

In a recent study<sup>3</sup> of vicinal <sup>13</sup>C-<sup>13</sup>C coupling in aliphatic and alicyclic <sup>13</sup>C-labeled acids, the experimental magnitudes for dihedral angles near 0° ranged from 1.9 to 2.4 Hz and for angles near 180° the values ranged from 3.6 to 5.2 Hz, in reasonable correspondence with calculated results for butanoic acid in Table II. The shifts in the maxima from the usual 0 and 180° values<sup>3</sup> may be attributable to the dependence of this type of coupling on two dihedral angles.

The large differences in the <sup>13</sup>C-<sup>13</sup>C coupling constants for the *cis* conformations of 2-butanol and butanoic acid follow the experimental trends but have no counterpart in vicinal H-H coupling. For the *cis* conformation of butanoic acid the oxygen atom is in close proximity (1.70 Å) to the hydrogen atoms on the C<sub>4</sub> carbon atom. It is possible that the oxygen and hydrogen atoms constitute the electronic path for transfer of spin information between the two carbon atoms.

**Acknowledgments.** The authors wish to express thanks to Dr. J. L. Marshall and Dr. D. E. Miiller for providing a copy of their manuscript while this one was in preparation. We also thank Mr. Frank Wians, Jr., for computational assistance and the University of Arizona Computer Center for use of their facilities.

(3) J. L. Marshall and D. E. Miiller, *J. Amer. Chem. Soc.*, **95**, 8305 (1973).

(4) Queen Elizabeth II Research Fellow, 1973-1974.

D. Doddrell,<sup>4</sup> I. Burfitt

Department of Organic Chemistry, The University of New England  
Armidale, N.S.W. 2351, Australia

J. B. Grutzner

Department of Chemistry, Purdue University  
West Lafayette, Indiana 47907

M. Barfield\*

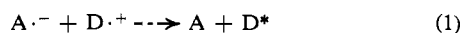
Department of Chemistry, University of Arizona  
Tucson, Arizona 85721

Received October 14, 1973

### A Comparison of Optical Excitation and Chemiluminescence. Variation of Fluorescence Quantum Efficiency with Selective Population of Vibrational Levels

Sir:

This paper reports the first example of systematically increasing the fluorescence efficiency of a compound by selectively populating various vibrational levels of the excited state, based on the specific difference between optical excitation and chemiluminescence.<sup>1,2</sup> In chemiluminescence, energy from a chemical reaction is converted into light; the type of chemiluminescence involved in this report is due to homogeneous charge transfer in a cation-anion annihilation reaction, which can be represented as



followed by



When the ions A<sup>·-</sup> and D<sup>·+</sup> are prepared *in situ* by electrochemical means, the term "electrogenerated

chemiluminescence," often abbreviated as "ECL," applies.<sup>3-9</sup> The conversion of one form of energy into another is among the most fundamental problems in science, and recent advances in ECL have been related to improving that conversion efficiency ( $\Phi_{ECL}$ ). Advantageous experimental conditions were found to be the use of low polarity solvents including mixed "heteropolar" solvents such as acetonitrile-benzene<sup>7-9</sup> and lowering the supporting electrolyte concentration.<sup>9</sup> These improvements<sup>7-9</sup> did not directly involve the fluorescence efficiency,  $\Phi_f$ , and the relevant literature<sup>3,4</sup> including the recent paper by Schwartz, Blakeley, and Robinson<sup>10</sup> assumed that the optical quantum yield has a limit set by the fluorescence quantum efficiency measured from optical excitation ( $\Phi_{f, optic}$ ); *i.e.*, even if eq 1 were 100% efficient,  $\Phi_{ECL}$ , representing the combined process of eq 1 and eq 2, was regarded as having the upper limit  $\Phi_{f, optic}$ .

