measuring competitive kinetic hydrogen isotope effects in the IR laser photolysis of 2-methyl-2-propoxide-*1,1,1-d₃* (**1**) and 2-methyl-2-propoxide-*1,1,1,3,3,3-d₆* (**2**). Simultaneous detection of the relative intensities of the partially deuterated product enolate ions permitted measurement and separation of both secondary and primary effects.

An unusually large secondary isotope effect (loss of CH_3 favored over loss of CD_3; pulsed laser, 1.9 (1.2/D) for **1** and 1.7 (1.2/D) for **2**; CW laser, 6.9 (1.9/D) for **1**) and a small primary effect (pulsed, 1.6 for **1** and **2**; CW, 2.0 for **1**) were observed.[11,12] Before these results could be interpreted it was imperative to ensure that the small primary effect was not an artifact of the pumping process. In a multiple-channel system, the branching ratio (isotope effect) is a function of the excess energy of the reacting species, which for an IRMP process is primarily determined by the CO_2 laser pumping rate. Since pulsed CO_2 lasers can give large pumping rate constants, it is likely that the ions are decomposing somewhat above threshold.[14] So that the intensity dependence of the isotope effects could be investigated, the d_3 alkoxide **1** was subjected to low-power continuous-wave (CW) CO_2 laser photolysis.[15] In this case, the reacting ions must be decomposing right at threshold. These experiments indicate only a slight change in the primary effect (2.0) but a very large amplification of the secondary effect (6.9).

We believe that the isotope effect results are consistent only with a stepwise mechanism (eq 2). The unusually large secondary effect essentially requires a severe loosening of the methyl group in the transition state relative to the ground-state reactant.[16] Such a requirement is easily fulfilled by invoking an intermediate methyl radical[17] or anion in which the ν_2 umbrella mode is considerably looser than that in a bound methyl (617 vs. 1364 cm^{-1}). The small primary effect is indicative of a highly asymmetric transition state, consistent with the large exothermicity (ca. 35–40 kcal/mol) of the second step in eq. 2. While the small primary effect may also be consistent with a bent four-center transition state (eq 1), it is difficult to rationalize the large secondary effect in terms of the relatively tight transition state in this concerted mechanism. The most convincing evidence against the concerted pathway is the large difference in energy dependence of the secondary and primary effects (i.e., the extreme variation in the secondary effect with little change in the primary effect). In a concerted mechanism involving only one transition state, the secondary and primary effects which result only from differences in zero-point energies and state sums[18] would be expected to exhibit similar energy dependences. This large difference in energy dependence of the isotope effects strongly suggests that the secondary effect

occurs in a rate-limiting step while the primary effect occurs in a subsequent rapid product-determining step. Our multistep scheme (eq 2) can easily accommodate the large variation in the secondary effect due to the rate-limiting first step (loss of methyl), and the slight changes in the primary effect that would be expected for such an exothermic hydrogen transfer in the second step.[19]

This general stepwise mechanistic scheme can easily be extended to a variety of reactions. Since the photochemically generated intermediate in this scheme is also an intermediate in a proton-transfer reaction, bimolecular reaction dynamics[20] can be probed. These and related studies that rely heavily on the present mechanistic study will be forthcoming.

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Rose Bengal and Nonpolar Derivatives

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Dyes were first used to sensitize oxidation by Windaus and Brunken[1] after the phenomenon of photodynamic action had been discovered by Raab in 1900.[2] Many synthetic applications of dye-sensitized oxidation processes preceded the papers of Foote and Wexler[3] and Corey and Taylor,[4] which established that singlet oxygen, a reactive intermediate originally postulated by Kautsky and de Bruijn,[5] was responsible for such processes.

