Electron Ejection and Fluorescence in Aqueous β-Naphthol Solutions

By Michael Ottolenghi

The ultraviolet photochemistry of aqueous β-naphthol solutions was investigated using specific scavengers for solvated electrons (N_2O, H_3O^+, and acetone) and for hydrogen atoms (C_2H_5OH). It was found that the excited β-naphtholate ion undergoes an electron ejection process while the neutral β-naphthol molecules undergo both electron ejection and dissociation into hydrogen atoms and β-naphthoxyl radicals. The pH dependence of the quantum yields of these processes is similar to that found by Förster and Weller for the relative fluorescence of the β-naphthol molecule and the β-naphtholate ion. It is thus concluded that electron ejection occurs mainly from the first singlet, fluorescence-emitting, excited state, in thermal equilibrium with the medium.

Introduction

In a previous paper[1] the photochemistry of the phenolate ion in aqueous solution was investigated in the presence of specific scavengers for solvated electrons (N_2O and acetone) using monochromatic light of 2288 and 2537 Å. The kinetic analysis of the dependence of the quantum yield on the scavenger concentration indicated that the excited phenolate ion undergoes a thermal ionization into a solvated electron and a phenoxyl radical, both in the same solvent cage. The limiting constant quantum yield, Γ, obtained at high [N_2O], represents total scavenging of solvated electrons from the photochemical cage. The magnitude of Γ is determined by the relative efficiency of the electron ejection process and the various ways of deactivation of the excited ion.

A brief spectroscopic study[1] indicated that the absorption bands of the phenolate ion in aqueous solutions are due to internal π–π^* excitations of the aromatic system and do not involve any considerable contribution of a C.T.T.S. (charge transfer to the solvent) transition. Such a transition leads to the formation of solvated electrons in the case of the Cl^-, Br^-, I^-, and OH^- ions in solution.[2-4] However, the exact nature of the excited state from which the electron ejection takes place, in the case of the phenolate ion, remained unclear. Irradiation at 2288 or 2537 Å. excites the ion to the second singlet excited state (the $^1B_{1u}$ state) which may, however, undergo radiationless transitions to lower excited states before ejecting the electron. Electron ejection may then take place from a lower state such as the lowest singlet (the $^1B_{2u}$ state), the lowest triplet (the $^3B_{2u}$ state), or even a C.T.T.S. state.

The purpose of the present work was to determine which of the various possible states is responsible for electron ejection from excited aromatic molecules and ions in solution. The choice of β-naphthol is due to the relatively high fluorescence efficiency of both ionized and neutral forms of this molecule. As it will become clear in the following sections, the main conclusions of this work are drawn from the analogies between fluorescence efficiencies and quantum yields for electron ejection in aqueous β-naphthol solutions.

Experimental

Radiation Source and Actinometry.—The radiation source was an Osram Cd/1 cadmium arc operated at 12 v. and 1.5 amp. The cadmium lines absorbed by the β-naphthol solutions were those in the range between 214 and 360 mμ. Actinometry was carried out, employing the uranyl oxalate actinometer, with a suitable correction for the inner filter effect of the oxalic acid for the 2288 Å. cadmium line. The light intensity was found to be in the range 2.0×10^{-7} to 3.4×10^{-7} einstein l.$^{-1}$ sec.$^{-1}$.

(1) J. Jortner, M. Ottolenghi, and G. Stein, *J. Am. Chem. Soc.*, **85**, 2712 (1963).

(2) J. Jortner, M. Ottolenghi, and G. Stein, *J. Phys. Chem.*, **66**, 2029 (1962).

(3) J. Jortner, M. Ottolenghi, and G. Stein, *ibid.*, **66**, 2037 (1962).

(4) J. Jortner, M. Ottolenghi, and G. Stein, *ibid.*, submitted for publication.
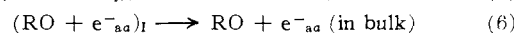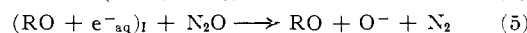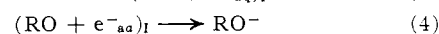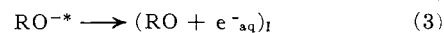
Photochemical Procedure.—Reaction vessels were adapted for vacuum photochemical experiments from $1 \times 1 \times 4$ cm. or $1 \times 3 \times 4$ cm. spectrophotometric cells. The procedure in experiments involving N_2O was previously described.[3] The pressure of the gas evolved on irradiation was determined by means of a McLeod gage and a Pirani L.K.B. gage. The chemical composition of the gas was ascertained by combustion in the presence of hydrogen or oxygen, or by comparing the readings on the McLeod gage with those on the Pirani gage, after a suitable calibration.

The pH below pH 3.1 was adjusted by means of H_2SO_4; CH_3COOH–CH_3COONa buffer was employed in the range $4 <$ pH < 5, K_2HPO_4–NaH_2PO_4 buffer in the range $6 <$ pH < 8, and H_3BO_3–KCl buffer in the range $7.9 <$ pH < 10.5. The buffer concentration in all solutions was 5×10^{-3} M. Above pH 12 the pH was adjusted by means of $NaOH$. In all cases total absorption of light by the β-naphthol molecule or the β-naphtholate ion could be assumed.

Determination of Fluorescence Intensities.—The apparatus for the fluorescence measurements consisted of a xenon arc as the light source and two Bausch and Lomb monochromators, for both exciting and emitted light. An EMI 6256B photomultiplier was used as the detector for the emitted radiation, the intensity of which was measured at 414 mμ.

