for **1b**) and a concomitant absorbance increase around 330–340 nm. During the first few microseconds after the laser flash, formation of a second, more strongly absorbing intermediate was observed in the range of 330–360 nm. Shown in Figure 1 is a representative waveform that has a triphasic appearance: step, growth, and decay. The time-resolved growth and subsequent decay of the transient absorption both obeyed first-order kinetics. In agreement with related work,^{6,8,9} the initial step (<50 ns) is attributed to formation of ketene **2**, the growth to the hydrolysis of **2** yielding enediol **3**, and the final decay to tautomerization of the enol to carboxylic acid **4**.

The kinetic data reported below were determined with **1b** in acidic solutions. A less comprehensive set of kinetic data obtained with **1a** was consistent with that quoted here. Ketene **2** hydrolysis took place with a constant rate throughout the pH range of 1–6, $k_0 = (1.1 \pm 0.1) \times 10^6 \text{ s}^{-1}$. In basic solutions, the rate constant for the growth increased linearly with hydroxide ion concentration; linear least-squares analysis of the data in basic solutions gave a catalytic coefficient $k_{\text{OH}^-} = 3.8 \pm 0.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ from the slope, and an uncatalyzed term, $k_0 = 1.2 \pm 0.2 \times 10^6 \text{ s}^{-1}$, from the intercept (Figure 2, curve a).

The rates of ketonization of **3** follow a V-shaped pH profile, Figure 2, curve b. In acidic solutions the rate increased linearly with increasing acid concentration and approached a maximum value of $2.5 \times 10^5 \text{ s}^{-1}$ below pH 2. The lower rates in buffered and basic solutions were measured on a conventional discharge flash setup. Rates in acetate, phosphate, and TRIS buffer solutions were linearly dependent on buffer concentration. General base catalysis was quite strong, especially in the TRIS buffers, which made it difficult to obtain reliable intercepts from the buffer dilution plots. The data were analyzed using a constrained Bayesian linear regression model. The posterior distributions of the linear parameters k_i , subject to the inequality condition $k_i \geq 0$, were obtained using a Gibbs sampler.²² The slopes and intercepts determined from buffer dilution plots at constant buffer ratio are collected in Table 1.

The thermal stability of **1a** and **1b** in basic solutions was sufficient to extend the measurements up to 0.1 N NaOH. However, the photoproduct was unstable to the reaction conditions and slowly formed colored products after the decay of enediol **3** to acid **4**. Flash photolysis of either 1-bromo-2-naphthol or 2-bromo-1-naphthol in aqueous base gave very weak, complex transient decay curves which showed no similarity with those

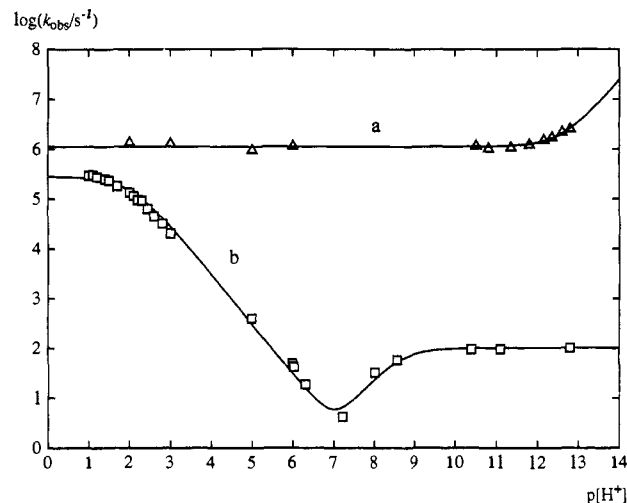


Figure 2. pH rate profiles for the hydrolysis of ketene **2** (curve a) and the ketonization of enediol **3** (curve b). The fitted curves were obtained by nonlinear least squares fitting to the appropriate rate law (eq 8 for curve b).

observed with the diazonaphthoquinones. Thus, the bromonaphthols are inadequate as precursors to monitor ketene **2** by flash photolysis in aqueous base, although the former did give a significant yield of **2** upon photolysis in an argon matrix.

