### Macroscopic Diffusion Control in High-Pressure Photochemistry

Katsuhiro Tamura\* and Sigeru Sugiyama

Department of Chemical Engineering, Faculty of Engineering, Tokushima University, Minamijosanjima-cho, Tokushima 770, Japan

W. J. le Noble\*

Department of Chemistry, State University of New York, Stony Brook, New York 11794

# Received April 10, 1984

In contrast to the wealth of available information concerning pressure effects on thermal reactions in solution,<sup>1</sup> little is known about such effects in photochemistry. Fortunately, this picture has begun to change in recent years.<sup>2</sup> In one review, attention has been called<sup>3</sup> to an experimental difficulty that must be appreciated if mechanistic conclusions are to be drawn for photochemical reactions from high-pressure observations. The basic problem is that one must be able to guarantee equal light availability in all parts of the unstirred solution.

There are two common ways in which such experiments may fail in this necessity. First, because of the mechanical weakness of the high-pressure windows, apertures are always small, generally 3-7 mm in diameter. The optical cells inside can be-and often are-of much larger diameter; this means that only a small fraction of the solution is receiving radiation at any time. One possible solution of this problem is to use light baffles at the far end of the pressure vessel to scatter the radiation throughout; another is to use an optical cell the diameter of which matches the aperture. The investigator who now finds that he can irradiate only a small amount of solution may be tempted to use high concentrations and/or a vessel and cell of extended length. But this defeats the purpose of guaranteeing uniform exposure as the forward part of the solution absorbs the light, leaving the farther portion in darkness even though it is formally in the light path.

These complications do not play a significant role in those experiments where only product distributions are measured and used to draw conclusions.<sup>4</sup> However, there are several reports now in which the time dependence of a single product concentration is recorded. In some of these, a pressure-induced retardation occurred, closely resembling the decrease in diffusion rate as measured by the effect of pressure on viscosity, and the conclusion was drawn that diffusion was controlling the reaction. While these conclusions may well be correct, where the experimental descriptions do not guarantee uniform light access, one must entertain the alternative possibility that the diffusion control may have operated at the macroscopic rather than at the chemical level. We record an experiment here to make this point. In it, norbornadiene (N) is irradiated in toluene solution with benzophenone as sensitizer (S), to give quadricyclane (Q); the concentration



**Figure 1.** High-pressure vessel: (1) body of the vessel  $(130 \times$  $130 \times 130$  mm); (2) fused quartz; (3) optical cell (sample solution); (4) cell holder; (5) window plug.

is measured as a function of time and pressure.

### **Experimental Section**

The vessel and cell<sup>5</sup> used are shown in Figure 1, the combination permits irradiation of the entire solution. The vessel was thermostated at 25 °C and connected to a hand-operated Hikari Koatsukiki KP-3A pump and a Naganoseiki NKS-5000 Bourdon gauge; the hydraulic fluid was a 2:1 (v:v) mixture of glycerin and ethanol. The pressure range employed was from 0.1-150 MPa (1 MPa  $\approx$  10 atm). The norbornadiene, quadricyclane, toluene, and benzene used (the latter as internal standard) were distilled and the benzophenone was crystallized from hexane prior to use. The presence of oxygen was minimized by means of extensive nitrogen bubbling. Analysis was done by means of GLC; use was made of a Hitachi 164 F with a 1-m column at 70 °C and Bentone 34 + DDP on Uniport KA (5 + 5%).

Partial molar volumes were determined with the relation

$$\bar{\mathbf{V}}_2 = \frac{M_2}{\rho_{\rm m}} + M_2 (1 - W_2) \frac{\mathrm{d}(1/\rho_{\rm m})}{\mathrm{d}W_2} \tag{1}$$

where the subscript 2 represents the solute,  $\bar{V}$  is the partial molar volume, M the molecular weight,  $\rho_m$  the density of the solution, and W the weight fraction. Plots of the reciprocal of the density vs. the weight fraction of the solute were approximately linear;  $\overline{V}_2$  at infinitive dilution was determined by extrapolation to zero concentration.

### **Results and Discussion**

When the concentrations of N and S are both 0.22 mol kg<sup>-1</sup>, one observes that Q is formed at a rate that is essentially first order in N at all pressures examined. The thermal reverse reaction at 25 °C is too slow to interfere; pseudo-first-order rate plots were linear with correlation coefficients in excess of 0.99. When the rate constants are plotted against pressure, the curve obtained can be fitted to  $\ln k = a + bp + cp^2$ , and the pseudo activation volume at zero pressure estimated by means of the equation  $\Delta V^*$  $= -RT (\delta \ln k / \delta p)_{\rm T} = -bRT$ . The value obtained equals  $+18 \text{ cm}^3 \text{ mol}^{-1}$ 

Since the photoisomerization of N proceeds<sup>6</sup> via the steps I–V, it would at first glance seem reasonable to at-

Asano, T.; le Noble, W. J. Chem. Rev. 1978, 78, 407.
 (2) (a) Brauer, H.-D.; Schmidt, R.; Kelm, H. in "High Pressure Chemistry"; Kelm, H., Ed., D. Reidel; Boston, MA, 1978; p 521 ff. (b) Isaacs, N. S. "Liquid Phase High Pressure Chemistry", Wiley: New York, 1992. 1981

<sup>(3)</sup> Reference 1, p 479.