The results presented here demonstrate that such need not be the case and indeed that an upper limit on  $\Phi_{ECL}$  set by  $\Phi_{f, optic}$  does not exist in the general sense, the reason being that fluorescence efficiency may strongly depend for some compounds on the mode of excitation. Specifically, the fluorescence quantum efficiency of a luminescor may be much lower when optical excitation is used than when chemical energy is converted to light.

To readily demonstrate such a difference in fluorescence quantum efficiency, a compound having a low  $\Phi_{f, optic}$  is best suited. In addition, the chemiluminescence route to excited-state production should clearly avoid some established causes of the low  $\Phi_{f, optic}$ . A suitable compound is thianthrene (TH) having  $\Phi_{f, optic} = 3.6\%$ ,  $\Phi_{t, optic} = 94\%$ .<sup>11</sup> In addition, for thianthrene the optical excitation maximum (4.77 eV) differs significantly from the emission maximum (2.84 eV), and this leads to a situation where intersystem crossing from the vibrationally "hot" Franck-Condon state (R\*†) to the triplet becomes a prominent route in the time evolution of TH\*.

The chemical energy available from eq 1 is found from the standard oxidation and reduction potential of D and A, respectively, according to

$$\Delta H_r^\circ = E^\circ_{(A/A^{\cdot-})} - E^\circ_{(D/D^{\cdot+})} + 0.10 \text{ eV} \quad (3)$$

where the last term is the currently used estimate of  $T\Delta S^\circ$ , needed when direct measurement of  $[\partial\Delta G^\circ/\partial T]_p$  is lacking for the system. The reduction potentials of the various A species are given in Table I, together with the calculated  $\Delta H_r^\circ$  values. We note that the lesser  $|\Delta H_r^\circ|$  values are still sufficient to populate the <sup>1</sup>TH\* state (2.84 eV) but progressively lower

(3) D. M. Hercules, *Accounts Chem. Res.*, **2**, 301 (1969).

(4) R. Bezman and L. R. Faulkner, *J. Amer. Chem. Soc.*, **94**, 6331 (1972).

(5) C. P. Keszthelyi, H. Tachikawa, and A. J. Bard, *J. Amer. Chem. Soc.*, **94**, 1522 (1972).

(6) N. E. Tokel, C. P. Keszthelyi, and A. J. Bard, *J. Amer. Chem. Soc.*, **94**, 4872 (1972).

(7) C. P. Keszthelyi and A. J. Bard, *J. Electrochem. Soc.*, **120**, 241 (1973).

(8) C. P. Keszthelyi, *J. Electrochem. Soc.*, **120**, 39C (1973).

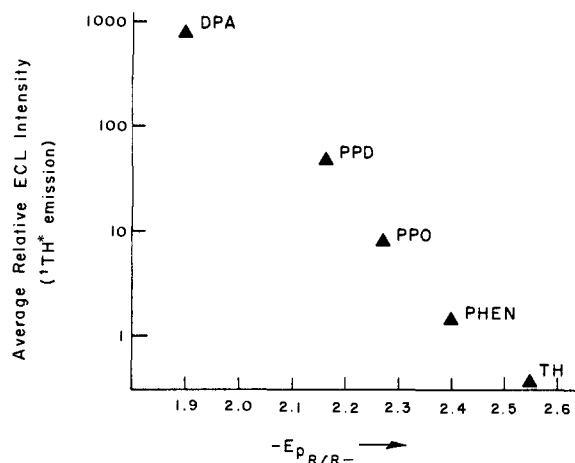
(9) A. J. Bard, C. P. Keszthelyi, H. Tachikawa, and N. E. Tokel, "Chemiluminescence and Bioluminescence, Proceedings of the 1972 International Conference," M. J. Cormier, D. M. Hercules, and J. Lee, Ed., Plenum Press, New York, N. Y., 1973, pp 193-208.

(10) P. M. Schwartz, R. A. Blakeley, and B. B. Robinson, *J. Phys. Chem.*, **76**, 1868 (1972).

(11) J. M. Bonnier and R. Jardon, *J. Chim. Phys. Physicochim. Biol.*, **68**, 428 (1971).

