

ligand. Furthermore, it suggests that, for rapid turnover in electron transport, a low-spin complex with a weakly coordinated sixth ligand may be a prerequisite.¹⁶

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank Dr. C. T. Lin for a preliminary temperature-jump measurement.

(16) Parallel experiments on ferric myoglobin azide, which exists in spin equilibrium at pH 7,⁶ give similar results, *i.e.*, the spin-equilibrium relaxation occurs within the heating risetime of 5 μ sec. This relaxation process is considerably more rapid than the formation and dissociation of the azido ferrimyoglobin.¹⁷

(17) D. E. Goldsack, W. S. Eberlain, and R. A. Alberty, *J. Biol. Chem.*, **240**, 4312 (1965); **241**, 2653 (1966).

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Received October 11, 1973

High-Pressure High-Resolution Nuclear Magnetic Resonance. Pressure Dependence of the Proton Chemical Shift of Chloroform in Aromatic Solvents

Sir:

Recent experiments on the high-pressure high-resolution nmr have shown that the technique provides a very useful means of studying the behavior of a molecule in the liquid phase at high pressure.¹

In the previous paper,^{1c} one of us described a convenient device in which a pressure-resisting glass cell was connected to a thermal expansion type pressure generator and a piezometer to realize the high-resolution nmr experiment up to near 1700 kg cm⁻². The device, however, required considerable skill and effort to be constructed for the correct functioning. To overcome this difficulty, we have developed a method of connecting the glass cell with standard high-pressure equipment, and, in the course of the nmr experiments utilizing the improved apparatus, we have found a notable pressure dependence of the proton chemical shift of chloroform in aromatic solvents.

The apparatus mainly consists of a stainless steel nozzle (NZ), a glass nozzle (NZG) fixed in (NZ) with an epoxy adhesive, and a glass cell having a long tail of flexible capillary, the end of which is fixed in (NZG) with the adhesive.² The (NZ) was mounted to the ordinary high-pressure system consisting of a 5000 kg cm⁻² Bourdon gauge³ and a 3000 kg cm⁻² hand pump. The nmr measurements were carried out on a JEOL 3H-60 high-resolution spectrometer operating at 60 MHz, and the present sample cell, having i.d. \approx 1 mm, proved satisfactory to perform easily the high-resolution measurement to establish $\Delta\nu_{h/2} \approx$ 1 Hz for the chloroform resonance. The chemical shifts were determined by linear interpolation between known audio frequency side bands to obtain the accuracy of ± 0.1 to ± 0.2 Hz. The temperature of the sample, measured by the procedure described in the previous paper,^{1c} was

(1) (a) D. J. Wilbur and J. Jonas, *J. Chem. Phys.*, **55**, 5840 (1971); (b) J. Jonas, *Rev. Sci. Instrum.*, **43**, 643 (1972); (c) H. Yamada, *Chem. Lett.*, 747 (1972); (d) J. Jouanne and J. Heidberg, *J. Magn. Resonance*, **7**, 1 (1972); (e) D. J. Wilbur and J. Jonas, *ibid.*, **10**, 279 (1973).

(2) Detailed description will appear elsewhere.

(3) Calibrated with Aminco dead weight tester.

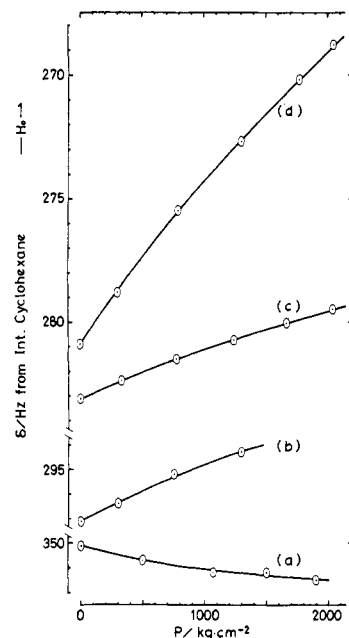


Figure 1. Pressure dependence of the chloroform proton chemical shift for chloroform (a) and chloroform in benzene (b), in mesitylene (c), and in 1,3,5-triisopropylbenzene (d).

estimated to be maintained at 29–30° throughout the experiment.