A few percent of the transient absorption resulting from flash photolysis of **1b** decayed on the microsecond time scale in basic solutions, i.e., the initial growth, attributed to ketene hydrolysis, was immediately followed by a partial decay on a similar time scale. We cannot offer an assignment of this transient absorbance change.²³ The major part decayed by a clean first-order reaction which was independent of hydroxyl ion concentration at pH > 10, $k'_0 = 105 \pm 5 \text{ s}^{-1}$. This reaction is attributed to carbon protonation of the enol dianion by water. On a still longer time

(23) The decay of a minor part of the transient absorption increased linearly with $[\text{OH}^-]$ at low base concentrations and approached a plateau of ca. $6 \times 10^5 \text{ s}^{-1}$ at $\text{p}[\text{H}^+] = 11.5$. Degassing the solutions had no effect on this transient. Although this is the behavior qualitatively expected for the enediolate **3**⁻ reacting through the dianion **3**²⁻, such an assignment is quantitatively inconsistent with the isotope exchange measurements on **4** (*vide infra*). Also, it would leave the major contribution to the transient decay unassigned. A referee has raised the question whether aggregation of the poorly soluble diazoquinone precursors **1a** and **1b** could be the cause for the unassigned transient. This is unlikely because similar transients appear when 2-bromophenol⁶ (cf. the Discussion in this paper) or sulfonated diazonaphthoquinones⁶ (A. J. Kresge, personal communication) are flash photolyzed in aqueous base.

Table 1. Catalytic Coefficients for the Ketonization of **3** Determined from Buffer Dilution Plots at Constant Buffer Ratio, Ionic Strength $I = 0.1$, 25 °C

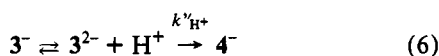
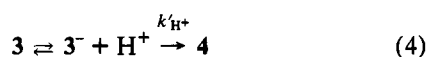
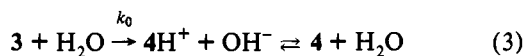
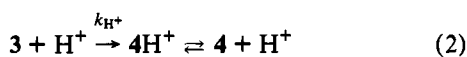
buffer	buffer ratio [HA]/[A ⁻]	p[H ⁺] ^a	no. of points	slope M ⁻¹ s ⁻¹	intercept s ⁻¹
acetate ^b	0.37	5.00	8	(2.4 ± 0.1) × 10 ⁴	(4.0 ± 0.3) × 10 ²
acetate ^b	0.037	6.0	8	(4.2 ± 0.1) × 10 ³	50 ± 4
TRIS ^c	0.35	8.57	11	(6.56 ± 0.05) × 10 ⁴	59 ± 10
TRIS ^c	1.4	8.00	11	(4.9 ± 0.3) × 10 ⁴	33 ± 25
TRIS ^c	8.1	7.21	10	(1.71 ± 0.01) × 10 ⁴	4.2 ± 1.0
phosphate ^d	3.0	6.30	10	(4.8 ± 0.2) × 10 ³	19 ± 4
phosphate ^d	5.9	6.02	11	(4.9 ± 0.1) × 10 ³	43 ± 5

^a Proton concentrations were calculated from ionization concentration quotients^{b-d} at ionic strength $I = 0.1$ M; glass electrode readings were within ± 0.1 of the calculated p[H⁺] values. ^b pK_a = 4.57: Harned, H. S.; Ehlers, R. W. *J. Am. Chem. Soc.* **1933**, *55*, 652. ^c pK_a = 8.12: Bates, R. G.; Hetzer, H. B. *J. Phys. Chem.* **1961**, *65*, 667. ^d Grzybowski, A. K. *J. Phys. Chem.* **1958**, *62*, 555 gives pK_a^o = 7.20; activity coefficients needed to calculate pK_a ($I = 0.1$ M) = 6.78 were taken from Bates.²¹

scale of minutes, formation of the blue species was observed. The kinetics of this process were complex, showing an induction period following the decay of 3²⁻, and were not studied in detail.

$$\log(k_{\text{obs}}/s^{-1}) = \log \left\{ k_{\text{H}^+}[\text{H}^+] + (k_0 + k'_{\text{H}} + K_{\text{a}}^{\text{E}}) + \frac{(k'_0 + k''_{\text{H}}K_{\text{a}}^{\text{E}})K_{\text{a}}^{\text{E}}}{[\text{H}^+]} + \frac{k''_0K_{\text{a}}^{\text{E}}K_{\text{a}}^{\text{E}}}{[\text{H}^+]^2} \right\} - \log \left\{ 1 + \frac{K_{\text{a}}^{\text{E}}}{[\text{H}^+]} + \frac{K_{\text{a}}^{\text{E}}K_{\text{a}}^{\text{E}}}{[\text{H}^+]^2} \right\} \quad (1)$$

A general expression describing the pH profile for ketonization of benzofulvenediol is given in eq 1. To derive this function, reactions 2–7 were considered as possible mechanisms for the ketonization of enediol **3** and its anions. Ketonization of the enediol involves protonation on carbon which can occur on either of the three species **3**, 3⁻, or 3²⁻. In the absence of general acids, only the proton and neutral water are considered as proton sources. It was assumed that the protonation equilibria at enol oxygen (⇌) are established rapidly on the time scale of the rate-determining protonation reactions (→) at carbon.



