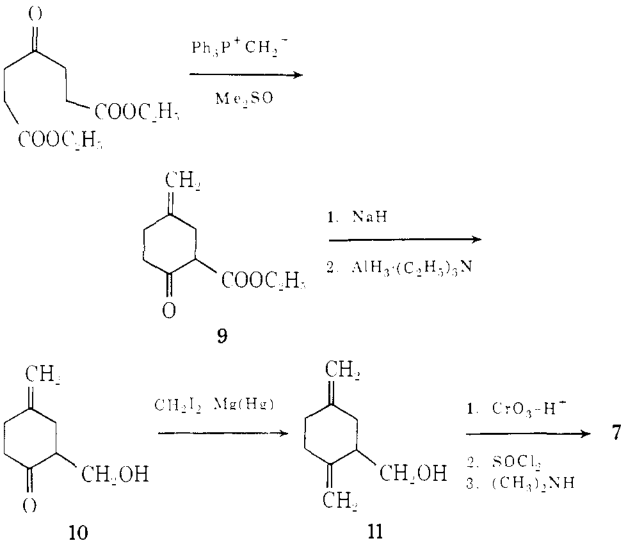
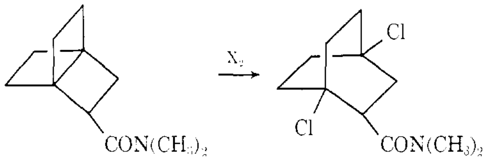
The structure of the minor product **8** from the ring opening of **6** was deduced from the compound's origin and the spectral data: ir (CCl_4) ν 1635, 892 cm^{-1}; nmr (CCl_4, 270 MHz) δ 5.71 (1 H, s), 4.64 (2 H, 4-Hz apart), 3.00 (3 H, s), 2.88 (3 H, s), 2.52 (2 H, t, J = 6 Hz), 2.24 ppm (6 H, br s). The structure of **7** was arrived at similarly (see Figure 1b) and was confirmed by unambiguous synthesis of the compound (Chart II).

Chart II



Reaction of diethyl γ-ketopimelate (Aldrich) with an excess of methylenetriphenylphosphorane in Me_2SO provided for the introduction of an exocyclic methylene group and subsequent Dieckmann condensation to the carboethoxycyclohexanone **9** in 60% yield, bp 59–60° (1 Torr). Rapid salt formation from the β-keto ester interfered with further methylenation under basic conditions. Treatment[11] of the sodium enolate of **9** in glyme with aluminum hydride–triethylamine in benzene led to reduction of the ester group alone and gave the hydroxymethyl ketone **10** in 50% yield, bp 58–60° (20 mTorr). This compound could be methylenated satisfactorily (70%) with methylene iodide–magnesium amalgam[12] giving the diene **11**, which was taken on without complete purification. Adjustment of oxidation state and subsequent production of the requisite amide were done as illustrated and need no further comment. The final product was shown to be identical spectroscopically and chromatographically with the amide **7** formed from thermal cleavage of the propellane **6**.

The [2.2.2]propellane **6** reacts very rapidly with chlorine to give **12**, mp 121.5–122.5°, the product of addition across the central bond. The structure of **12** was confirmed by an independent, unambiguous synthesis of the compound. Diels–Alder reaction of 1,2,3,4-tetrachloro-1,3-cyclohexadiene with excess acryloyl chloride at 140° for 3 days gave a mixture of adducts that was taken directly to the corresponding mixture of dimethylamides (72% overall; 5 parts endo, mp 196–197°; 1 part exo, mp 110.5–111.5°). Reduction of these, together or alone, with hydrogen over palladium-on-carbon in methanolic sodium hydroxide gave **12** in excellent yield. The propellane **6** reacts instantly with bromine at −70° to give the dibromo adduct **13**, mp 117–118°. No doubt these reactions reflect sp$^{<3}$ hybridization of the tetrasubstituted bridgehead atoms (taken on to meet the structural demands of the carbon skeleton), a weak central bond formed to a significant degree by σ overlap of p orbitals, and the great strain inherent in the [2.2.2]propellane system.[13]



6

12, X = Cl
13, X = Br

Acknowledgments. Generous support of this work by the National Science Foundation is recognized with thanks. We are grateful to Dr. J. C. Kauer of Du Pont for a sizable sample of tetrachlorocyclohexadiene.