When immobilized to polystyrene/divinylbenzene beads, the xanthene dye rose bengal (**1**) is unique in being an effective heterogeneous photosensitizer.[6] In the context of understanding the site of immobilization of the dye to the polymer support,[6a]

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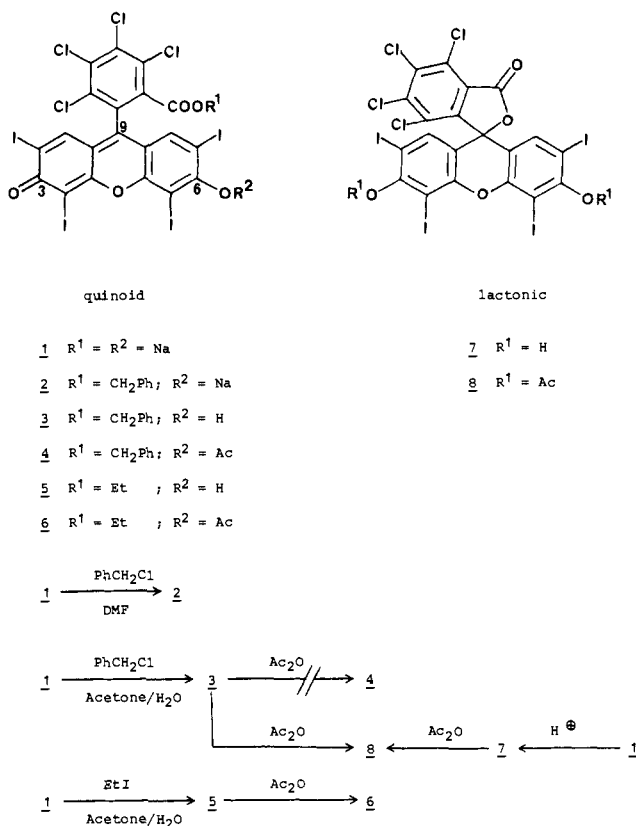(2) Raab, O. *Z. Biol. (Munich)* **1900**, *39*, 524.

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Communications to the Editor

Scheme I

quinoid   lactonic

1 $R^1 = R^2 = Na$

2 $R^1 = CH_2Ph; R^2 = Na$

3 $R^1 = CH_2Ph; R^2 = H$

4 $R^1 = CH_2Ph; R^2 = Ac$

5 $R^1 = Et; R^2 = H$

6 $R^1 = Et; R^2 = Ac$

7 $R^1 = H$

8 $R^1 = Ac$

$$1 \xrightarrow[DMF]{PhCH_2Cl} 2$$

$$1 \xrightarrow[Acetone/H_2O]{PhCH_2Cl} 3 \xrightarrow[]{Ac_2O} \not\longrightarrow 4$$

$$3 \xrightarrow[]{Ac_2O} 8 \xleftarrow[]{Ac_2O} 7 \xleftarrow[]{H^{\oplus}} 1$$

$$1 \xrightarrow[Acetone/H_2O]{EtI} 5 \xrightarrow[]{Ac_2O} 6$$

an investigation of chemical reactions of rose bengal was undertaken. In spite of the enormous volume of literature on structural and spectroscopic characteristics of the fluorescein dyes such as rose bengal and their excited states,[7] and an even more enormous volume of literature on synthetic[8] and other applications of these compounds,[9] 1 is structurally complicated, difficult to

Table I. Spectral Data of the Rose Bengal Derivatives[a]

	$\nu_{C=O}$, cm^{-1}	ν_{OH}, cm^{-1}	λ_{max}, nm	solvent
1	<1600		558, 519	MeOH
2	1730		564, 524	MeOH
3 (5)	1730	3410	564, 524	MeOH
			496, 407	CH$_2$Cl$_2$
6	1780, 1730		494, 400	MeOH
			494, 395	CH$_2$Cl$_2$
7	1770	3430	558, 519	MeOH
			<300	CH$_2$Cl$_2$
8	1780		<300	MeOH
			<300	CH$_2$Cl$_2$