Results and Discussion

Photochemistry of the β-Naphtholate Ion.—In previous investigations[1-4] it has been shown that electron ejection from excited molecules and ions in solution may be detected by means of specific scavengers for solvated electrons, such as proton donors (H_3O^+, $H_2PO_4^-$, NH_4^+, etc.), acetone, or N_2O. Because of the restriction of the high alkalinity, N_2O was employed in the β-naphtholate system. Solutions of 2×10^{-3} M β-naphthol, at pH values above 12, were equilibrated with N_2O at various pressures and then irradiated. The gas evolved on irradiation was found to be pure N_2, its quantum yield $\gamma(N_2)$ depending on the N_2O concentration but not on the pH (when pH > 12). The experimental results are reported in Table I. As in other systems previously investigated,[1-4] we attribute the nitrogen evolution to the formation of solvated electrons from the excited β-naphtholate ion followed by scavenging by N_2O, according to the kinetic scheme

$$RO^- \xrightarrow{h\nu} RO^{-*} \qquad (1)$$

$$RO^{-*} \longrightarrow RO^- \qquad (2)$$

$$RO^{-*} \longrightarrow (RO + e^-_{aq})_I \qquad (3)$$

$$(RO + e^-_{aa})_I \longrightarrow RO^- \qquad (4)$$

$$(RO + e^-_{aq})_I + N_2O \longrightarrow RO + O^- + N_2 \qquad (5)$$

$$(RO + e^-_{aa})_I \longrightarrow RO + e^-_{aa} \text{ (in bulk)} \qquad (6)$$

where the parentheses denote the photochemical cage in which the solvated electron e^-_{aq} is formed with the β-naphthoxyl radical, RO. The dependence of γ-(N_2) on [N_2O] is due to competition between the cage scavenging (eq. 5) and the geminate cage recombination, eq. 4. This dependence may be quantitatively represented by Noyes' equation[5]

$$\gamma(N_2) = \gamma_r + \Gamma_e' 2a \sqrt{\pi k_{N_2O + e^-_{aa}}[N_2O]} \qquad (7)$$

(5) R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955); **78**, 5486 (1956).
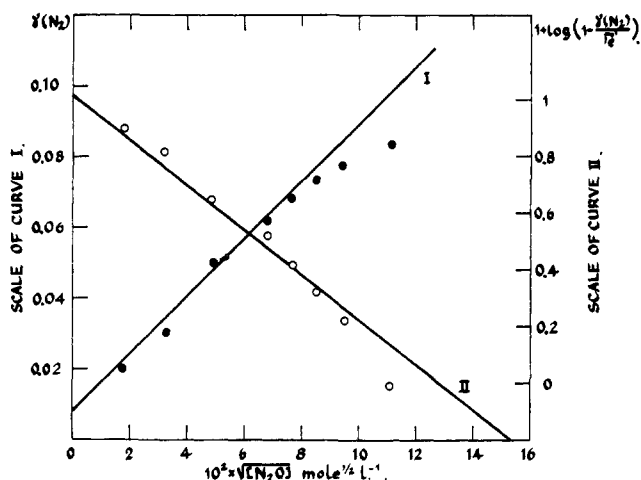
Fig. 1.--Cage scavenging of solvated electrons by N_2O: curve I, plot according to eq. 7; curve II, plot according to eq. 8.

$\Gamma_e{}'$ is the yield of formation of the pair $RO + e^-{}_{aq}$ in the photochemical cage I, a is a parameter depending on the solvent and on the nature of the radicals in the cage,[5] and γ_r is the "residual yield"[2] representing the quantum yield of radicals escaping cage recombination by diffusion into the bulk, when $[N_2O] = 0$. Equation 7 is an approximation valid only at relatively low $[N_2O]$ values. A more general relation valid over the whole $[N_2O]$ range, derived[2] on the basis of Noyes' theoretical treatment,[4] is

$$\ln\left\{1 - \frac{\gamma(N_2)}{\Gamma_e}\right\} = \ln\left\{1 - \frac{\gamma_r}{\Gamma_e'}\right\} - \frac{2a}{1 - \frac{\gamma_r}{\Gamma_e'}} \sqrt{\pi k_{N_2O + e^-{}_{aq}}[N_2O]}$$

(8)

Equations 7 and 8 are not applicable at very low N_2O concentrations when the rates of scavenging and bulk recombination are comparable, i.e., when $\gamma(N_2) < \gamma_r$. In our system (see Table I) total scavenging is obtained at $[N_2O] > 1.4 \times 10^{-2}$ M, when $\gamma(N_2)$ reaches the limiting value of $\gamma(N_2) = 9.2 \times 10^{-2}$, which should thus be identified as the yield of formation of $e^-{}_{aq}$ and RO in the photochemical cage at 25°. We may therefore assume $\Gamma_e' = 9.2 \times 10^{-2}$. The plot of the experimental results of Table I according to the cage scavenging eq. 7 and 8 is given in Fig. 1. The deviation from linearity at high $[N_2O]$, in the plot according to eq. 7, is due to the above-mentioned limitation of this equation. The slight deviation in the plot of eq. 8 has been discussed for other cage-scavenging systems[2] and attributed to a time dependence of the diffusion-controlled rate constant $k_{N_2O + e^-{}_{aq}}$. From the slopes in Fig. 1 one gets $2a\sqrt{\pi k_{N_2O + e^-{}_{aq}}} = 8.7$ $l.^{1/2}$ mole$^{-1/2}$ when this parameter is calculated from the plot of eq. 7. When the calculation is according to eq. 8, the value $2a\sqrt{\pi k_{N_2O + e^-{}_{aq}}} = 17.5$ $l.^{1/2}$ mole$^{-1/2}$ is obtained. A factor of 1–3 between the values of the parameter $2a\sqrt{\pi k}$ as calculated from the slopes of eq. 7 and 8 has been observed in all systems in which these equations are applicable and have been previously discussed.[2] In both treatments we get $\gamma_r < 8.0 \times 10^{-3}$, indicating a very efficient cage recombination of RO and $e^-{}_{aq}$. We may thus conclude that our experimental results are quantitatively consistent with the operation of the cage scavenging kinetic scheme (eq. 1–6), thus excluding other charge transfer mechanisms, such as a direct interaction of N_2O with the excited ion, which could also lead to electron capture and nitrogen evolution.