It can be seen from the shape of the observed pH rate profile (Figure 2, curve b) that several of these reactions do not contribute significantly to the observed overall decay rate. A contribution from reaction 2 should produce an increase of k_{obs} at the low end of the pH scale (first term of eq 1). This was not observed; the decay rate of **3** remained constant at ca. 2.5×10^5 s⁻¹ up to [H⁺] = 1 M, i.e., $k_{\text{H}^+} < 1 \times 10^5$ M⁻¹ s⁻¹. Furthermore, reactions 5 and 6, which appear in the third term of eq 1, give rise to a pH-independent, horizontal contribution in the pH profile between the first and second ionization constant of **3**, pK_a^E and pK_a^E. Again, this was not detectable so that these terms may be neglected. Finally, a consideration of linear free energy relationships (cf. the Discussion) shows that the contribution from reaction 4 should be many orders larger than that from reaction 3, which has the same pH-dependence. Therefore, only reactions 4 and 7 are needed to reproduce the observed pH rate profile and

Table 2. Summary of Rate and Equilibrium Constants Measured in Aqueous Solution at 25 °C

reaction (Scheme 1)	constant/unit ^a	indenecarboxylic acid	cyclopentadiene carboxylic acid ^b
4 ⇌ 4 ⁻ + H ⁺	pK _a ^K /M	4.50 ± 0.03	4.71 ± 0.02
4 ⁻ ⇌ 3 ²⁻ + H ⁺	pK _a ^K /M	15.2 ± 0.2	13.7 ± 0.04
4 ⇌ 3	pK _E	9.3 ± 0.3	6.71 ± 0.2 ^d
4 ⇌ 3 ⁻	pK _E	6.6 ± 0.3	3.3 ± 0.2 ^d
3 ⇌ 3 ⁻ + H ⁺	pK _a ^E /M	1.90 ± 0.05	1.31 ± 0.05
3 ⁻ ⇌ 3 ²⁻ + H ⁺	pK _a ^E /M	8.3 ± 0.2	10.4 ± 0.1 ^d
3 ⁻ + H ⁺ → 4	k'_{\text{H}^+}/M ⁻¹ s ⁻¹ c	(2.21 ± 0.04) × 10 ⁷	(2.2 ± 0.3) × 10 ⁷
3 ²⁻ + H ₂ O → 4 ⁻ + OH ⁻	k''_0/s ⁻¹ c	105 ± 5	(9.6 ± 0.9) × 10 ⁵ d

^a All equilibrium constants are concentration quotients determined at ionic strength $I = 0.1$ M, 25 °C, in aqueous solution. ^b Data taken from ref 8. ^c These observed rate constants may include a contribution from the formation indenecarboxylic acid upon ketonization.²⁶ ^d These data are probably incorrect; cf. the Discussion.

eq 1 simplifies to eq 8.

$$\log(k_{\text{obs}}/s^{-1}) = \log \left\{ k'_{\text{H}^+}K_{\text{a}}^{\text{E}} + \frac{k''_0K_{\text{a}}^{\text{E}}K_{\text{a}}^{\text{E}}}{[\text{H}^+]^2} \right\} - \log \left\{ 1 + \frac{K_{\text{a}}^{\text{E}}}{[\text{H}^+]} + \frac{K_{\text{a}}^{\text{E}}K_{\text{a}}^{\text{E}}}{[\text{H}^+]^2} \right\} \quad (8)$$

In the acidic range (pH < 5), the terms containing the denominator [H⁺]² under the log functions of eq 8 may be neglected, and the rate law simplifies further to eq 9. Linear regression of the data in the pH range of 1–3 to the inverse of eq 9 gave $k'_{\text{H}^+} = (2.21 \pm 0.04) \times 10^7$ M⁻¹ s⁻¹ and $K_{\text{a}}^{\text{E}} = (1.26 \pm 0.10) \times 10^{-2}$ M, pK_a^E = 1.90 ± 0.05.

$$k_{\text{obs}} \cong \frac{k'_{\text{H}^+}K_{\text{a}}^{\text{E}}[\text{H}^+]}{[\text{H}^+] + K_{\text{a}}^{\text{E}}} \quad (\text{pH} < 5) \quad (9)$$