---

[11] The method follows from a suggestion in N. M. Yoon and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 2927 (1968). The reagent was purchased from Lithium Corporation of America.

[12] G. Cainelli, F. Bertini, P. Grasselli, and G. Zubiani, *Tetrahedron Lett.*, 5153 (1967).

[13] The [2.2.2]propellane **6** does not react with oxygen at a noticeable rate. This is quite unlike the much less strained propellanes 1,3-dehydroadamantane[14] and [3.2.1]propellane[15] which copolymerize with oxygen extremely readily. These contain a cyclopropane unit.

[14] R. E. Pincock, J. Schmidt, W. B. Scott, and E. J. Toruka, *Can. J. Chem.*, **50**, 3958 (1972).

[15] K. B. Wiberg and G. J. Burgmaier, *J. Amer. Chem. Soc.*, **94**, 7396 (1972).

[16] Shell Research Foundation Predoctoral Fellow.

Philip E. Eaton,* George H. Temme III[16]
Searle Chemistry Laboratory, Department of Chemistry
The University of Chicago, Chicago, Illinois 60637

Received July 17, 1973

Triboluminescence of Hexaphenylcarbodiphosphorane. Emission from a Molecular Excited State Populated by Mechanical Stress

Sir:

The phenomenon of triboluminescence, the emission of light caused by application of mechanical stress to crystals, has been known since the 17th century.[1] Although a wide variety of organic and inorganic crystals are triboluminescent,[2] the specific mechanisms of the excitation and the excited-state origins of the emission are not known for most of the crystals studied.[3] In some cases, the emissions originate from triboelectrification[4] of the solid. Evidence for an electrical mechanism was provided by the observation that the triboluminescence of *cis*-4-octene in an atmosphere of neon exhibited the red glow of an electrical discharge in that gas.[5] The triboluminescence of zinc sulfide crystals has been attributed[3] to an electroluminescent mechanism on the basis of the correspondence between the electro- and triboluminescence spectra. In this communication we report the triboluminescence spectrum

---

[1] G. Wiedemann and F. Schmidt, *Ann. Phys. Chem.*, **54**, 606 (1895). Triboluminescence was first named in this reference. It takes its prefix from the Greek "tribein," to rub.

[2] G. Wolff, G. Gross, and I. N. Stranske, *Z. Elektrochem.*, **56**, 420 (1952).

[3] P. A. Thiessen and K. Meyer, *Naturwissenschaften*, **57**, 423 (1970).

[4] S. DePaoli and O. P. Strausz, *Can. J. Chem.*, **48**, 3756 (1970).

[5] M. C. Hoff and C. E. Boord, *J. Amer. Chem. Soc.*, **72**, 2770 (1950).