It should be noted that the quantum yields reported in Table I refer to the polychromatic cadmium radiation in the range 214–360 mμ. An experiment in which
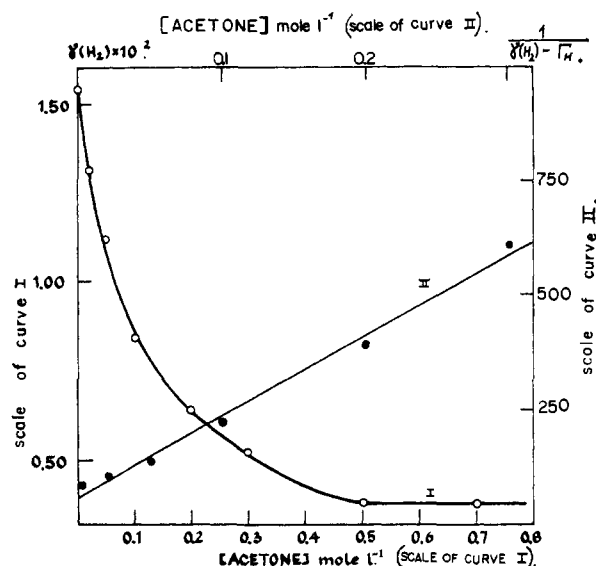

Fig. 2.—Curve I, the dependence of $\gamma(H_2)$ on acetone concentration at pH 2.0 in the presence of 0.75 M ethanol; curve II, test of the dependence of $\gamma(H_2)$ on the acetone concentration according to eq. 13.

a 4 N CH_3COOH filter (cutting off light below 2400 Å.) was placed between the light source and the cell showed that 65% of the chemical change was due to the 214 and 229 mμ lines. The value of Γ_e' for both of these lines, which excite the molecule to the second singlet state, has the value of 0.102. That for the longer wave lengths below 360 mμ, where excitation is to the first singlet, has the value of 0.077.

TABLE I

THE DEPENDENCE OF $\gamma(N_2)$ ON N_2O CONCENTRATION IN SOLUTIONS OF 2 × 10^{-3} M β-NAPHTHOL AT pH ≥ 12

| $[N_2O]$, mole l.$^{-1}$	pH	$\gamma(N_2)$
1.95×10^{-2}	14	9.0×10^{-2}
1.95×10^{-2}	13.5	9.2×10^{-2}
1.95×10^{-2}	12	9.2×10^{-2}
1.95×10^{-2}	13	9.1×10^{-2}
2.00×10^{-2}	13	9.2×10^{-2}
1.47×10^{-2}	13	9.2×10^{-2}
1.23×10^{-2}	13	8.3×10^{-2}
8.8×10^{-3}	13	7.7×10^{-2}
7.3×10^{-3}	13	7.3×10^{-2}
5.8×10^{-3}	13	6.8×10^{-2}
4.7×10^{-3}	13	6.2×10^{-2}
2.4×10^{-3}	13	5.05×10^{-2}
1.06×10^{-3}	13	3.0×10^{-3}
3.1×10^{-4}	13	2.0×10^{-3}
. . .	13	$<4.0 \times 10^{-4}$

Photochemistry of the Neutral β-Naphthol Molecule. —The photochemistry of un-ionized β-naphthol was investigated in acid solutions at pH < 2 in order to ascertain whether photochemical electron ejection is a characteristic of the solvated anion or may also occur in the case of the neutral molecule. Experiments were carried out in acid solutions where H_3O^+ acts very efficiently as electron scavenger,[2] according to

$$H_3O^+ + e^-{}_{aq} \longrightarrow H + H_2O \qquad (9)$$
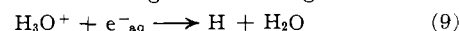
Ethanol was employed as a scavenger for hydrogen atoms[1-4] formed either by reaction 9 or, possibly, by a direct dissociation of the excited neutral molecule. On irradiation pure H_2 was evolved. According to the experimental results of Table II, there is no gas evolution in the absence of ethanol, indicating that H_2 formation proceeds via H atoms, scavenged by the al-

cohol according to

$$H + C_2H_5OH \longrightarrow H_2 + C_2H_4OH \qquad (10)$$
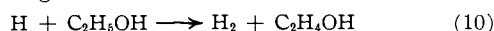
The quantum yields in Table II also indicate that total scavenging of H atoms is obtained when $[C_2H_5OH] > 0.75\ M$. However, no information can be obtained from the data as to the mechanism by which hydrogen atoms are formed. In order to clarify this point we investigated the effect of added acetone on the quantum yields of H_2 evolution. The experimental results are presented in Fig. 2, curve I. It has been shown[1,6]

TABLE II

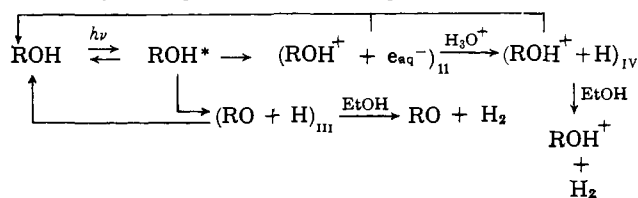QUANTUM YIELDS FOR H_2 EVOLUTION FROM ACID β-NAPHTHOL SOLUTIONS IN THE PRESENCE OF C_2H_5OH

pH[a]	Scavenger system		$\gamma(H_2)$
	For solvated electrons	For hydrogen atoms	
0.6	$2.5 \times 10^{-1}\ M\ H_3O^+$	$0.75\ M$ EtOH	1.60×10^{-2}
0.9	$1.26 \times 10^{-1}\ M\ H_3O^+$	$0.75\ M$ EtOH	1.48×10^{-2}
1.75	$1.8 \times 10^{-2}\ M\ H_3O^+$	$0.75\ M$ EtOH	1.52×10^{-2}
1.75	$1.8 \times 10^{-2}\ M\ H_3O^+$	$1.2\ M$ EtOH	1.56×10^{-2}
1.75	$1.8 \times 10^{-2}\ M\ H_3O^+$	...	$<2.0 \times 10^{-4}$
2.0	$10^{-2}\ M\ H_3O^+$	$0.75\ M$ EtOH	1.56×10^{-2}

