MTPA ester[7c,10] with Eu-fod shift reagent, but may be ~1%, The double homologation should reduce the enantiomer of **5** to the 0.01% level.

The functional group compatibility of the new procedure was tested in the simple synthesis of *exo*-brevicomin (**10**; western pine beetle, *Dendroctonus brevicomis*)[11,12] outlined in Scheme II. (−)-Pinanediol[1,9] as chiral directing group led to the natural enantiomer of **10**, $[\alpha]^{23}_{\mathrm{D}}$ +81.1° (c 1.4, ether) [lit, $[\alpha]^{25}_{\mathrm{D}}$ +84.1°,[12a] +81.5°[12b]], which contained 2% *endo*-brevicomin by GC,[11a] 3% by 200-MHz NMR (t at δ 0.97[11a]). Most of the loss in stereoselectivity occurred during the displacement of chloride by benzyl oxide. The intermediate **9**, reported as an oil,[12b] matched the reported IR, mass spectral, and NMR data[13] but crystallized and could thus be freed from its diastereomer, from ether/pentane, mp 30-31 °C, $[\alpha]^{23}_{\mathrm{D}}$ −13.4° (c 3.4, $CHCl_3$).

Acknowledgment. We thank the National Science Foundation for a grant (CHE-8025229) and the Boeing Corp. for a gift in support of the Nicolet 200-MHz NMR instrument.

Supplementary Material Available: Preparation and characterization of new cmpounds (**3–9**) and NMR curves showing diastereomeric purity of **3c**, **3f**, and **6** (7 pages). Ordering information is given on any current masthead page.

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[13] We thank Professor Fraser-Reid for a copy of the 60-MHz NMR spectrum of **9**.

Light-Induced Reversible pH Change

Masahiro Irie

The Institute of Scientific and Industrial Research
Osaka University, Suita, Osaka, Japan

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Although a stopped-flow pH jump is a suitable technique for kinetic studies in aqueous solution,[1] its use is limited to relatively slow processes ($\tau > 10^{-3}$ s), and it can not be applied to reactions in complex systems such as vesicles or membranes. In contrast to this technique, a laser-induced pH jump,[2] using an appropriate proton or hydroxide ion emitter, is a more convenient method for perturbing chemical and biochemical reactions by a proton or hydroxide ion pulse. It is applicable to closed systems such as reactions inside vesicles, and the time necessary for pH change can be reduced to less than 10^{-9} s with a short laser pulse. The light-induced pH jump is of particular interest in connection with the function of bacteriorhodopsin. Bacteriorhodopsin uses light energy to translocate protons across the membrane. The cell uses the energy stored in the electrochemical gradient for ATP synthesis.[3]

Clark et al. and Gutman et al. adopted 2-naphthol-6-sulfonate, 2-naphthol-3,6-disulfonate, and 8-hydroxypyrene-1,3,6-trisulfonate as proton emitters. These compounds, ArOH, release protons in the photoexcited state and the reprotonation of ArO^- takes place within 0,1–1 μs at $(H^+) = 10^{-4}$–10^{-5} M.[2] The rapid recombination limits the application to specific reactions.

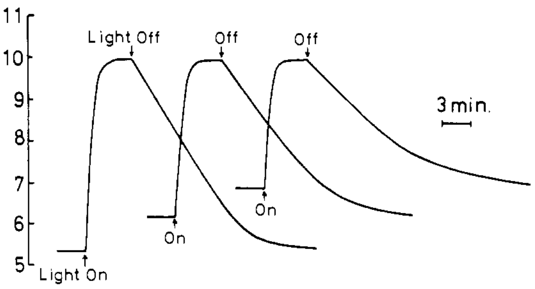
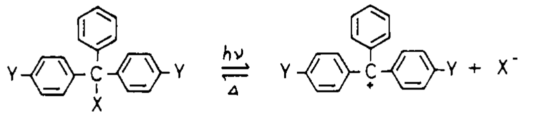


Figure 1. Light-induced pH increase of aqueous solutions containing 4,4′-bis(dimethylamino)triphenylmethane leucohydroxide (4.8×10^{-4} mol/L) and dodecyltrimethylammonium chloride (0.1 mol/L) at 35 °C. Initial pH was controlled by the addition of sodium hydroxide solution.

