Transient Raman Observation of Quinoxaline Aqueous Protonation Kinetics

S. M. Beck and L. E. Brus*

Bell Laboratories
Murray Hill, New Jersey 07974

Received February 9, 1981

Fast transient electronic absorption and emission spectroscopy are sensitive and useful methods for monitoring condensed phase reaction dynamics. Nevertheless, a limitation of these techniques is an inability to determine actual chemical structures of transient species from their broad and featureless spectra in many important chemical and biological processes. Often circumstantial arguments are employed, and several distinct species may have nearly the same absorption spectrum. There is a clear need for a practical transient spectroscopy directly yielding structural and/or vibrational data. In this communication we describe how nanosecond-time-resolved spontaneous Raman spectroscopy can provide such information in aqueous solution at modest solute concentrations.

A 5×10^{-3} M quinoxaline (1,4-diazanaphthalene) solution is irradiated with a ~25-mJ, 355-nm pulse (time width ~10 ns) from a Nd-YAG laser, thus creating transient species via electronic excitation of quinoxaline. After a delay of Δt ns, the sample is irradiated with a ~40-mJ, 532-nm pulse from the same laser. Spontaneous Raman scattering of the second pulse is analyzed by a computer-controlled small triple spectrograph-gated, intensified reticon optical system. The complete Raman spectrum is recorded for each 532-nm pulse. The spectra from $\sim 5 \times 10^3$ pulses are summed to produce a Raman spectrum of the system at time Δt after excitation. The spatially superimposed beams are brought to a line focus in a windowless, flowing solution stream. A detailed experimental description will be subsequently given.[1]

Traces A and F of Figure 1 show the spectra at pH 5.0 and 1.7 when the exciting ultraviolet beam is blocked. The H_2O solvent appears as a sloping continuous background with a broad maximum near 1700 cm^{-1}. Superimposed are three relatively intense, sharp peaks at 1424, 1374, and 770 cm^{-1}, as well as other weaker peaks, representing the ground S_0 state nonresonant Raman scattering of aqueous quinoxaline. The positions and intensities agree well with the literature spectra[2] taken under low-power CW irradiation, thus demonstrating that the high peak power 532-nm beam remains in the region of linear, spontaneous Raman scattering. The S_0 spectra are unchanged for pH ≥ 1.7 in agreement with the reported pK_a (S_0) = 0.56.[3]

Traces B–E show the $\Delta t = 15$ ns spectra for both beams as a function of pH. Three strong additional peaks (labeled T_1) at 1505, 1182, and 973 cm^{-1} are observed, in addition to the S_0 peaks. We assign these lines to the lowest π–π^* triplet T_1 state of quinoxaline, in agreement with earlier transient absorption studies which reported T_1 quinoxaline produced by subnanosecond intersystem crossing.[4] The triplet–triplet absorption spectrum of quinoxaline peaks near 440 nm, with a weak tail extending beyond 600 nm. Therefore the 532-nm pulse lies in a region of weak transient absorption, and the T_1 spectrum is enhanced by a modest resonance Raman effect. This T_1 resonance Raman enhancement is far less intense than utilized in earlier nanosecond transient Raman reports for hemoglobin[5] and (2,2′-bipyridine)ruthenium(II),[6] for example.