[a] The pH was adjusted by means of H_2SO_4.

that acetone reacts very efficiently with solvated electrons in a process which does not lead to gas evolution, while its reactivity with H atoms is relatively low.[7] An examination of curve I in Fig. 2 shows that $\gamma(H_2)$ decreases from the value $\gamma(H_2) = 1.56 \times 10^{-2}$, in the absence of acetone, to a constant limiting value of $\gamma(H_2) = 3.8 \times 10^{-3}$ obtained at high acetone concentrations. As the acetone concentration is too low to compete for H atoms with $0.75\ M$ ethanol,[7] we conclude that the decrease in $\gamma(H_2)$ with increasing acetone concentration is due to competition between reaction 9 and the reaction

$$e^-_{aq} + CH_3COCH_3 \longrightarrow (CH_3COCH_3)^- \longrightarrow$$
$$\text{nongaseous prod.} \quad (11)$$
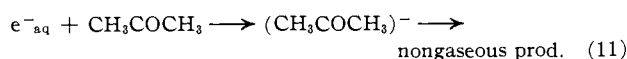
However, the fact that $\gamma(H_2)$ does not decrease below the limiting value of $\gamma(H_2) = 3.8 \times 10^{-3}$ indicates that some other process is responsible for part of the H atom formation, besides reaction 9. We suggest that this limiting yield of hydrogen is due to hydrogen atoms formed directly from excited β-naphthol molecules. This may be represented by the general scheme

$$
\begin{array}{c}
\overbrace{\text{ROH} \underset{\rightleftarrows}{\overset{h\nu}{}} \text{ROH*} \longrightarrow (\text{ROH}^+ + e_{aq}^-)\underset{11}{\overset{H_3O^+}{\longrightarrow}} (\text{ROH}^+ + H)_{IV}}\\
\uparrow \qquad \qquad \Big\downarrow \qquad \qquad \qquad \qquad \Big\downarrow \text{EtOH}\\
\text{(RO + H)}_{III} \xrightarrow{\text{EtOH}} \text{RO + H}_2 \qquad \text{ROH}^+ \\
\qquad \qquad \qquad \qquad + \\
\qquad \qquad \qquad \qquad H_2
\end{array}
$$

where we assume that all radical pairs are formed in photochemical cages. The independence of $\gamma(H_2)$ on H_3O^+ and ethanol concentrations (see Table II) indicates that total scavenging of solvated electrons and hydrogen atoms may be assumed when $[H_3O^+] > 10^{-2}\ M$ and $[C_2H_5OH] > 0.75\ M$. In this concentration range we may therefore neglect the recombinations of pairs II, III, and IV and set $\Gamma_H = 3.8 \times 10^{-3}$ and $\Gamma_e = 1.18 \times 10^{-2}$, where Γ_H is the quantum yield of formation of hydrogen atoms in cage III (derived from $\gamma(H_2)$ at high acetone concentrations) and Γ_e that of solvated electrons formation in cage I (derived from the value $\gamma(H_2) = 1.56 \times 10^{-2}$ in the absence of acetone, i.e., $\Gamma_e + \Gamma_H = \Gamma_e + 3.8 \times 10^{-3} = 1.56 \times 10^{-2}$). It should be noted that the influence of the

(6) J. Rabani and G. Stein, J. Chem. Phys., **37**, 1865 (1962).
(7) S. Nehari and J. Rabani (to be published) report the value $k_{ethanol+H}/k_{acetone+H} = 5-10$.
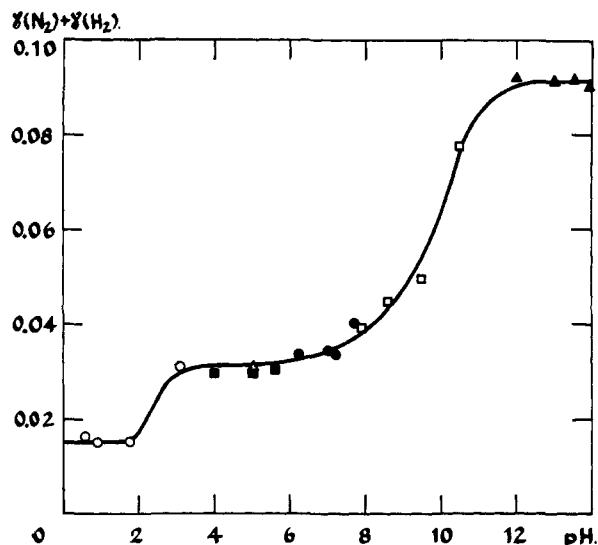

Fig. 3.—The pH dependence of the quantum yield for gas evolution in the photochemistry of β-naphthol; pH adjusted with: ▲, NaOH; □, borate buffer; ●, phosphate buffer; ■, acetate buffer; △, unbuffered; ○, H_2SO_4.

added acetone on $\gamma(H_2)$ is not concerned with the radical recombination in cage II and its only effect is that of competing with H_3O^+ for the solvated electrons, which at pH < 2, are totally scavenged even in the absence of acetone. $\gamma(H_2)$ in acetone-containing solutions when pH < 2 and $[C_2H_5OH] = 0.75\ M$ should thus be represented by

$$\gamma(H_2) = \Gamma_H + \Gamma_e \frac{k_9[H_3O^+]}{k_9[H_3O^+] k_{11}[\text{acetone}]} \qquad (12)$$

which may be rearranged to

$$\frac{1}{\gamma(H_2) - \Gamma_H} = \frac{1}{\Gamma_e} + \frac{k_{11}[\text{acetone}]}{\Gamma_e k_9[H_3O^+]} \qquad (13)$$

The agreement of the experimental results with eq. 13 is clearly proved by curve II in Fig. 2. From the slope of the straight line the rate constant ratio $k_9/k_{11} = 3.3$ was calculated. This value is the same as that obtained in radiation chemistry experiments[6] and in our previous treatment for the solvated electrons formed from the excited phenolate ion.[1] We may thus conclude that the results in acid solutions agree quantitatively with the scheme suggested above.