We adopted triphenylmethane leucohydroxide as hydroxide ion emitters. Triphenylmethane leuco derivatives are well-known photochromic molecules, which dissociate into ion pairs under ultraviolet irradiation with production of intensely colored triphenylmethyl cations. The cations thermally recombine with counterions as in eq 1.[4] These compounds have long been employed advantageously for their color change on photoirradiation rather than for the chemical property change.[4,5] According to the reaction scheme 1, triphenylmethane leucohydroxide derivative (**1**, X = OH) functions as a light-induced hydroxide ion emitter. Investigations of the derivatives have indicated that the dissociation proceeds very rapidly (within 40 ns) in high quantum yield.[4,6]



(1)

(1)

Although triphenylmethane leucohydroxide has promise as a hydroxide ion emitter, one serious disadvantage is its very low solubility in water. To overcome this difficulty, the following two methods have been employed: (1) solubilization using surfactants; (2) chemical modification to water soluble form.

Figure 1 shows the light-induced pH increase from various initial pHs in aqueous solution containing 4,4′-bis(dimethylamino)triphenylmethane leucohydroxide (**1**, X = OH, Y = $N(CH_3)_2$)[7] and cationic surfactant, dodecyltrimethylammonium chloride. The initial pH was controlled by the addition of sodium hydroxide solution. A high-pressure mercury lamp (Ushio, 1 kW) was used as a light source, and the irradiation wavelength was limited to the ultraviolet region ($410 > \lambda > 280$ nm) using glass filters (Toshiba UV-D25 and UV-31). The pH was measured by a conventional pH meter (Horiba F-7ss).[8] In the most pronounced case, the pH was increased from 5.4 to 10.0 by irradiation.[9] After removal of the light, the pH returned to the initial value after 15 min in the dark. The cycle, an increase in pH by irradiation and a return in the dark, could be repeated several times without any noticeable fatigue. No change in pH was detected in the absence of 4,4′-bis(dimethylamino)triphenylmethane leucohydroxide. Photoirradiation of an aqueous solution of malachite

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[7] 4,4′-Bis(dimethylamino)triphenylmethane leucohydroxide was prepared by treating phenyllithium with Michler's ketone in ether. Anal. Calcd for $C_{23}H_{26}N_2O$: C, 79.73; H, 7.56; N, 8.09. Found: C, 80.02; H, 7.63; N, 7.85.

[8] To avoid any photoirradiation effect onto the electrode, light was focused to the solution below the electrode. The cell (15 × 15 × 45 mm) is made of quartz and the solution sample (6 mL) was stirred with a magnetic stirrer during the measurement.

[9] The pH change was also confimed by using a pH probe such as pyranine fluorescence probe (Kano, K.; Fendler, J. H. *Biochim. Biophys. Acta* **1978**, *509*, 289).

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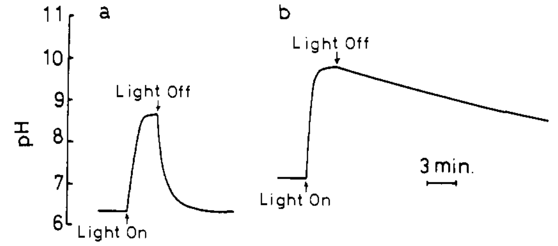


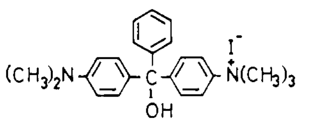
Figure 2. Light-induced pH increase of aqueous solutions containing (a) compound **2** (5×10^{-3} mol/L) and (b) compound **3** (1×10^{-3} mol/L) at 30 °C.

green oxalate did not induce any detectable increase of pH. These results present unambiguous evidence that the large pH increase is ascribable to photodissociation of the leucohydroxide.

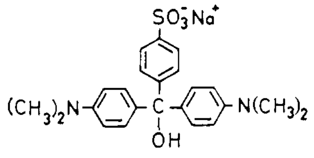
Ultraviolet light pumps the leucohydroxide, surrounded by surfactants, to the excited state. The excited leucohydroxide dissociates into ion pairs, triphenylmethyl cation and hydroxide anion, and the hydroxide ion is released from the surfactants to the aqueous phase, causing the increase in pH.

The amount of the ejected hydroxide ion is a function of the quantum yield of the dissociation, the concentration of the emitter, and the light intensity. The rapid increase of pH to the photostationary pH of 10.0 under present experimental conditions (the emitter concentration is 4.8×10^{-4} mol/L) suggests that the quantum yield is fairly large. By changing the light intensity with use of neutral density filters, the photostationary pH could be controlled. The pH with full light intensity, 9.9, decreased to 6.3 when the intensity was reduced to 0.008. Titration of this solution with sodium hydroxide demonstrated that the pH change corresponds to 90% reduction of the photoejected hydroxide ions. The light-intensity dependence suggests second-order recombination decay of the hydroxide ions.