Similarly in the basic region (pH > 7), the terms under the log functions of eq 8 that do not contain [H⁺] in the denominator may be neglected, and the rate law simplifies to eq 10. Linear regression of the data obtained in basic solutions (pH 11–13), and in TRIS buffers, to the inverse of eq 10 gave $k''_0 = 105 \pm 5$ s⁻¹, and $K_{\text{a}}^{\text{E}} = (5 \pm 3) \times 10^{-9}$ M, pK_a^E = 8.3 ± 0.2. The large uncertainty in K_{a}^{E} arises from the large errors in the intercepts of the buffer dilution plots (Table 1). The rates of disappearance of the enol determined in aqueous HCl (0.001–0.1 M), NaOH (0.001–0.1 M), and the extrapolated intercepts referring to zero buffer concentration are shown in Figure 2, curve b. The rate and equilibrium constants obtained by least-squares fitting are collected in Table 2.

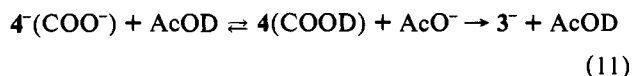
$$k_{\text{obs}} \cong \frac{k''_0K_{\text{a}}^{\text{E}}}{[\text{H}^+] + K_{\text{a}}^{\text{E}}} \quad (\text{pH} > 7) \quad (10)$$

Picosecond Flash Photolysis. A preliminary study of the initial photoprocesses was done by subpicosecond excitation of **1a** and **1b** at 248 nm in acetonitrile solution. In both cases, ketene **2** was

formed with a rate of about $2 \times 10^{10} \text{ s}^{-1}$ following excitation. The nature of these primary photoprocesses has not yet been established. Over half the initial bleaching of starting material **1b** was restored during this process. Keeping in mind that the quantum yield of disappearance of **1b** (in aqueous acid) is only 34%, this strongly suggests that the observable primary process should be attributed to the decay of the excited state of **1b** and not to the alleged ketocarbene intermediate undergoing Wolff rearrangement.

Isotope Exchange Kinetics. The solubility of indene-3-carboxylic acid (**4**) in aqueous DCl was too low to provide reliable kinetic data of isotopic exchange by ^1H NMR spectroscopy. Instead, acetate buffer was employed which increased the solubility of **4** due to partial ionization to 4^- . The NMR measurement was made at 25°C in D_2O solution which contained a high concentration of acetate buffer ($[\text{OAc}^-] = 0.414 \text{ M}$ and $[\text{DOAc}] = 0.197 \text{ M}$) in order to swamp a possible contribution of **4** ($[\text{4}] = 0.021 \text{ M}$) as a general acid catalyst. The extent of deuteration of **4** was measured by monitoring the allylic proton signal intensity at $\delta = 3.53 \text{ ppm}$; the aromatic protons provided an internal standard. The disappearance of the allylic proton signal intensity fitted well to a first-order rate law and gave $k_{\text{obsd}}^{\text{exch}} = (2.87 \pm 0.16) \times 10^{-4} \text{ s}^{-1}$. The rate of ketonization of 3^- was determined by flash photolysis of diazoquinone **1b** in water with the same buffer composition as above, $k_{\text{obsd}}^{\text{K}} = (4.4 \pm 0.2) \times 10^3 \text{ s}^{-1}$. The rate in D_2O was $940 \pm 50 \text{ s}^{-1}$ which amounts to a kinetic isotope effect of $k_{\text{obsd,H}_2\text{O}}^{\text{K}}/k_{\text{obsd,D}_2\text{O}}^{\text{K}} = 4.7 \pm 0.4$.

The following assumptions were made in order to determine the rate of enolization of **4**, k^{E} , from the observed rate of deuteration, $k_{\text{obsd}}^{\text{exch}}$: (i) Under the conditions of the NMR experiment, isotopic exchange at C_1 of **4** is dominated by the mechanism shown in eq 11,