Photochemistry at Intermediate pH Values.—The quantum yields for gas evolution in the intermediate range $3.1 < pH < 12$ are presented in Table III. In all experiments the concentration of the solvated electron scavenger, $[N_2O] = 1.95 \times 10^{-2}\ M$ or $[H_3O^+] > 10^{-2}\ M$, was sufficient for total scavenging of solvated electrons either from cage I or from cage II, and the same for the scavenging of H atoms by $0.75\ M$ ethanol from cages III and IV (the only exception are the experiments in strongly alkaline solutions, at pH > 12, where ethanol could not be used because of the formation of $C_2H_5O^-$ ions). Figure 3, which summarizes the data of Tables I, II, III, gives the pH dependence of the sum $\gamma(H_2) + \gamma(N_2)$, over the whole pH range. Considering the high scavenger concentrations this sum may be identified as that of γ_H (the quantum yield of H atoms formed by direct dissociation of ROH*), γ_e (the quantum yield of solvated electrons due to electron ejection from ROH*), and γ_e' (the quantum yield of solvated electrons due to electron ejection from RO$^-$*).

Fluorescence Intensities in the Presence of N_2O.— The fluorescence intensity in $10^{-4}\ M$ β-naphthol solu-

TABLE III

QUANTUM YIELDS OF H_2 AND N_2 IN THE RANGE $2 < pH < 12$ IN AQUEOUS SOLUTIONS OF 2×10^{-3} M β-NAPHTHOL

pH	Buffer system	Scavengers For solvated electrons	For hydrogen atoms	$\gamma(H_2) \times 10^3$	$\gamma(N_2) \times 10^2$
3.08	H_2SO_4	1.95×10^{-2} M N_2O	0.75 M EtOH	1.6 ± 1.2^a	2.96
4.05	Acetate	1.95×10^{-2} M N_2O	.75 M EtOH	2.0 ± 1.2^a	2.80
5.0	Acetate	1.95×10^{-2} M N_2O	.75 M EtOH	1.6 ± 1.2^a	2.64
5.0	Unbuffered	1.95×10^{-2} M N_2O	.75 M EtOH	2.0 ± 1.2^a	2.92
5.6	Acetate	1.95×10^{-2} M N_2O	.75 M EtOH	2.8 ± 1.2^a	2.76
5.6	Acetate	$\cdots$	.75 M EtOH	3.0 ± 0.3	..
6.24	Phosphate	1.95×10^{-2} M N_2O	.75 M EtOH	2.0 ± 1.2^a	3.20
6.98	Phosphate	1.95×10^{-2} M N_2O	.75 M EtOH	1.6 ± 1.2^a	3.22
7.17	Phosphate	1.95×10^{-2} M N_2O	.75 M EtOH	2.4 ± 1.2^a	3.16
7.73	Phosphate	1.95×10^{-2} M N_2O	.75 M EtOH	1.6 ± 1.2^a	4.00
7.73	Phosphate	$\ldots$	.75 M EtOH	3.0 ± 0.3	..
7.73	Phosphate	$\ldots$	$\ldots$	<0.4	..
7.9	Borate	1.95×10^{-2} M N_2O	.75 M EtOH	1.6 ± 1.2^a	3.75
8.6	Borate	1.95×10^{-1} M N_2O	.75 M EtOH	1.6 ± 1.2^a	4.50
9	Borate	$\ldots$	.75 M EtOH	2.0 ± 0.3	..
9.50	Borate	1.95×10^{-2} M N_2O	.75 M EtOH	$<1.6^a$	5.00
10.1	Borate	$\ldots$	.75 M EtOH	1.2 ± 0.2	..
10.5	Borate	1.95×10^{-2} M N_2O	.75 M EtOH	$<1.6^a$	7.70
12	NaOH	1.95×10^{-2} M N_2O	.75 M EtOH	$\ldots$	9.60

^{a} Experimental difficulties in the determination of small amounts of H_2 in the presence of an excess of N_2 prevented an accurate determination of these values.

tion at pH 13 in the presence of 1.9×10^{-2} M N_2O was measured and compared to that in the same solution, evacuated and without N_2O. The fluorescence was excited either at 229 mμ or at 349 mμ. In both experiments there was no significant effect of N_2O on the fluorescence intensity.
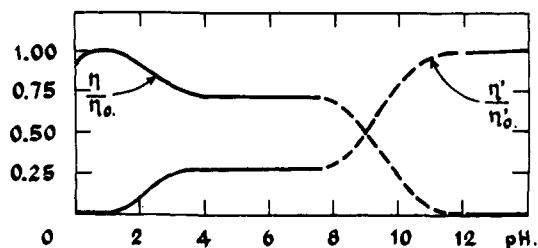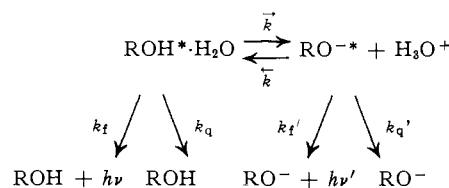

Fig. 4.—The pH dependence of η/η_0 and η'/η'_0 (after A. Weller; see ref. 9).