<sup>(4)</sup> For examples: (a) Tanaka, F.; Sasaki, M.; Osugi, J. Rev. Phys. Chem. Jpn. 1971, 41, 18. (b) le Noble, W. J.; Tamura, K. Tetrahedron Lett. 1977, 495. (c) Neuman, R. C.; Berge, C. D. Tetrahedron Lett. 1978, 1709. (d) Hamann, S. D.; Linton, M.; Sasse, W. H. F. Aust. J. Chem. 1980, 33, 1419.

<sup>(5)</sup> le Noble, W. J.; Schlott, R. Rev. Sci. Instrum. 1976, 47, 770. (6) Hautala, R. R.; Little, J.; Sweet, F. Sol. Energy 1977, 19, 503.

$$S \rightarrow {}^{1}S^{*}$$
 (I)

$${}^{1}\mathrm{S}^{*} \rightarrow {}^{3}\mathrm{S}^{*}$$
 (II)

$$^{3}S^{*} \rightarrow S$$
 (III)

$${}^{3}\mathrm{S}^{*} + \mathrm{N} \xrightarrow{k_{d}} \mathrm{S} + {}^{3}\mathrm{N}^{*}$$
 (IV)

$${}^{3}N^{*} \xrightarrow{\kappa_{r}} Q$$
 (V)

tribute the adverse pressure effect to diffusion-controlled competition between steps III and IV. Indeed, the rate constant for the energy transfer process can be expressed in terms of the Debye equation

$$k_{\rm d} = 8RT/3000\eta \tag{2}$$

where  $\eta$  is the viscosity. This equation is usually employed for viscous solvents such as glycerin, but it has been applied to nonviscous solvents like hexane ( $\eta = 0.3cp$  at 25 °C) as well; for instance, Dubois and Van Hemert<sup>7</sup> evaluated first excited singlet lifetimes of naphthalene and benzene derivatives in *n*-hexane this way in spite of the low viscosity. At 30 °C, the viscosity of toluene increases experimentally with pressure to 150 MPa,<sup>8</sup> and a value for  $\Delta V_d^*$  can be estimated from these data: it equals +17 cm<sup>3</sup> mol<sup>-1</sup>. The two volume terms are therefore equal within the margin of error of ±2 cm<sup>3</sup> mol<sup>-1</sup>, and diffusion control is strongly implicated. Nevertheless, the inference that step IV is rate controlled is wrong: since  $k_d \approx 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>, the lifetime of the triplet  $\tau(^3S^*) \approx 10^{-6}$  s in deoxygenated solutions, and [N]  $\approx 0.2$  mol kg<sup>-1</sup>, the fraction of  $^3S^*$ quenched by N must be very close to unity.

The key feature is this experiment is of course the high concentration of S. The toluene cut-off occurs at about 270 nm; at longer wavelengths, the extinction coefficient of S averages<sup>9</sup> about 60 at the main emission lines of the mercury source (313 and 366 nm). We furthermore found the absorption spectrum of S to be unaffected by pressure. With a concentration of S at 0.22 mol kg<sup>-1</sup>, virtually all of the useful light is absorbed in the first millimeter or so, and the N in the bulk of the solution must diffuse into this thin layer in order to be sensitized. Indeed, in experiments in which this concentration was lowered to about 0.001 mol kg<sup>-1</sup>, the pressure dependence of the pseudo rate constant vanished.

A final word about the reaction volume, found as the difference between  $\bar{V}_Q$  (94.9) and  $\bar{V}_N$  (102.6) to be about -8 cm<sup>3</sup> mol<sup>-1</sup>. This net contraction is not reflected in an enhanced conversion rate under pressure. Since molecular shapes and dipoles are not affected significantly by such modest pressures,<sup>10</sup> absorption spectra generally do not change very much.<sup>11</sup> The chemical bonds in the excited state are usually somewhat longer than in the ground state, and there are polarity changes in many instances as well. These changes are at the basis of Ubbelohde's proposal<sup>12</sup> that hydrostatic pressure may well affect the reactions of photoexcited molecules much more than thermal processes; however, this suggestion has thus far not been borne out experimentally. The reason for this is probably that it essentially ignores the Franck-Condon factor: the changes in volume follow the absorption step. It may be assumed that the overall volume decrease in the present instance arises during the rapid and irreversible cascading steps and

- (11) Hamann, S. D.; Linton, M. Aust. J. Chem. 1975, 28, 701.
- (12) Ubbelohde, A. R. Nature (London) 1966, 209, 28.

the effect of pressure on these steps is not revealed by the pseudo kinetics.