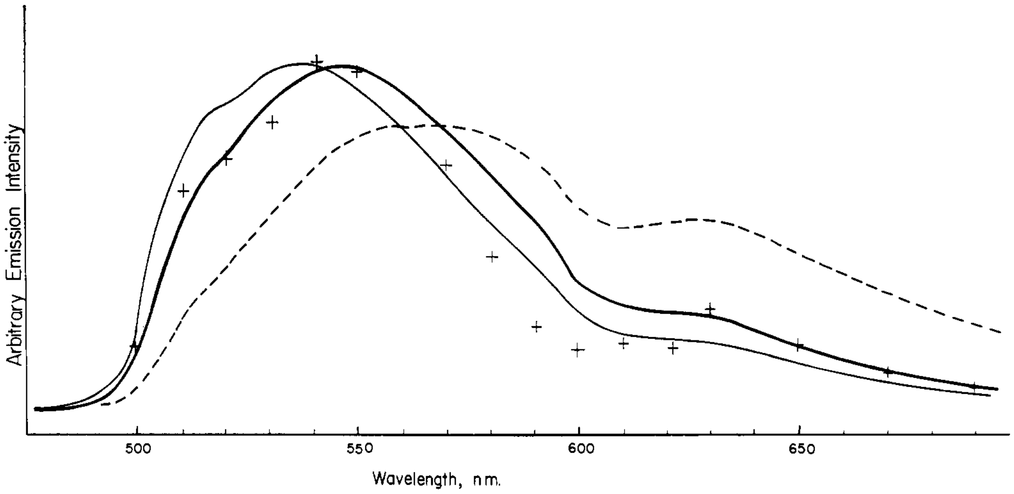


Figure 1. Luminescence spectra of (Ph$_3$P)$_2$C: (—) methyltetrahydrofuran glass, 77 °K; (—) solid-state crystals, 77 and 298 °K; (+++) triboluminescence, 298 °K. The emission maxima are normalized to the same value. (-----) Methyltetrahydrofuran solution, 298 °K, intensity not normalized.

and the crystal and the rigid glass ultraviolet excitation spectra of hexaphenylcarbodiphosphorane, (Ph$_3$P)$_2$C (I), and provide the first evidence that triboluminescence can originate from a purely molecular excited state. Spectroscopic evidence indicates that no chemical change results from the production of the triboluminescence.

Hexaphenylcarbodiphosphorane was prepared by the reported method,[6] recrystallized twice from diglyme, and washed twice with pure hexane. The bright yellow monoclinic crystals (space group *C*2)[7] are moisture sensitive and were handled in a dry nitrogen atmosphere. The triboluminescence spectrum was obtained by grinding 0.5-g samples with glass, chromel, and stainless steel rods. The emission intensity of a triboluminescent flash at a given wavelength and the total intensity were measured simultaneously using two detectors. Triboluminescence was observed under nitrogen, argon, and ambient atmospheres with no change in color. The gradual decrease in emission intensity which was recorded as the crystals were ground to an increasingly fine powder probably arises because the plunger could no longer apply sufficient stress to the microcrystals comprising the powder. The powder from which the triboluminescence had been observed retained spectral properties identical with those of the fresh, unground samples. All uv excitation emission spectra were obtained using mercury excitation at wavelengths below 3800 Å.

The triboluminescence spectrum and the uv excitation spectrum of I in a methyltetrahydrofuran glass at 77 °K are almost identical (Figure 1). The excitation spectrum of the solid crystals is the same at 77 and 300 °K and is given in the figure for comparison. This is the first compound for which the triboluminescence has been shown to originate from an excited state of a discrete molecule (contrasted with an excited state characteristic of the crystal). The small bathochromatic shift of the triboluminescence maximum compared with that of the uv excitation spectrum of the solid may result in part from the effect of pressure on the crystal.[8] The lifetime of the emission in MeTHF glass at 77 °K is 0.11 ± 0.01 msec at 5500 and 6300 Å. At 298 °K in fluid solution the lifetimes have an upper limit of about 10 μsec, shorter than that of our flash. For comparison, triphenylphosphine has a phosphorescence maximum at 3970 Å with a lifetime of 14 msec.[9] The change in relative intensities of the 5500 and 6300 Å maxima with temperature is shown in the figure. Although both maxima have the same apparent lifetime at 298 and at 77 °K, we cannot exclude the possibility that the 6300-Å band is a different emitting state with a very short lifetime such that the only measured luminescence decay at 6300 Å arises from the vibronic manifold of the 5500 Å emission. The shoulder at 5130 Å is due to the hydrolysis decomposition product, Ph$_3$P=CHP(O)Ph$_2$ (II). We have found that the emission spectrum of II consists of two maxima at 5130 and 5250 Å. The small shift of the emission maximum and the lowest energy absorption maxima which occur when the central carbon is protonated suggest that the transition does not involve the nonbonding electron pair on the central carbon and may be tentatively assigned as a π–π^* phosphorescence involving the partial double bond character of the central carbon and phosphorus atoms. Support for this assignment is provided by our inability to find an emission from (CO)$_3$NiC(PPh$_3$)$_2$ in the visible region of the spectrum.