Relations between Electron Ejection and Fluorescence in Ultraviolet-Irradiated β-Naphthol Solutions.—

Förster[8] investigated the pH dependence of the fluorescence emission in aqueous solutions of aromatic hydroxy compounds and was able to show that in many cases the "blue" emission of the RO^- ion was still considerable even when the solutions where irradiated at pH values up to 5–8 units below the pK_a of the ground state compound. This behavior was attributed to a partial establishment of the excited state equilibrium

$$ROH^* \cdot H_2O \rightleftharpoons RO^{-*} + H_3O^+ \qquad (14)$$
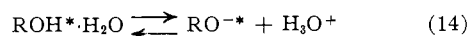
whose pK value (pK*) was supposed to be lower by 5–8 units than that of the ground state, the difference pK $-$ pK* depending on the nature of the hydroxy compound. These arguments were later given a quantitative basis by Weller,[9-11] who carefully investigated the pH dependence of the fluorescence of α- and β-naphthol and 2-naphthol-5-sulfonate solutions. His results for β-naphthol are reproduced in Fig. 4, where η_0 is the quantum yield of the "ultraviolet" emission of the β-naphthol molecule below pH 1, and η'_0 that of

(8) Th. Förster, *Naturwiss.*, **36**, 186 (1949); *Z. Elektrochem.*, **54**, 531 (1950).

(9) A. Weller, *ibid.*, **56**, 662 (1952).

(10) A. Weller, *Z. physik. Chem.* (Frankfurt), **15**, 438 (1958).

(11) A. Weller in "Progress in Reaction Kinetics," Vol. I, Pergamon Press, New York, N. Y., 1961, p. 189.

the "blue" emission of the β-naphtholate ion above pH 12.5; η and η' are the quantum yields for "ultraviolet" and "blue" emissions at intermediate pH values. By applying steady-state kinetics to the scheme

$$ROH^* \cdot H_2O \underset{\overleftarrow{k}}{\overset{\overrightarrow{k}}{\rightleftharpoons}} RO^{-*} + H_3O^+$$

$$k_f \swarrow \quad \searrow k_q \qquad k_f' \swarrow \quad \searrow k_q'$$

$$ROH + h\nu \quad ROH \qquad RO^- + h\nu' \quad RO^-$$

Weller[9] derived analytical expressions for the ratios η'/η'_0 and η/η_0 as functions of $[H_3O^+]$ and of the constant parameters $\overrightarrow{k}$, $\overleftarrow{k}$, $\tau_0 = 1/k_f + k_q$, and $\tau'_0 = 1/k_f' + k_q'$. These expressions, refined later in order to account for effects of transient reaction rates[10] and of ionic strength,[11] were found to agree with the experimental behavior in Fig. 4 and enabled the calculation of pK*. (For β-naphthol, pK* = 2.8, compared to pK = 9.23 in the ground state.)
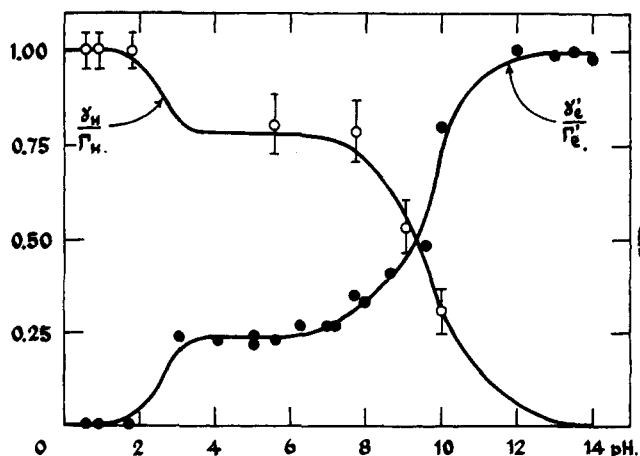

Fig. 5.—The dependence of γ_H/Γ_H and γ_e'/Γ_e' on the pH.

The similarity of the trend of the pH dependence of η'/η'_0 (Fig. 4) to that of the sum $\gamma(H_2) + \gamma(N_2) = \gamma_H + \gamma_e + \gamma'_e$ (Fig. 3) is obvious. This similarity induced us to analyze separately the pH dependence of the electron ejection from RO^{-*} and those of H atom

formation or electron ejection from ROH^{-*}. In the absence of a direct measurement of γ_e' we calculated this parameter according to the relation

$$\gamma_e' = \gamma(H_2) + \gamma(N_2) - \gamma_H - \gamma_e$$

However γ_e could not be separately determined and had to be calculated according to $\gamma_e \cong \gamma_H \Gamma_e/\Gamma_H = 3.1\gamma_H$, i.e., by assuming that the ratio of solvated electrons to H atoms formed from ROH^* is not affected by the pH. Thus

$$\gamma_e' = \gamma(H_2) + \gamma(N_2) - 4.1\gamma_H$$

Above pH 2 in 0.75 M C_2H_5OH solutions (with or without N_2O being present) all H atoms are scavenged by the alcohol ($k_{N_2O + H} < k_{C_2H_5OH + H}$) so that $\gamma_H = \gamma(H_2)$. (Below pH 2, in the absence of N_2O, $\gamma(H_2) = \gamma_H + \gamma_e = \Gamma_H + \Gamma_e$.) Thus, above pH 2, $\gamma_e' = \gamma(N_2) - 3.1\gamma(H_2)$. As no experimental values of $\gamma(H_2)$ are available at pH > 12, we estimated this parameter by extrapolation of the pH dependence of $\gamma(H_2)$ above pH 10; $\gamma(H_2) = \gamma_H$ is, however, so small in this region that the values of γ_e' are unaffected by this approximation, and we may assume $\gamma_e' = \Gamma_e'$. The plots of γ_H/Γ_H and γ_e'/Γ_e' vs. the pH are presented in Fig. 5. Because of the inaccuracy in the determination of $\gamma(H_2)$ in experiments where an excess of N_2 was present, we assumed γ_H to be represented by the H_2 yield in N_2O-free solutions, i.e., when no N_2 is evolved. We have not plotted γ_e/Γ_e because of the lack of separate, independent experimental values of γ_e. The results in this work will not distinguish between electrons ejected from ROH^* and those ejected from RO^{-*}. This parameter has been calculated above from γ_H by means of the relation $\gamma_e = \gamma_H(\Gamma_e/\Gamma_H)$. Obviously a plot in which these calculated values of γ_e are employed is the same as that of γ_H/Γ_H and does not provide any additional information.