Two simple methods for preparing water-soluble compounds are to introduce a quaternary amine or a sulfonate into the structure. Compounds **2** and **3** were synthesized.[10] Both compounds were quite soluble in water and showed reversible photochromic behavior. Figure 2 shows the photoresponse of the pH of aqueous solutions containing **2** (a) and **3** (b). The relatively low photostationary pH value of aqueous solution containing **2** is attributable to the fast recombination rate of the ion pairs. The positive charge on the quaternary amine in addition to that of the photogenerated triphenylmethyl cation may accelerate the recombination rate due to the increase in Coulombic force. Sulfonated triphenylmethane leucohydroxide (**3**) showed a similar photoresponse of pH on irradiation, although return of the pH in the dark was very slow. The slow recovery of pH may be explained by the absence of a strong Coulombic force between sulfonated triphenylmethyl cation and hydroxide ion.



(**2**)



(**3**)

The hydroxide emitters described here, triphenylmethane leucohydroxide derivatives, may be useful for controlling many aspects of chemical reactions in aqueous solutions as well as in vesicles.

Registry No. **1** (X = OH; Y = H), 76-84-6; **1** (X = OH; Y = N(CH$_3$)$_2$), 510-13-4; **2**, 84961-00-2; **3**, 6362-29-4.

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(10) Compound **2** was prepared by treating 4,4'-bis(dimethylamino)triphenylmethane leucohydroxide with methyl iodide in toluene in sealed glass at 90 °C in the dark for 20 h. Anal. Calcd for $C_{24}H_{29}N_2OI$ (**2**): C, 59.02; H, 5.98; N, 5.73. Found: C, 59.02; H, 5.92; N, 5.65. Compound **3** was prepared by directly sulfonating compound **1** by chlorosulfonic acid. Anal. Calcd for $C_{23}H_{26}N_2O_4S$ (**3**): C, 61.59; H, 5.62; N, 6.25. Found: C, 61.60; H, 5.95; N, 6.22.

η^8 Coordination of Planar $C_8H_8^{2-}$ to Vanadium. Structural Characterization of $(\eta^8\text{-}C_8H_8)V[(C_2H_5)_2C_2B_4H_4]$[1]

Robert G. Swisher, Ekk Sinn, Greg A. Brewer, and Russell N. Grimes*

Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

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Cyclooctatetraenide dianion, $C_8H_8^{2-}$, a planar 10π-electron aromatic system, forms symmetrically bonded (η^8) sandwich complexes with large metals including the actinides,[2a,b] lanthanides (in which the metal–ligand bonding is mainly ionic),[2c] and second-row transition metals (especially zirconium[2d-f]), but η^8 coordination to first-row transition metals is rare;[3] structurally established examples are limited to several titanium complexes, all oxygen-sensitive,[4] in one of which[4d] the crystallographic R factor is 21%.

We report here the preparation and X-ray structure determination of the vanadacarborane title complex (**1**), which represents, to our knowledge, the first example of η^8 binding of a C_8 ring to a first-row transition metal other than titanium. The metal in **1** is the smallest atom yet shown to coordinate symmetrically to a ring as large as planar $C_8H_8^{2-}$ (estimated[5] covalent radii of V and Ti are respectively 1.22 and 1.32 Å). At this writing, **1** is the only structurally characterized vanadium–cyclooctatetraene complex of any geometry, although mass spectrometric evidence for ions such as $(C_5H_5)V(C_8H_8)^+$ has been observed in ion–molecule reactions.[6]

Compound **1** was obtained in the in vacuo reaction of $K_2C_8H_8$ with the nido-carborane anion $[2,3\text{-}(C_2H_5)_2C_2B_4H_5]^-$ and VCl_3 (~equimolar ratio) in tetrahydrofuran (THF) for 2 h at 0 °C followed by warming to room temperature. Workup in air and chromatography in 25% CH_2Cl_2 in n-hexane on a silica gel plate gave **1** as a dark green air-stable solid, mp 240 °C dec, R_f 0.47, yield 41 mg (0.14 mmol, 3.2% of theory). The EI mass spectrum exhibits a strong parent group with a high-mass cutoff at m/e 286, corresponding to the $^{51}V^{13}C^{12}C_{13}{}^{11}B_4{}^1H_{22}{}^+$ ion, and a base peak at m/e 155, which is assigned to $V(C_8H_8)^+$. The parent envelope is closely consistent with the pattern calculated from natural isotope distributions except that slight loss of hydrogen is indicated. The IR spectrum (KBr pellet) contains an intense B–H doublet at 2530 and 2500 cm^{-1}, a strong C_2H_5 multiplet between 2880 and 2980 cm^{-1}, and weak C–H stretching bands at 3025 and 3075 cm^{-1} attributed to the C_8H_8 ligand. The paramagnetism of **1** precluded obtaining useful NMR data.

X-ray diffraction data were collected on a crystal of **1** grown from benzene solution, and the structure (Figure 1) was solved by standard Patterson and Fourier procedures.[7] The complex

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