Figure 1 summarizes the pressure dependences of the proton chemical shift of chloroform (a) and chloroform (20 mol %) in benzene (I), mesitylene (II), and 1,3,5-triisopropylbenzene (III) (b, c, and d, respectively) relative to cyclohexane (5 mol %) used as an internal reference. The pressure dependence was also measured for solutions of 10 mol % chloroform in II and 45 mol % chloroform in III. In both cases the result was similar to the observation (c) and (d), respectively. From this fact, it may possibly be said that the present data approximately represent the pressure shifts expected for very dilute solutions of chloroform in aromatics. Since the experiments use the internal referencing system, it is only possible to center the discussion about the difference of chloroform and cyclohexane in the degree of interaction with surrounding molecules. Chloroform differs from cyclohexane in polarity and also in shape and size of the molecule, which gives rise to the observed pressure dependences of the chemical shifts relative to the reference.

Little displacement to lower field (a) with increasing pressure is noted for the chloroform resonance in the absence of the aromatic solvent. This is interpreted in terms of the preferred reinforcement of the self-association of chloroform molecules, which promotes the polarization of the H-CCl₃ bond (decrease in σ_E)⁴ and also intensifies the dispersion interaction between the molecules (decrease in σ_w).⁴ In aromatic solvents, on the other hand, the resonance shifts to higher field (b, c, d) with increasing pressure. This might generally be explained by the picture that chloroform, in preference to the cyclohexane, gets closer with increasing pressure to the aromatic molecule to experience the increased diamagnetic anisotropy effect of the ring with a resultant increase in σ_a which should overshadow the op-

(4) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

posed effect due to accompanying changes in σ_w and in σ_E . It is interesting, however, to note that the chloroform in III, as compared with those in the other solvents, shows the marked pressure shift, since the aromatic solvent shifts (ASIS) of chloroform resonance induced by I, II, and by III are shown to be nearly identical with each other at ordinary pressure.⁵ Thus the observation (d) can hardly be explained by the simple model in which the chloroform proton in III is located much closer to the ring and consequently displays much larger pressure shift. One plausible explanation may be that the approach of the chloroform proton, with increasing pressure, to the ring of III overcrowded on its periphery with bulky side chains might be allowed only in the limited region near the sixfold axis of the ring where the proton feels the highest diamagnetic field.

Continuing studies, examining the pressure dependence of chloroform resonance in various solvents in relation to the density changes of the solutions are now being carried out, and a more detailed discussion will appear in the near future.

Acknowledgment. The writers are indebted to Professors Tadashi Makita and Hironobu Kubota of Kobe University for their invaluable advice and for making facilities available for carrying out the calibration of our high-pressure gauge. This work has been supported in part by a Grant in Aid for Fundamental Scientific Research from the Ministry of Education, Japan.

(5) H. Yamada, T. Ishihara, and T. Kinugasa, unpublished data.

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Received November 7, 1973

Quantum Chain Processes. A Novel Procedure for Measurement of Quenching Parameters. Evidence That Exothermic Triplet-Triplet Energy Transfer Is Not Diffusion Limited and an Estimation of the Efficiency of Exothermic Quenching in a Solvent Cage

Sir:

The *assumption* of diffusion-limited exothermic triplet-triplet energy transfer in fluid organic solvents has allowed the calculation of the lifetimes of electronically excited molecules and the rate constants of many important photochemical processes.¹ However, inspection of the literature reveals that the assumption of diffusion controlled quenching is moot.² One of the

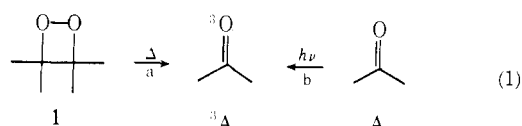
(1) For an excellent review see A. A. Lamola in "Energy Transfer and Organic Photochemistry," Wiley-Interscience, New York, N. Y., 1969.