which involves formation of the reactive neutral form of **4** in a preequilibrium, followed by C_1 deprotonation of **4** by the acetate ion. The latter step is irreversible in D_2O . This mechanistic assumption is consistent with the observed catalytic coefficients of acetate buffers at $\text{p}[\text{H}^+] = 5.0$ and 6.0 for the rate of ketonization of 3^- (the reverse of the second step in eq 11), as the ratio of the slopes k_{bu} is approximately equal to the relative amount of AcOH in the two buffer mixtures. It is also consistent with an estimate based on linear free energy relations described in the Discussion. The kinetic isotope effect of 4.7 is consistent with rate determining deprotonation at C_1 in the second step. (ii) The preequilibrium constant of eq 11 stands for the equilibrium of deuterium exchange between two carboxylic acids of very similar acid strength, $K_{(11)} = K_{\text{a}}^{\text{AcOD}}/K_{\text{a}}^{\text{K}}$. We assume that $K_{(11)}$ is not affected by either ionic strength or isotopic composition of the solvent (H_2O or D_2O), i.e., that the activity coefficients of the anions, γ_{AcO^-} and γ_{3^-} , as well as the isotope effects for H/D substitution in the two carboxylic acids will essentially cancel. Thus, $K_{(11)} = 0.86$, calculated from the ionization quotients of AcOH²⁴ and of **4** in H_2O at ionic strength $I = 0.10 \text{ M}$, is assumed to hold for the conditions of the NMR experiment, i.e., D_2O solvent and ionic strength $I = 0.414 \text{ M}$. Any error introduced by this assumption should be small compared to other uncertainties. (iii) Secondary and solvent kinetic isotope effects on the second step of eq 11 are neglected. A reasonable estimate for the α -H secondary isotope effect in the exchange of the second hydrogen of **4** carrying one deuterium at C_1 is $2k_{\text{HD}}/k_{\text{HH}} = 0.9 \pm 0.1$.²⁵ This would amount to a negligible effect on the overall

process of hydrogen exchange, which fitted well to a single exponential rate law. Thus we assume that $k_{\text{HD}} \cong 1/2 k_{\text{HH}}$ which introduces a statistical factor of $1/2$ relating the rate of enolization to the rate of isotope exchange, $k_{\text{obsd}}^{\text{exch}} = 1/2 k^{\text{E}}$. (iv) It is assumed that the observed decay rate of **3**, $k_{\text{obsd}}^{\text{K}}$, is equal to the rate of the reaction $3 \rightarrow 4$ (see, however, below). Assumptions (i)–(iii) lead to eq 12 as the relation between the required rate of enolization of **4** and the observed rate of deuteration.

$$k^{\text{E}} = 2k_{\text{obsd}}^{\text{exch}} \frac{0.86[\text{AcOD}] + [\text{AcO}^-]}{0.86[\text{AcOD}]} \quad (12)$$

Based on assumption (iv) the equilibrium constant $K_{(11)} = k^{\text{E}}/k_{\text{obsd}}^{\text{K}}$ is then calculated as $(4.5 \pm 0.5) \times 10^{-7}$, from which $\text{p}K_{(11)}^{\text{E}} = \text{p}K_{(11)} + \text{p}K_{\text{a}}(\text{AcOH}) - \text{p}K_{\text{a}}^{\text{K}} = 6.4 \pm 0.2$, and $\text{p}K_{\text{E}} = \text{p}K_{(11)} + \text{p}K_{\text{a}}(\text{AcOH}) - \text{p}K_{\text{a}}^{\text{E}} = 9.0 \pm 0.3$ are obtained.²⁴

Recent work by Kresge and co-workers²⁶ shows that assumption (iv) may not be valid, as ketonization of **3** initially yields significant amounts of indene-1-carboxylic acid along with **4**, which is the predominant product after workup. This implies that the observed rate of ketonization may be larger than the rate of reaction $3 \rightarrow 4$ required here, since it is equal to the sum of the rates for reactions $3 \rightarrow 4$ and $3 \rightarrow$ indene-1-carboxylic acid. Any contribution of the latter reaction will make $k_{3 \rightarrow 4}$ smaller than the observed rate of ketonization and hence increase the equilibrium constant K_{E} derived therefrom. The necessary correction to $\text{p}K_{\text{E}}$ is probably less than -0.3 (corresponding to a 1:1 yield of both isomers), but we prefer to quote the higher bound of our uncorrected values as an upper limit defined by this measurement, $\text{p}K_{\text{E}} \lesssim 9.3$, $\text{p}K_{\text{E}}^{\text{E}} \lesssim 6.6$. Note that the $\text{p}K_{\text{a}}$ values derived from the pH profile are not affected by the ratio of indenecarboxylic acid isomers formed on ketonization.

Discussion

Both α -diazonaphthoquinones (**1a** and **1b**) undergo the expected photochemistry in acidic aqueous solution,^{6,8,9} namely Wolff rearrangement and hydrolysis of the resulting ketene (**2**) to give indene-3-carboxylic acid (**4**) through benzofulvene-8,8-diol (**3**), Scheme 1.