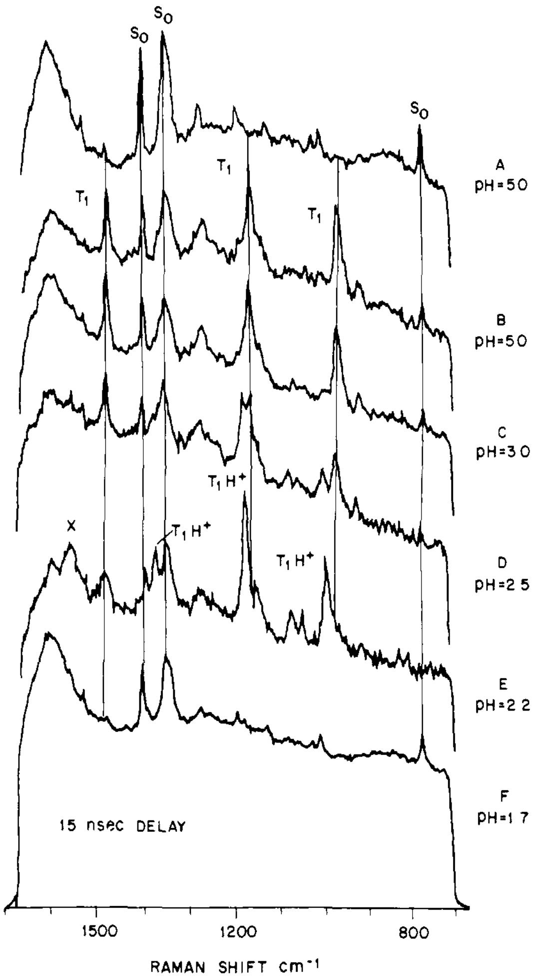


Figure 1. Raman spectra (700–1700-cm^{-1} range) of 5×10^{-3} M aqueous quinoxaline for indicated pH values. The traces have been offset vertically for clarity; trace F shows the strength of the H_2O background relative to the quinoxaline S_0 peaks. Traces A and F were taken with the UV beam blocked; traces B–E were taken with both beams ($\Delta t = 15$ ns) and show transient species labeled T_1 and T_1H^+. The vertical lines demonstrate the shift of T_1H^+ lines to higher frequency than those of T_1. The instrumental resolution of these spectra is about 5 cm^{-1} (fwhm).

The T_1 spectrum evolves as a function of Δt and pH. For $\Delta t = 15$ ns, the spectrum shifts to higher frequency below pH ≃2.5, with strong bands at 1397, 1192, and 1004 cm^{-1}. For $\Delta t = 56$ ns, the same spectral changes occur near pH ≃3.2 as shown in Figure 2. An unprotonated S_0 molecule is initially excited, and we observe a reaction caused by the kinetic approach of H_3O^+ to the free base T_1 molecule. These data yield an essentially diffusion-controlled bimolecular rate constant $k = (1.7 \pm 0.3)10^{10}$ $M^{-1}\ s^{-1}$. As pK_a (T_1) ≃ 5.0,[3] the T_1 molecule should protonate readily, and the simpliest interpretation is that a diffusion-controlled T_1 protonation occurs.

This reaction was not discovered when the T_1 transient absorption was observed as a function of pH in this same range.[4] It was observed that H_3O^+ quenched the T_1 absorption with a ~17-fold slower rate constant $k = 9.7 \times 10^8$ $M^{-1}\ s^{-1}$. The reaction we have discovered must cause only a subtle change in the triplet absorption. The fact that the observed decay of the triplet absorption is slower than the rate of protonation suggests that the protonated species T_1H^+ also absorbs at 532 nm and exhibits a modest resonance Raman effect.

These preliminary results demonstrate the utility of fast transient Raman spectroscopy in unraveling chemical dynamics. The Raman spectra of T_1 and T_1H^+ should ultimately help establish the corresponding chemical structures. The method in fact shows

---

(1) S. Beck and L. E. Brus, to be published.

(2) H. F. Shurvell and J. W. Russell, *J. Raman. Spectrosc.*, **3**, 407 (1975).

(3) A. Grabowski, J. Herbich, E. Kirkor-Kaminska, and B. Pakula, *J. Lumin*, **11**, 403 (1976).

(4) D. V. Bent, E. Hayon, and P. N. Moorthy, *J. Am. Chem. Soc.*, **97**, 5066 (1975).

(5) J. M. Friedman and K. B. Lyons, *Nature (London)*, **284**, 570 (1980).

(6) R. F. Dallinger and W. F. Woodruff, *J. Am. Chem. Soc.*, **101**, 4391 (1979).