[a] $\nu_{C=O}$ in KBr and λ_{max} in MeOH and CH$_2$Cl$_2$.
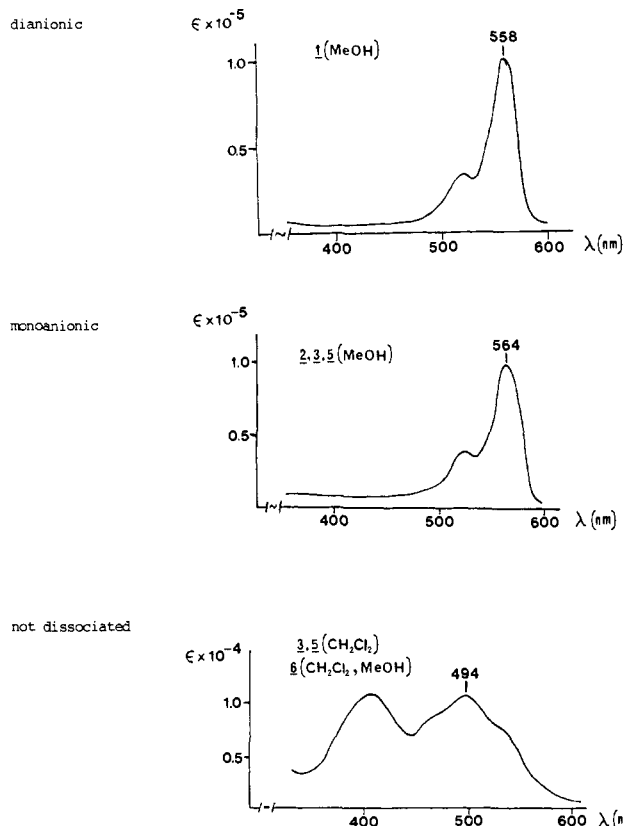
dianionic

monoanionic

not dissociated

Figure 1. Absorption spectra of the rose bengal derivatives in the visible region as a function of the dissociation state.

purify,[10] and sufficiently perverse so as to isomerize, ionize, or in other ways modify as a function of solvent even in the unlikely event that something approaching a pure material is obtained at one stage or another in the purification process.

We have established the molecular composition of nonpolar analogues of rose bengal and, in the process, have clarified the structural characteristics of the parent dyestuff. Our experiments

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suggest caution in the use of rose bengal for photophysical experiments in view of the various structural isomers available to the molecule in differing environments. Each of these structural isomers may have different excited-state characteristics for they have obviously different spectra.

Rose bengal (**1**) was heated in DMF with 1.5 equiv of benzyl chloride as a model for the reaction with chloromethylated polystyrene/divinylbenzene. We demonstrate below that the benzyl ester **2** was produced (Scheme I). When repeated with 2.5 equiv of benzyl chloride in an attempt to convert both the carboxylate and the phenolate centers of **1** into an ester and an ether, respectively, the reaction led to the same deep purple product, **2**, which was insoluble in CH_2Cl_2. The absorption spectrum of **2** in MeOH had the same shape as that of **1** with a small red shift of the absorption maximum, and the IR of **2** was that of an ester (1730 cm^{-1}) (Table I, Figure 1). Elemental analysis indicated the incorporation of only one benzyl group in both experiments.

The reaction of benzyl chloride and rose bengal in acetone/water (50:50) afforded a bright orange-red product **3**, which was soluble in CH_2Cl_2, leading to a solution of the same color.[11] A solution of **3** in MeOH, however, had a distinctly different deep red color. The IR spectrum of **3** showed an OH stretch at 3410 cm^{-1} suggesting deprotonation of the phenolate function. The absorption spectrum in MeOH of both **2** and **3** was the same, whereas the spectrum of **3** in CH_2Cl_2 was totally different (Figure 1).

It has been reported repeatedly that the planes of the 2′-carboxyphenyl group and of the xanthene moiety of fluorescein dyes are perpendicular to one another and that the latter is largely responsible for the absorption characteristics of the molecule in the visible region.[7h,n,o,s] Therefore, it was concluded that upon a change of solvent from MeOH to CH_2Cl_2 a major change takes place in the xanthene portion of **3**. The benzyl ester of rose bengal has a protonated phenol group under the latter conditions, the protonation being due to the hydrochloric acid formed from partial hydrolysis of benzyl chloride in the aqueous solvent in which the reaction was carried out. While **3** is soluble in CH_2Cl_2, its monosodium salt, **2**, is not. When **3** is dissolved in a more polar solvent, MeOH, the phenolic OH bond dissociates. Additional structural proof was obtained by the addition of a few drops of HCl to either a solution of **2** or **3** in MeOH. The absorption spectrum of the resulting solution was the same as that of a solution of **3** in CH_2Cl_2. The acidity of the phenolic proton and the solvent dependence of the structure of **3** might interfere with its effectiveness as a singlet oxygen sensitizer, especially in the synthesis of acid-sensitive hydroperoxides.