In conclusion, we have shown by means of the sensitized photoconversion of norbornadiene into quadricyclane under high pressure that the diffusion control often observed in such experiments may be ascribable to macroscopic diffusion rather than to impeded motion at the molecular level.

Acknowledgment. K. Tamura acknowledges a Grant-in-Aid for Science Research from the Ministry of Education, Science and Culture. W. le Noble thanks the NSF for financial support and Dr. H.-D. Brauer (Frankfurt) for correspondence.

**Registry No.** Norbornadiene, 121-46-0; quadricyclane, 278-06-8; benzophenone, 119-61-9.

# Electric Second Hyperpolarizability as a Novel Probe to the Stability of Dianions. Case Study: Four Conformers of C<sub>6</sub>H<sub>8</sub><sup>2-</sup>

J. Waite\* and M. G. Papadopoulos

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Vas. Constantinou 48, Athens 501/1, Greece

#### Received March 12, 1984

The main question which is addressed in this paper is the effect of changes in shape of a molecular anion on its electric response to the environment, with particular reference to its stability. This is an important problem because it is known that the interactions of an anion with its environment (e.g., the solvent) control the chemistry of anionic species.<sup>1,2</sup>

In this computational study we have chosen four isomers of  $C_6H_8^{2-}$ , all of which have been prepared<sup>3-6</sup> and their relative stabilities reported.<sup>6</sup> We also provide evidence for a factor which contributes to the lower stability of the "linear" dianion 2 (Figure 1), in comparison to 1, as shown by experiment. It is noted that the problem of relative stability of cross and linearly conjugated dianions has been subjected to considerable theoretical and experimental research.<sup>3,6-10</sup> Here a novel point of view is contributed to this discussion.

The response of a molecular anion to its environment is monitored by the average electric polarizability,  $\alpha$ , and the second hyperpolarizability,  $\gamma$ .<sup>11,12</sup> Several authors have

- (8) Clark, T.; Wilhelm, D.; Schleyer, P. v. R. Tetrahedron. Lett. 1982, 23, 3547.
  - (9) Inagaki, S.; Hirabayashi, Y. Chem. Lett. 1982, 709.
  - (10) Gund, P. J. Chem. Educ. 1972, 49, 100.
- (11) Buckingham, A. D.; Orr, B. J. Q. Rev. Chem. Soc. London 1967, 21, 195.

<sup>(7)</sup> Dubois, J. T.; Van Hemert, P. L. J. Chem. Phys. 1964, 40, 923.
(8) Bridgman, P. W. "The Physics of High Pressure"; Dover Publications, Inc.: New York, 1970; p 344.

 <sup>(9)</sup> Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; p 3.

<sup>(10)</sup> Benson, S. W.; Berson, J. A. J. Am. Chem. Soc. 1964, 86, 259.

<sup>(1)</sup> Stevenson, G. R.; Pourlan, M. J. Phys. Chem. 1982, 86, 1871.

<sup>(2) (</sup>a) Brauman, J. L.; Blair, L. K. J. Am. Chem. Soc. 1970, 92, 5986.

<sup>(</sup>b) Waite, J.; Papadopoulos, M. G. J. Mol. Struct. 1984, 108, 247.
(3) Bates, R. B.; Hess, B. A.; Ogle, C. A.; Schaad, L. J. J. Am. Chem.

Soc. 1981, 103, 5052. (4) Bahl, J. J.; Bates, R. B.; Gordon, B., III. J. Org. Chem. 1979, 44,

<sup>2290.
(5)</sup> Bates, R. B.; Beavers, W. A.; Greene, M. G.; Klein, J. H. J. Am. Chem. Soc. 1974, 96, 5640.

 <sup>(6)</sup> Inagaki, S.; Kawata, H.; Hirabayashi, Y. J. Org. Chem. 1983, 48, 2928.

<sup>(7)</sup> Rusinko, A., III; Mills, N. S.; Morse, P. J. Org. Chem., 1982, 47, 5198.

<sup>(12)</sup> The first hyperpolarizability,  $\beta$ , being a vectorial quantity, is very sensitive to geometry changes, but it was not considered an appropriate probe for this study since in two of the four cases  $\beta$  is zero by symmetry.