0002-7863/81/1503-2495$01.25/0

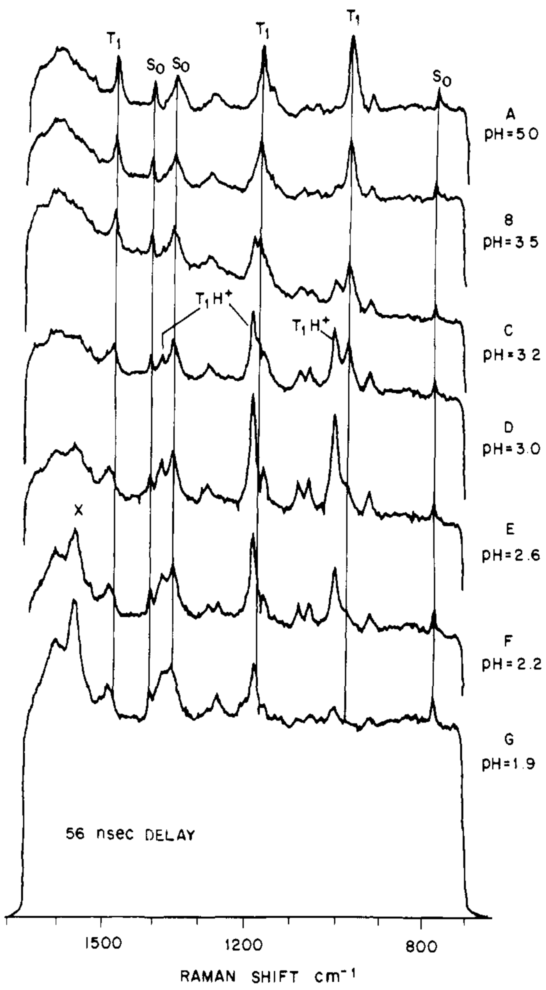


Figure 2. Raman spectra as a function of pH with both laser beams and Δt = 56 ns. "X" refers to an unidentified transient species.

further evolution of T_1H^+ at the lowest pH values in Figure 2 where one or more new species ("X") begin to appear. A more detailed and systematic study in progress will help to unravel the complete dynamics.[1]

Acknowledgment. We thank P. M. Rentzepis and J. M. Friedman for useful discussions of transient Raman phenomena.

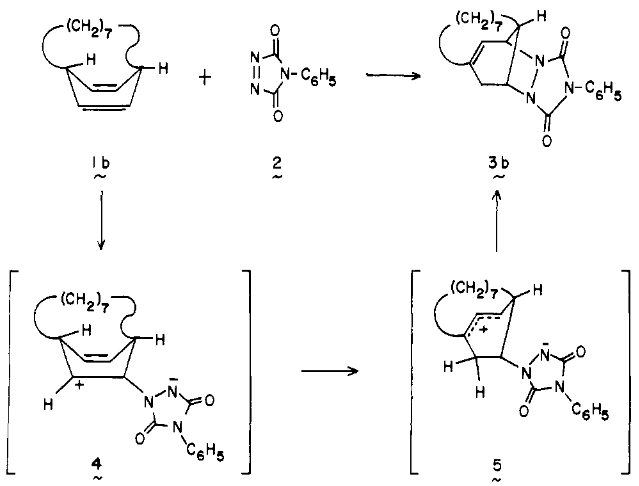
Anomalous Cycloaddition Reactions of Distorted Cyclohexa-1,4-dienes. Cycloaddition of *N*-Phenyltriazolinedione to (i,o)-Bicyclo[*n*.2.2]alkadienes

Paul G. Gassman* and Rebecca C. Hoye

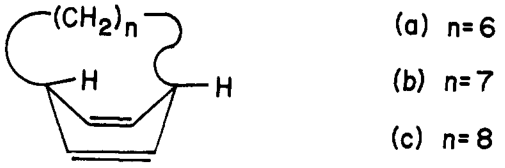
Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