Flash photolysis of **1a** and **1b** in acetonitrile produces a long-lived intermediate absorbing weakly near 330 to 340 nm that was formed with a rate of ca. $2 \times 10^{10} \text{ s}^{-1}$ and is assigned to ketene **2**. In aqueous media, the ketene readily reacts with water to give enol **3**, and this reaction was observed by the time-resolved growth of transient absorption at 330–360 nm. The rate of ketene hydrolysis is independent of acid concentration down to 0.1 M but increases with increasing hydroxide ion concentration in strong base (Figure 2, curve a).

The ketonization process $3 \rightarrow 4$ is accelerated by acid down to $\text{pH} \approx 2$ where acid catalysis saturates. Such behavior is characteristic for predissociation of an enediol to the more reactive enediol anion; above pH 2 the rate of carbon protonation on 3^- increases with increasing proton concentration. Once the equilibrium shifts to the neutral enediol **3**, increased acid strength does not further accelerate the reaction, because increased acid concentration is compensated by decreased concentration of the reactive species 3^- . Thus, saturation of acid catalysis defines the first ionization constant of the enediol **3**, $\text{p}K_{\text{a}}^{\text{E}} = 1.90 \pm 0.05$. In basic solutions, the ketonization rate increases with increasing hydroxide concentration in the weakly basic region, where 3^- predominates, and quickly reaches its maximum rate of $105 \pm 5 \text{ s}^{-1}$ beyond the second acidity constant of the enol, $\text{p}K_{\text{a}}^{\text{E}} = 8.3 \pm 0.2$ (Figure 2, curve b).

Interpretation of the flash photolytic data obtained in basic solution was hampered by two problems: (i) We could not ascertain that indene-3-carboxylic acid **4** is the only photoproduct

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Table 3. Calculated Rate Constants for the Rate-Determining Carbon Protonation Reactions, Eqs 2-7 (cf. Text)

reaction i	rate symbol	p <i>K</i> _i	α_i	log(<i>k</i> _i)
2	<i>k</i> _{H⁺}	-2.3 ^a	0.47	3.2
3	<i>k</i> ₀	11.5 ^b	0.63	-6.9
4	<i>k</i> _{H⁺}	-11.1	0.37	≅7.34
5	<i>k</i> ₀	2.7 ^b	0.53	0.0
6	<i>k</i> _{H⁺}	-15.2	0.33	8.7
7	<i>k</i> ₀	-1.4 ^b	0.48	2.6

^a The acidity of protonated methyl benzoate, p*K*_a = -7.0, was taken from the following: Bagno, A.; Lucchini, V.; Scorrano, G. *J. Phys. Chem.* **1991**, *95*, 345 and was used as a substitute for the unknown acidity of protonated indenecarboxylic acid. ^b p*K*_w (*I* = 0.1 M) = 13.80.²¹

formed by irradiation of the α -diazonaphthoquinones in basic solutions, because **4** is unstable under these conditions and reacts within minutes to a complex, highly colored product mixture. It was observed, however, that an authentic mixture of **4** and **1b** in aqueous base reacts similarly in the dark. (ii) The transient absorption observed after hydrolysis of ketene **2** partly decays on a time scale of microseconds. The origin of this fast decay is unknown.²³ Nevertheless, we are confident that the assignment of the major, much slower decay observed in basic solutions to the reaction of dianion **3**²⁻ with water, eq 7, is correct for the following reasons. Based on this assignment we obtain an enolization constant for **3** which is consistent with an independent determination of this value (*vide infra*). Moreover, the kinetic and thermodynamic data based on this assignment form a self-consistent set by the criteria of linear free energy relationships, as is shown next.

An *a priori* estimate of the rate constants *k*_i for carbon protonation, eqs 2-7, can be obtained from their free energies of reaction, $\Delta_i G^\circ$, using a Brønsted-type approach, eq 13, in combination with Marcus theory²⁷ to estimate the Brønsted parameter α_i , eq 14.

$$\log(k_i/k_{\text{ref}}) = \alpha_i \log(K_i/K_{\text{ref}}) \quad (13)$$

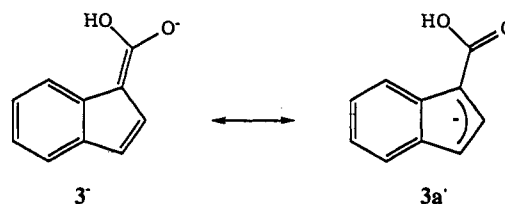
$$\alpha_i = 0.5 + \Delta_i G^\circ / (8\Delta G_0^\ddagger) \quad (14)$$