In order to block the phenolate function, an attempt was made to prepare the 6-*O*- acetyl derivative of **3** by refluxing with acetic anhydride. Surprisingly, this reaction did not yield the expected orange-red 6-*O*-acetyl rose bengal benzyl ester, **4**, but the colorless diacetyl derivative of the lactonic form of rose bengal, **8** (IR band at 1780 cm^{-1}). Its structure was also firmly established by independent synthesis from **1** via the lactonic modification of rose bengal, **7**.[12] Both **7** and **8** are colorless compounds soluble in CH_2Cl_2 with no absorption in the visible region and no absorption for **8** in MeOH. The absorption spectrum of **7** in MeOH, however, is the same as that of **1** indicating complete dissociation with accompanying conversion to the quinoid modification. We suggest that **8** is formed instead of **4** as a consequence of the highly polarized character of the C–O bond in the benzyl ester. After the introduction of the first acetyl function at the 6-O position, the 3-O attacks acetic anhydride aided by an electron push caused by attack of the ester oxygen on the slightly positively polarized C(9). This forces elimination of the benzyl cation.

In a slightly different approach, **1** was converted to its ethyl ester **5**, which has a less polarized C–O bond.[13] Refluxing with acetic anhydride yielded the bright red colored 6-*O*-acetyl rose bengal ethyl ester, **6** (1780 and 1730 cm^{-1} for acetyl and carboxylate esters, respectively).[14] The absorption spectrum of **6** is the same in MeOH and in CH_2Cl_2. The evolution of the spectra of **1–6** with structure resembles that observed for the ionization of eosin.[7q] Furthermore, a 6-O monoester of fluorescein described recently had an absorption spectrum similar to **8**, though shifted to shorter wavelengths.[15]

The work presented above shows the elusive structural nature of rose bengal and the dependence of its structure on subtle changes of environment. The close relationship between the dissociation state of the xanthene moiety of rose bengal and the appearance of the absorption spectrum has been clearly established.

Preliminary experiments have shown that **6** is a useful singlet oxygen sensitizer. Our work is continuing with an investigation of the experimentally discernable differences in the photochemistry of the structurally modified rose bengal derivatives.[16]

(14) Spectral parameters of **6**: UV–vis λ_{max} (log ϵ) 494 nm (4.03), 395(4.22), λ_{min} (log ϵ) 441 nm (3.87); 80 MHz ^{1}H NMR (CDCl₃, Me₄Siδ, 0.98 (t, CH₃, 3 H, *J* = 7.1 Hz), 2.48 (s, CH₃C=O, 3 H), 4.01 (q, CH₂, 2 H, *J* = 7.1 Hz), 7.41 (s, 1 H, xanthene H), 7.65 (s, 1 H, xanthene H).
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On the Stability of the Polygonal H$_n$ Systems. Simple Models of Aromaticity and Antiaromaticity

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Aromaticity and antiaromaticity have been the most difficult and the most fascinating subjects in organic chemistry ever since Kekule's intuitive idea in 1865.[1] The Hückel aromaticity rule has played the leading role in the theory of aromaticity[2] providing one a simple method of prediction that in the cyclic conjugate π-electron system such an aromaticity appears if the number of the atoms in the conjugated system is $4n + 2$ whereas antiaromatic unstability dominates if the number is $4n$. The Hückel rule is generally obtained by solving the secular equation consisting of unspecified quantities, α and β, which are called Coulomb and resonance integrals. Although most of aromaticity and antiaromaticity are realized in the π-electron systems, the Hückel secular determinant does not restrict the type of basic atomic orbitals. This suggests that such an effect can be reproduced in the arrangement of hydrogen atoms serving a simple model for energetic analysis of aromaticity or antiaromaticity. Along such a guiding line, we performed an MO theoretical calculation on the system placed as a regular polygons.

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(12) Compound **7** was prepared by dropwise addition of concentrated HCl to an aqueous solution of **1**. Then, **8** was prepared by refluxing **7** with acetic anhydride.
(13) Synthesis of **5** by refluxing a solution of **1** with 5 equiv of ethyl iodide in acetone/water 50% v/v. When a smaller excess of EtI is used a $\nu_{C=O}$ corresponding to a lactone is found in the IR spectrum.