Received January 9, 1981

Scheme I



Bridged 1,4-cyclohexadiene derivatives are known to undergo a wide range of cycloaddition reactions. Among the most studied is bicyclo[2.2.1]hepta-2,5-diene which undergoes a homo-Diels–Alder reaction with a wide variety of dienophiles.[1] In the case of highly polarized dienophiles, it has been suggested that zwitterionic intermediates are involved.[2] Similar cycloaddition reactions have been observed with bicyclo[2.2.0]hexa-2,5-dienes,[3] bicyclo[2.2.2]octa-2,5-dienes,[4,5] and bicyclo[3.2.2]nona-6,8-dienes.[4] In contrast, 1,4-cyclohexadiene reacts with diethyl azodicarboxylate, dimethyl acetylenedicarboxylate, tetracyanoethylene, and *N*-phenyl-1,2,4-triazoline-3,5-dione (PTAD) to yield, as primary intermediates, ene type products.[1,6] In view of the difference between 1,4-cyclohexadiene and its bridged derivatives, we decided to explore the reactions of (i,o)-bicyclo[*n*.2.2]alkadienes of general formula **1** with dienophiles. We now wish to report unprecedented cycloaddition reactions of *N*-phenyl-1,2,4-triazoline-3,5-dione (**2**) with **1**.



1

Stirring of a chloroform solution of **1b**[7] with **2** at 25 °C for 12 h gave a crystalline 1:1 adduct (**3b**), mp 146–148 °C, in 86% yield.[8] The initial structural assignment was based on a combination of ^{1}H and ^{13}C NMR; ^{1}H NMR (benzene-d_6) δ 7.72 (1 H, m), 7.20–6.85 (4 H, aromatic), 5.38 (H_4, d, $J_{3,4}$ = 6 Hz), 4.09 (H_3, d of d, $J_{3,4}$ = 6 Hz, $J_{2,3}$ = 4 Hz), 3.90 (H_1, m) 2.61 (H_6, $J_{5,6}$ = 18 Hz),[9] 1.85 (2 H, H_2,[10] H_5, $J_{5,6}$ = 18 Hz,[9] $J_{1,5}$ = 4 Hz), and 1.70–0.38 (14 H, br m). Irradiation at δ 2.2 removed all coupling

---

[1] Ullman, E. F. *Chem. Ind.* (*London*) **1958**, 1173. Blomquist, A. T.; Meinwald, Y. C. *J. Am. Chem. Soc.* **1959**, *81*, 667. Hall, H. K. *J. Org. chem.* **1960**, *25*, 42. Kobuke, Y.; Sugimoto, T.; Furakawa, J.; Tueno, T. *J. Am. Chem. Soc.* **1972**, *94*, 3633. Krespan, C. G.; McKusick, B. C.; Cairns, T. L. *Ibid* **1961**, *83*, 3428. Cookson, R. C.; Dance, J. *Tetrahedron Lett.* **1962**, 879. Heuber, C. F.; Donoghue, E.; Dorfman, L.; Stuber, E. A.; Danielli, N.; Wenkert, E. *Ibid.* **1966**, 1185. Schrauzer, G. N.; Glockner, P. *Chem. Ber.* **1964**, *97*, 2451. Tabushi, I.; Yamamura, K.; Yoshida, Y.; Togashi, A. *Bull. Chem. Soc. Jap.* **1975**, *48*, 2922; Gillis, B. T.; Hagarty, J. D. *J. Org.Chem.* **1967**, *32*, 330.

[2] Sasaki, T.; Eguchi, S.; Sugimoto, M.; Hibi, F. *J. Org. Chem.* **1972**, *37*, 2317.

[3] Iwamura, H.; Tanabe, Y.; Kobayashi, H. *Tetrahedron Lett.* **1976**, 1987.

[4] Fickes, G. N.; Metz, T. E. *J. Org. Chem.* **1978**, *43*, 1057.

[5] Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1964**, *86*, 1434.

[6] Longone, D. T.; Smith, G. L. *Tetrahedron Lett.* **1962**, 205. Jacobson, B. M. *J. Am. Chem. Soc.* **1980**, *102*, 886.

[7] Gassman, P. G.; Bailey, T. F.; Hoye, R. C. *J. Org. Chem.* **1980**, *45*, 2923.

[8] Satisfactory elemental analyses and/or exact mass molecular weights were obtained on all new compounds.

0002-7863/81/1503-2496$01.25/0