As a parameter for the intrinsic barrier of proton transfer to carbon we use $\Delta G_0^\ddagger = 15 \text{ kcal mol}^{-1}$, an average taken from two recent estimates of this value for related systems.²⁸ The results are not very sensitive to the choice of the parameter ΔG_0^\ddagger . The free energies of reaction for the rate-determining steps, eqs 2-7, are calculated from the equilibrium constants determined in this work (Table 2). Reaction 4 was chosen as a reference in eq 13, i.e., $k_{\text{ref}} = k_{(4)} = k'_{\text{H}^+} = 2.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, and $K_{\text{ref}} = K_{(4)} = K_a^E K_E = 1.3 \times 10^{11}$. The equilibrium constants for the rate determining step in reactions 2-7, the resulting estimates for α_i , and the calculated rate constants *k*_i are collected in Table 3. In agreement with experimental findings, only two of the reactions 2-7, reactions 4 and 7, are expected to make a significant contribution to the observed rate profile. The estimated contribution from reaction 2, which is proportional to [H⁺] at the low end of the pH-scale, is over two orders of magnitude less than the observed, pH-independent rate attributed to reaction 4 up to the highest acid concentration used, [H⁺] = 1 M. The contributions by reactions 5 and 6 are pH-independent in the central part of the pH-profile and are estimated as $\log(k'_0/s^{-1}) = 0.0$ and $\log(k''_{\text{H}^+} K_a^E/s^{-1}) = 0.4$, respectively; both of these estimates are somewhat less than the lowest value of $\log(k_{\text{obs}}/s^{-1}) = 0.6$ at the bottom of the pH-profile, and, hence, a least-squares fit of the experimental data to eq 1 does not provide a significant value for the parameter

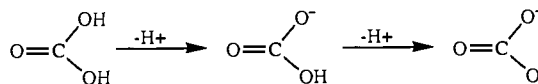
$(k'_0 + k''_{\text{H}^+} K_a^E)$. On the other hand, the rate calculated for reaction 7, $\log(k''_0/s^{-1}) = 2.6$, agrees satisfactorily with the observed rate in aqueous base, $\log(k_{\text{obs}}/s^{-1}) = 2.0$. In view of this analysis, use of the simplified rate law, eq 8, is justified. A least-squares fit of the complete set of data to eq 8 is shown in Figure 2, curve b. The parameters resulting from the fit were virtually identical with those given in Table 2 which were obtained from the linear regressions of eqs 8 and 9.

The four acidity constants for the first and second ionization of carboxylic acid **4** and enediol **3** (Scheme 1) can be combined to thermodynamic cycles giving the enolization constants of **4** and **4**⁻: $pK_E = pK_a^K + pK_a^K - pK_a^E - pK_a^E = 9.5 \pm 0.5$ and $pK'_E = pK_a^K - pK_a^E = 6.9 \pm 0.4$. Upper limits for the same values were obtained independently as the ratio of rate constants of enolization and ketonization, $pK_E \lesssim 9.3$, $pK'_E \lesssim 6.6$ (cf. the section on isotopic exchange kinetics). Combination of these results gives $pK_E = 9.3 \pm 0.3$ and $pK'_E = 6.6 \pm 0.3$ as our best estimates for the enolization constants of carboxylic acid **4**.

Ionization of benzofulvenediol (**3**) is facilitated by partial delocalization of negative charge from oxygen (**3**⁻) into the benzocyclopentadienyl moiety (**3a**⁻). Therefore, the acidity of **3** is much higher than that of the enol of a simple carboxylic acid such as mandelic acid, $pK_a^E = 6.6$.²⁹ The first and second ionization constants of **3** are about two orders of magnitude larger than those of carbonic acid ($pK_a = 3.9$ and 10.25),³⁰ a structurally related compound. Thus, remarkably, the benzocyclopentadienyl moiety excels carbonyl oxygen as an electron acceptor.