An examination of Fig. 4 and 5 clearly reveals a striking analogy between the pH dependence of the relative fluorescence intensities of RO^{-*} and ROH^* with that of the relative quantum yields of electron ejection from RO^{-*} (γ_e'/Γ_e') and H atom formation from ROH^* (γ_H/Γ_H), respectively. As in the case of the "blue" fluorescence yields, electron ejection from RO^{-*} contributes to the total quantum yield of solvated electrons even at pH values far below the ground state pK of β-naphthol. Similarly, γ_H/Γ_H, like η/η_0, reaches unity only at pH values which are lower than the pK by 7–8 units. The relation $(\gamma_H/\Gamma_H) + (\gamma_e'/\Gamma_e') \cong 1$ holds here as $(\eta/\eta_0) + (\eta'/\eta_0') \cong 1$ holds for the relative fluorescence. More than that, the pH independent (constant) values $(\eta'/\eta_0')_{const} = 0.28$ and $(\eta/\eta_0)_{const} = 0.73$, in the region 4 < pH < 7, should be compared to the parameters $(\gamma_e'/\Gamma_e')_{const} = 0.25 \pm 0.04$ and $(\gamma_H/\Gamma_H)_{const} = 0.80 \pm 0.08$ in the same pH region. These arguments indicate that the electron ejection takes place from a relatively long-lived excited state of the molecule (or ion) capable of undergoing an acid–base equilibrium (eq. 14) before deactivation. The quantitative agreement between Fig. 4 and 5 prove that approximately the same parameters $\vec{k}$ and $\overleftarrow{k}$, τ_0 and τ_0' are involved in the two cases (see Weller's work[9] for the theoretical expressions of the plots in Fig. 4). We thus conclude that the same state is responsible for both fluorescence emission and electron ejection; i.e., the molecule, or ion, if excited to the second singlet excited state undergoes a rapid radiationless transition to the first singlet excited state, whose lifetime is long enough to permit the partial establishment of the equilibrium of eq. 14. The complete scheme representing the reactions undergone by ROH^* and RO^{-*} is
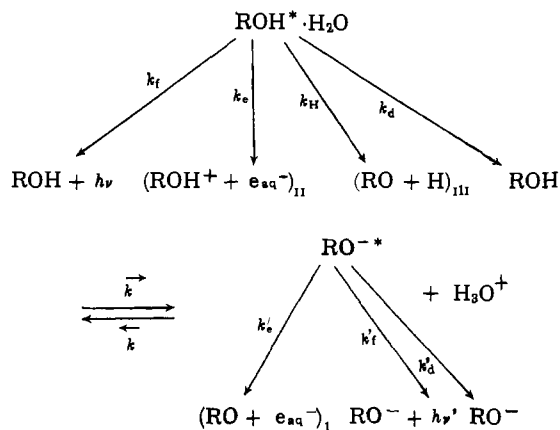
As mentioned above, excitation to the second singlet excited state, with the 214 and 229 mμ lines, leads to a value for the quantum yield which is higher by 30% than that of direct excitation to the first singlet by means of the lines above 229 mμ. This result probably suggests that some electron ejection may also occur directly from the second singlet before undergoing the radiationless transition to the emitting state. There may therefore be some contribution to the electron ejection which does not follow the pH dependence of the fluorescence emission. The deviations of the values of $(\eta'/\eta_0')_{const}$ and $(\eta/\eta_0)_{const}$ from those of $(\gamma_e'/\Gamma_e')_{const}$ and $(\gamma_H/\Gamma_H)_{const}$, respectively, may actually be due to such an effect.

The fact that an efficient electron scavenger such as 1.9×10^{-2} N_2O, capable of total electron scavenging, does not affect the fluorescence quantum yield η_0' clarifies two important points. First, it rules out a mechanism of direct electron transfer from RO^{-*} to N_2O, for in such a case N_2O would have acted as a quencher and a rise in $\gamma(N_2)$ should have been accompanied by a decrease in η'_0. This supports the conclusion which we have previously derived from the kinetic treatment, namely that N_2O reacts with a species formed from the excited state in a secondary process. The second point is that the recombination of RO and e^-_{aq} in cage I does not lead to the same excited (emitting) state, RO^{-*}, still capable of electron ejection. The recombination probably yields the ground state, so that once the pair $(RO + e^-_{aq})$ is formed, fluorescence can no more take place, even if e^-_{aq} is not scavenged by N_2O. This result differs from some electron–radical ion recombinations in glasses which have been shown to lead to the formation of excited species.[12] This suggests that the deactivation (quenching) rate constants k_q and k_q' should actually be replaced by the sums $k_q = k_e + k_H + k_d$ and $k_q' = k_e' + k_d'$, where k_d and k_d' represent deactivation by collision or radiationless transitions to the ground state. We may thus suggest that an important path of deactivation of excited organic molecules and ions in solution may be one of electron ejection to the solvent.

Our experimental results are consistent with electron ejection taking place mainly from the first singlet, thermalized, excited state of the β-naphthol molecule or ion. Meyer and Albrecht[13] and Kalantar and Albrecht[14] investigated the wave length dependence of the quantum yields for fluorescence, phosphorescence, and electron ejection (photooxidation) of N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) in glasses at 77°K. They observed a clear structure in the wave

(12) H. Linschitz, M. G. Berry, and D. Schweitzer, J. Am. Chem. Soc., **76**, 5833 (1954).

(13) W. C. Meyer and A. C. Albrecht, J. Phys. Chem., **66**, 1168 (1962).

(14) A. H. Kalantar and A. C. Albrecht, ibid., **66**, 2279 (1962).

length dependence of the quantum yield for photooxidation, not observed in those for fluorescence and phosphorescence. They concluded that electron ejection competes with thermal equilibration of the first excited singlet state. Thus in the rigid glass TMPD solution the electron ejection is a relatively fast process taking place, preferentially, from high vibrational levels. In aqueous solutions of β-naphthol it seems that this picture of vibronic photochemistry cannot be adopted. Electron ejection competes here with fluorescence emission so that k_e and k_e' should be of the same order of magnitude as k_f and k_f', i. e., $k_e \cong k_e' = 10^7\text{--}10^8$ sec.$^{-1}$.