(1) F. McCapra, *Essays Chem.*, **3**, 101 (1972).

(2) C. P. Keszthelyi, *Extended Abstr.*, **72-1**, 234 (1972).



**Figure 1.** Relationship between ECL intensity and energy available from the chemiluminescent reaction involving the thianthrene cation and various anions. (Cf. Table I for relevant additional information; the TH<sup>+</sup>/TH<sup>-</sup> pair gives no singlet TH\* emission; [DPA] was 0.75 mM due to its low solubility in ACN-0.1 M TBAP; other anion parent and TH concentrations were 1 mM.)

**Table I.** Energy Data<sup>a</sup> of Electrogenerated Chemiluminescence Systems with D = Thianthrene (TH).

$E^\circ(\text{TH}^+/\text{TH} \cdot^+)$  = +1.22 V vs. sce;  $E_s(\text{}^1\text{TH}^*)$  = 2.84 eV

A	$E^\circ_{(A/A \cdot^-)}$ <sup>a,b</sup> (V vs. sce) <sup>c</sup>	$-\Delta H_r^\circ$ , eV	Comment
9,10-Diphenylanthracene (DPA)	-1.85	2.97	d
2,5-Diphenyl-1,3,4-oxadiazole (PPD)	-2.14	3.26	e
2,5-Diphenyloxazole (PPO)	-2.25	3.37	e
Phenanthrene (PHEN)	-2.41	3.53	
Thianthrene (TH)	-2.54	3.66	f

<sup>a</sup> In dry, deaerated ACN-0.1 M TBAP containing 1 mM A (cf. d for DPA concentration). <sup>b</sup> Assuming the diffusion coefficients of A and A<sup>-</sup> are equal. <sup>c</sup> Recalculated from V vs. Ag reference (cf. Experimental Section). <sup>d</sup> 0.75 mM due to low solubility of DPA in ACN-TBAP. <sup>e</sup> Cf. N. P. Shimanskaya and V. D. Bezuglyi, *Zh. Obshch. Khim.*, **33**, 1683 (1963), for reduction in 92% methanol-water, where the reduction product is not the monoanion. <sup>f</sup> Unstable TH<sup>-</sup> makes  $E^\circ$  and  $\Delta H_r^\circ$  probably too small; an unstable anion can shift the reduction potential in the positive direction.

vibrational levels of it. In turn the probability of intersystem crossing to the triplet state decreases, and an increase in  $\Phi_f$  is predicted.

The ECL experiments were carried out under the same conditions and precautions reported earlier for the PPD-TH system;<sup>5</sup> the ECL cell has been described previously [Figure 1, ref 5], together with the electrochemical apparatus and Aminco-Bowman spectrofluorometer.<sup>5-8</sup> The ECL intensity ( $I_{\text{ECL}}$ ) for all systems was measured at 434 nm (the emission maximum of <sup>1</sup>TH\*) and an applied frequency of 50 Hz; this frequency is optimum for observing maximum  $I_{\text{ECL}}$  in these systems.<sup>8</sup> The relationship between <sup>1</sup>TH\* ECL emission and reduction potential of the various A species is shown in Figure 1. The very large changes in ECL efficiency are not explicable in terms of secondary effects such as differences in the quenching rate constants of the several A<sup>-</sup> species but suggest that a true variation of  $\Phi_f$  is involved. For the most efficient system in Figure 1, a chemiluminescence efficiency

greater than  $\Phi_{f,\text{optic}}$  has been measured,<sup>8,9</sup> while all the systems remain subject to a substantially less than unit efficiency of excited-state production in eq 1.