(2) (a) For examples supporting the contention that exothermic triplet-triplet energy transfer is diffusion limited in low viscosity organic solvents see G. Porter and F. Wilkinson, *Proc. Roy. Soc., Ser. A*, **264**, 1 (1961); K. Sandros, *Acta Chem. Scand.*, **18**, 2355 (1964); A. D. Osborne and G. Porter, *Proc. Roy. Soc., Ser. A*, **264**, 9 (1965). These papers appear to assume high fluidity ($\eta \sim 0.01$ P) and a transfer exothermicity of $\sim 2-3$ kcal/mol. (b) For a contrasting point of view see P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5715 (1967); P. J. Wagner and I. Kochevar, *ibid.*, **90**, 2232 (1968); K. S. Y. Lau, R. O. Campbell, and R. S. H. Liu, *Mol. Photochem.*, **4**, 315 (1972). In these latter studies only *indirect* evidence for nondiffusion limited triplet-triplet transfer was presented. (c) Research concerned with the occurrence of pure steric effects on the rate constant for exothermic triplet-triplet energy transfer is presently an active area and has resulted in both positive [P. J. Wagner, M. J. May, A. Haug, and D. R. Graber, *J. Amer. Chem. Soc.*, **92**, 5268 (1970); C. C. Wamser and P. L. Chang, *ibid.*, **95**, 2044 (1973)] and negative [P. J. Wagner, J. M. McGrath, and R. G. Zepp, *ibid.*, **94**, 6883 (1972), and references therein] results.

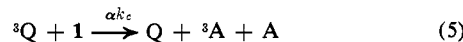
problems which arises in evaluating the reported data is the variation of methods employed to measure the important quantity k_q , the rate constant for quenching.³

The key idea of this report is that if a quantum chain reaction (a chain reaction in which electronic excitation is cycled through a number of steps) occurs, then the measurement of Stern-Volmer triplet quenching kinetics can lead to observed $k_q\tau$ values which differ significantly from the $k_q\tau$ values measured in the absence of a quantum chain. The difference between these measured $k_q\tau$ values can lead to information on the nature of the electronically excited triplet quencher 3Q , the rate constant of the quenching process, and the efficiency of exothermic triplet-triplet energy transfer in a solvent cage. Based on these ideas, we report here experiments which involve quantum chain reactions⁴ and which allow rapid determination of quenching parameters, evaluation of the assumption of diffusion limited triplet-triplet energy transfer, and an estimation of the efficiency of energy transfer within a solvent cage.

Equations 1-4 represent a standard scheme for exo-



thermic triplet-triplet energy transfer,¹ based on triplet acetone (3A) as donor. This mechanism predicts that entry to 3A via thermolysis⁵ of tetramethyl-1,2-dioxetane (**1**) or via photoexcitation⁶ of acetone, *i.e.*, path a and path b, respectively, in eq 1, should lead to the same Stern-Volmer constant (K_{sv}) which in turn will equal⁷ $k_q\tau_A$. A quantum chain reaction involving 3Q and **1** requires addition of steps 5 and 6 to the mechanism.



Notice that, although 3A is quenched in step 2, a new 3A reappears some of the time as a result of step 5. "Effective net quenching" of 3A depends on the extent of occurrence of step 5. The factors which determine the

(3) We feel that the best available data for the value of k_q will be obtained from studies in which the lifetime of the donor is measured. In this regard we take the value of k_q^{DIF} to be $\sim 1-2 \times 10^{10} M^{-1} \text{sec}^{-1}$ for acetonitrile solutions: A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968); W. R. Ware and H. P. Richter, *J. Chem. Phys.*, **48**, 1595 (1968).

(4) P. Lechtken, A. Yekta, and N. J. Turro, *J. Amer. Chem. Soc.*, **95**, 3027 (1973).

(5) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **94**, 2886 (1972); *Pure Appl. Chem.*, **33**, 363 (1973).

(6) For recent studies involved with acetone triplet in fluid solution see (a) R. W. Yip and W. Siebrand, *Chem. Phys. Lett.*, **13**, 209 (1972); (b) G. Porter, R. W. Yip, J. W. Dunston, A. J. Cessna, and S. E. Sugamori, *Trans. Faraday Soc.*, **67**, 3149 (1972) (c) R. O. Loutfy and R. O. Loutfy, *Can. J. Chem.*, **50**, 4052 (1972); (d) R. W. Yip, *et al.*, *ibid.*, **50**, 3426 (1972); (e) S. K. Dogra, R. O. Loutfy, S. E. Sugamori, and R. W. Yip, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1462 (1973).

(7) Direct measurement of quenching of acetone triplet by naphthalene in our laboratory (by single photon counting technique) results in a value of $k_q \sim 5 \times 10^9 M^{-1} \text{sec}^{-1}$. The only other value of a presumed triplet-triplet quenching rate constant for acetone in acetonitrile is the value reported in ref 6b where $k_q \sim 4 \times 10^9 M^{-1} \text{sec}^{-1}$ for 2,4-hexadien-1-ol as quencher.