These results should also be compared with those previously obtained by us[1-4] in the study of electron ejection from the solvated halide ions in their C.T.T.S. excited states. In these systems the excited state consists of an expanded electronic orbital centered by the respective halogen atom.[15,16] Electron ejection in this case consists of charge asymmetrization giving place to the separated solvated electron–halogen atom pair.[4] This is essentially a process of relative diffusion and thus faster by several orders of magnitude than the electron ejection in the case of excited β-naphthol or naphtholate, where electron ejection competes with a relatively slow deactivation.

(15) R. L. Platzman and J. Franck, "Farkas Memorial Volume," Jerusalem, 1952, p. 21.

(16) G. Stein and A. Treinin, *Trans. Faraday Soc.*, **55**, 108b (1959).

The Fluorescence of Carbon Disulfide Vapor

BY JULIAN HEICKLEN

For incident radiation between 2800 and 3600 Å., the primary process in CS_2, is given in eq. 2–4. The total emission between 4200 and 6500 Å. was measured. It was found that reaction 4 occurs on every collision, and that $k_3 = 3.0 \times 10^5$ sec.$^{-1}$. Results with added biacetyl are similar; the electronic energy is removed by collision and not transferred as such to the biacetyl.

Introduction

Apparently the emission from gaseous CS_2 has not been reported previously. The purpose of this paper is to establish the mechanism associated with luminescence.

The absorption spectrum has been obtained at high resolution by Lieberman[1] and Kleman.[2] More recently, a small note showing the absorption profile has appeared.[3] The first absorption starts at about 3600 Å., passes through a maximum near 3200 Å., and extends to 2600 Å.

Experimental

The optical equipment used to measure fluorescence is shown schematically in Fig. 1. The light source is an Osram-type XBO 1600 lamp. This high-pressure xenon lamp operates at 1600 w. and emits continuous radiation from 2000 Å. to the infrared region. The light is focused by a quartz lens onto the entrance slit of a Perkin-Elmer Model 98 monochromator and is spectrally dispersed by a Bausch and Lomb grating No. 33–53–09–29 which is blazed at 5000 Å. and has 1800 grooves per mm. The monochromator was calibrated with the line spectrum of a medium-pressure Hanovia mercury arc. This arc was used to measure the dispersion also.

After passing through a quartz lens, a Corning 7-54 filter, and a diaphragm opening, the radiation enters the fluorescence cell. The purpose of the lens is to focus the light at the center of the cell, whereas the filter removes any scattered radiation above 4000 Å.

The T-shaped stainless-steel cell is 5.0 cm. long and 2.5 cm. in diameter. The side arm extends 1.3 cm. and is also 2.5 cm. in diameter. Sapphire windows are mounted with "Eccobond 26" epoxy glue at both ends and on the side arm. A 6-mm. outlet at the top of the cell connects, through a stopcock, to an adjoining high-vacuum line.

The transmitted radiation is focused by a quartz lens onto an RCA 935 phototube. An ASCOP 541B-03 photomultiplier, operated at 1500 v., collects the fluorescent radiation that has left the side arm and has passed through a Wratten 2E filter. The filter transmits radiation above 4200 Å. and the photomultiplier is sensitive to 6500 Å.

(1) L. N. Lieberman, *Phys. Rev.*, **58**, 183 (1940); **59**, 106 (1941); **60**, 496 (1941).

(2) B. Kleman, Symposium of Molecular Structure and Spectroscopy, Columbus, Ohio, June, 1956.

(3) E. Treiber, J. Gierer, J. Rehnstrom, and K. E. Almin, *Acta Chem. Scand.*, **11**, 752 (1957).

The materials used were Allied Chemical C.P. grade CS_2 and Eastman Kodak White Label biacetyl. Pressures were measured on an alphatron which had been calibrated previously against a Wallace and Tiernan direct-reading pressure gage.

The absorption coefficients of CS_2 were measured at various wave lengths and with slit openings of 0.500 and 2.000 mm. Because the radiation was not truly monochromatic, the measured absorption coefficients are not necessarily constant with pressure if the absorption is large. Thus, the coefficients were obtained over the range of pressures which resulted in absorption of more than a few per cent. If less than about 10% of the light is absorbed, then the measured absorption coefficients become truly independent of pressure, because the quantity $\exp(-\epsilon_\lambda Cl)$ in the Beer's law expression can be approximately by $1 - \epsilon_\lambda Cl$. Here ϵ_λ is the absorption coefficient for wave length λ, C is the concentration, and l is the path length.

When pure CS_2 was studied, the fluorescent radiation was computed as the difference of the photomultiplier output with the cell full and empty. For CS_2–biacetyl mixtures, the background reading was measured when the cell contained the appropriate pressure of biacetyl. In this way, the correction is automatically made for the biacetyl emission. Readings were taken at eight wave lengths with slit openings of both 0.500 and 2.000 mm.

Results

The results with pure CS_2 are given in Table I and Fig. 2 and 3. In all cases, only the emitted light above 4200 Å. and below 6500 Å. was collected. The relative emission yield (emission per photon absorbed) for a given incident wave length Q_λ was measured at various pressures and two different slit-width settings.

In Table I, the ratios of the relative emission yields at various incident wave lengths to the emission yield with incident radiation centered at 3213 Å. are shown. There are three important observations to be made from Table I. These are: (1) Within the limits of the fairly large scatter of the data, there is no discernible trend in the values of the ratios with change in pressure. This is true even though the pressure has been varied by a factor of greater than 10^5 and the individual relative emission yields vary by a factor of about 10^4. The scatter in the data is most pronounced at the lowest pressures where the total emitted light was smallest. The average values of the ratios and the mean deviations are also listed in Table I. (2) Within