**Acknowledgment.** The many invaluable discussions with Professor Allen J. Bard are gratefully acknowledged.

Csaba P. Keszthelyi

Department of Chemistry, Louisiana State University  
Baton Rouge, Louisiana 70803

Received August 10, 1973

## High-Yield Syntheses of Monochloro Permethylated Polysilanes

Sir:

The reaction of 1,6-dichlorododecamethylhexasilane and an equimolar amount of methylmagnesium iodide in ethyl ether gave a 90% yield of 1-chloroterdecamethylhexasilane, a compound needed in our investigations of permethylated polysilanes. This yield is remarkable since the statistically predicted distribution of silicon-containing compounds is 50:25:25 for 1-chloroterdecamethylhexasilane, tetradecamethylhexasilane, and unreacted 1,6-dichlorohexasilane, respectively. The reactions for other  $\alpha,\omega$ -dichloropermethylpolysilanes with methylmagnesium iodide were studied to determine the yields of monochloropolysilanes as a function of chain length and to explore the nature of this high-yield reaction.

Halogenodemethylation with H<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>Cl<sup>1</sup> or with either HCl or CH<sub>3</sub>COCl in the presence of AlCl<sub>3</sub><sup>2</sup> has been used to prepare chloropermethylpolysilanes. However, for higher polysilanes, side reactions decrease yields considerably.<sup>3,4</sup> Halogenodephenylations of phenylmethylpolysilanes,<sup>2</sup> halogenation of methylated polysilylhydrides,<sup>5</sup> and halogenodealkoxylations of methylalkoxypolysilanes<sup>6</sup> also have been used but these intermediates are not readily available.

The yields of monochloropolysilanes obtained from the reaction of equimolar amounts of  $\alpha,\omega$ -dichloropolysilanes and methylmagnesium iodide at 30° are given in Table I. The nmr chemical shifts, given in Table II, of the protons of the -Si(CH<sub>3</sub>)<sub>2</sub>Cl group<sup>7</sup> differ sufficiently for the mono- and dichloropolysilanes for the relative amounts of these compounds to be measurable from integrated intensities. Therefore, yields were determined and reported from the nmr spectra of the reaction mixtures. These yields agree well with values obtained by fractional distillation.

(1) (a) M. Kumada and M. Ishikawa, *J. Organometal. Chem.*, **1**, 153 (1963); (b) M. Kumada, M. Ishikawa, and S. Maeda, *ibid.*, **2**, 478 (1964).

(2) H. Sakurai, K. Tominaga, T. Watanabe, and M. Kumada, *Tetrahedron Lett.*, 5493 (1966).

(3) M. Kumada and K. Tamao, *Advan. Organometal. Chem.*, **6**, 19 (1968).

(4) D. V. Stynes, Ph.D. Thesis, Northwestern University, Evanston, Ill., 1972.

(5) U. G. Stolberg, *Chem. Ber.*, **96**, 2798 (1963).

(6) M. Kumada, M. Yamaguchi, Y. Yamamoto, J. Nakajima, and K. Shiina, *J. Org. Chem.*, **21**, 1264 (1956).

(7) Chlorodi- and -trisilanes were identified by nmr.<sup>8</sup> 1,4-Dichlorooctamethyltetrasilane and 1,6-dichlorododecamethylhexasilane were identified by nmr and boiling points (C<sub>12</sub>H<sub>30</sub>Si<sub>6</sub>Cl<sub>2</sub>, bp 161-164° (1 mm), lit. 160-162° (0.8 mm); C<sub>8</sub>H<sub>22</sub>Si<sub>4</sub>Cl<sub>2</sub>, bp 78-80° (1 mm), lit. 76-78° (1 mm); Me(SiMe<sub>2</sub>)<sub>6</sub>Cl and Me(SiMe<sub>2</sub>)<sub>4</sub>Cl apparently have not been reported previously. *Anal.* Calcd for C<sub>13</sub>H<sub>30</sub>Si<sub>3</sub>Cl: Cl, 8.88. Found: Cl, 8.90. Calcd for C<sub>9</sub>H<sub>22</sub>Si<sub>2</sub>Cl: Cl, 12.52. Found: Cl, 12.53.

(8) R. West, F. Kramer, E. Carberry, M. Kumada, and M. Ishikawa, *J. Organometal. Chem.*, **8**, 79 (1967).