The rate and equilibrium constants governing the keto-enol equilibrium of **4** are summarized in Table 2 along with the results obtained previously⁸ for the parent system cyclopentadiene-1-carboxylic acid \rightleftharpoons fulvenediol. The two sets of data compare reasonably for those values which depend only on the pH-rate



profiles of the enediols in the acidic region. The acidity of fulvenediol is about four times that of the benzo derivative **3**. The same trend is more pronounced in the CH acidities of cyclopentadiene ($pK_a = 18.0$) and indene ($pK_a = 20.1$)³¹ where ionization develops a full charge in the five-membered ring. On the other hand, the large differences between the second acidity constants of the enediols, pK_a^E , and between the reaction rates of the dianion, *k*₀, are surprising, and, more important, the trends are opposite to those expected. Furthermore, analysis of the data for cyclopentadiene-1-carboxylic acid⁸ by the free energy relationship of eq 13 showed that the results were not self-consistent; based on the data given in Table 2, the rate of protonation of the dianion by water, *k''*₀, is calculated to be several orders of magnitude less than the observed value. This led us to scrutinize our previous results determined by flash photolysis of 2-bromophenol in basic solution, and a preliminary reinvestigation

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reveals that these are probably in error. The rate profile reported⁸ for the decay of fulvenediol in basic solutions appears to be of similar origin as the minor decay observed with **1a** in basic solutions.²³ A major slow decay with a rate constant of ca. 3 s^{-1} is also present; this has previously escaped our attention, because persistent end absorption reappears within minutes after the flash. We are currently reinvestigating the reaction kinetics of fulvenediol in buffer solutions and in base and will submit our findings shortly. For the time being, the values marked by footnote *d* in Table 2, which depend on the kinetic data obtained in basic solutions, should be disregarded.

Experimental Section

Instrumentation. NMR measurements were made on a 300-MHz instrument (Varian VX300). Kinetic flash photolysis on the millisecond time scale was done on a conventional system with a 1000-J electrical discharge through partly evacuated quartz tubes which produced a flash of 20 μs duration. Nanosecond laser flash photolysis was carried out with an excimer laser (Lambda Physik EMG101 MSC) operated on XeF (351 nm, pulse width 25 ns, ca. 100 mJ per pulse); the flash was perpendicular to the probing light from a pulsed Xe arc. The signal was recorded with a photomultiplier (EMI 9785QA) and was fed into a digitizer (Tektronix TDS 540). Rate constants were calculated by least-squares fitting of the transient waveforms with mono- or biexponential functions, as appropriate.³² The pump-probe flash photolysis system with picosecond time resolution was described previously.³³ It uses a pump pulse of 0.8 ps half-width at 248 nm and a delayed continuum probe pulse of the same duration ranging from 320 to 700 nm.

General Methods. For isolation of the photoproducts, 15 mg of **1b** were first dissolved in 1 mL of methanol and then added to an aqueous solution of appropriate pH, to give a total volume of 50 mL. The solutions were nitrogen-purged for 10 min before the irradiation. Continuous irradiation was carried out with a high-pressure mercury arc lamp equipped

with a 365 nm cut-off filter. The reaction progress was monitored by UV spectrometry. After the complete disappearance of **1b**, the aqueous solutions were neutralized (in the case of basic solutions) and extracted repeatedly with dichloromethane. The combined organic layers were washed with water and dried (Na_2SO_4), and the solvent was removed under reduced pressure.

Diazonaphthoquinones **1a** and **1b** are sparingly soluble in water; solutions up to about 10^{-4} M were prepared by ultrasonic treatment. Solutions of higher concentration for preparative work were prepared using a few percent of acetonitrile or methanol as cosolvents. Air-saturated solutions were used for most measurements; control experiments with degassed solutions showed that the results of the kinetic measurements were not affected significantly by the presence of air. Aqueous NaOH solutions (pH 10–12), aqueous HCl solutions (pH 1–3), and acetic acid (pH 4–6), phosphate (pH 6–8), and trishydroxymethylaminomethane (TRIS, pH 7–9) buffer solutions were employed. The ionic strength of all solutions was adjusted to 0.1 M by the addition of NaCl. Flash photolysis was done at ambient temperature ($23 \pm 2^\circ\text{C}$), but the solutions were always taken from a thermostat bath at 25.0°C shortly before the measurements.

Materials. Compounds **1a**³⁴ (recrystallized from ether; slowly decomposes as a solid at 0°C ; the decomposition product absorbs at $\lambda_{\text{max}} = 320 \text{ nm}$), **1b**³⁵ (purified by chromatography on neutral alumina with methylene chloride at 0°C followed by recrystallization from hexane; stable for months as a solid at 0°C), **4**³⁶ (purified by recrystallization), and 2-bromo-1-naphthol (purified by 2-fold sublimation)³⁷ were prepared according to the literature procedures. Commercial compounds were of best available purity.

Acknowledgment. This work was supported by the Swiss National Science Foundation. We thank Prof. Dr. A. J. Kresge for many helpful comments and for communicating his results on the initial product distribution of indenecarboxylic acids.²⁶

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