Although our data do not definitely exclude a triboelectric excitation mechanism, the correspondence of the triboluminescence and uv excitation spectra, the invariability of the luminescence with the nature of the atmosphere, and the decrease in intensity as the crystal size is decreased all suggest the possibility that the triboluminescence may arise from the strain exerted on molecules in the crystal. Our observations that triboluminescence can be repeatedly produced with no visible cracking of a crystal when a crystal of I is plunged into liquid nitrogen further support a strain mechanism. The low intensity of the tribolumines-

---

(6) F. Ramirez, N. B. Desai, B. Hansen, and N. McKelvie, *ibid.*, **83**, 3539 (1961); J. S. Driscoll, D. W. Grisley, J. V. Pustinger, J. E. Harris, and C. N. Matthews, *J. Org. Chem.*, **29**, 2427 (1964); G. H. Benim and C. N. Matthews, *J. Amer. Chem. Soc.*, **88**, 4198 (1966).

(7) A. T. Vincent and P. J. Wheatley, *J. Chem. Soc., Dalton Trans.*, 617 (1972).

(8) H. G. Drikamer and C. W. Frank, *Annu. Rev. Phys. Chem.*, **23**, 39 (1972).

(9) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

cence caused by cooling precluded measurement of the spectrum. Several of the most likely excitation mechanisms involving strain include phase transitions which halve the dimensions of the unit cell by changing the P–C–P bond angles or which allow formation of an intermolecular double bond. These possibilities are currently being investigated

Acknowledgment. We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work and Professor M. F. Nicol for the loan of some of the instruments.

(10) Contribution No. 3217.

Jeffrey I. Zink*
Department of Chemistry,[10] *University of California*
Los Angeles, California 90024

William C. Kaska
Department of Chemistry, University of California
Santa Barbara, California 93106

Received June 21, 1973

Preferred Direction of Proton Transfer between $C_2H_7^+$ and CO, CH_4, N_2O, and C_2H_4 at 300°K[1]

Sir:

In a recent publication,[2] Chong and Franklin purport to have observed thermodynamic equilibrium at 340°K for the proton transfer reaction

$$CH_5^+ + C_2H_6 \rightleftharpoons C_2H_7^+ + CH_4 \qquad (1)$$

The reaction was studied in a single ion source with p_{CH_4} maintained at 384 μ and $p_{C_2H_6}$ varied from 101 to 291 μ. The product to reactant ion ratios yielded an average value for the equilibrium constant of 4.94 ± 0.33 and a difference in proton affinities, $PA(C_2H_6) - PA(CH_4)$ of about 1 kcal mol^{-1}. From well-established values for the heats of formation of the other species involved in reaction 1, they calculate $PA(C_2H_6) = 127.0 \pm 1.05$ kcal mol^{-1}. This result does not agree with recent observations in our laboratory using the flowing afterglow technique.[3]

We have been employing this technique to study proton transfer reactions of the type

$$XH^+ + Y \rightleftharpoons YH^+ + X$$

starting in each direction. Thermalization of the protonated reactant is ensured by allowing it to undergo thousands of collisions prior to entry into the reaction region. Determination of the preferred direction of the reaction under these conditions establishes the relative proton affinity of X and Y.

Such studies, both in the forward and reverse directions, of the following reactions showed that proton transfer at 300°K occurs preferentially in the direction in which the reactions are written

$$N_2OH^+ + C_2H_6 \rightleftharpoons C_2H_7^+ + N_2O \qquad (2)$$

$$COH^+ + C_2H_6 \rightleftharpoons C_2H_7^+ + CO \qquad (3)$$

$$C_2H_7^+ + C_2H_4 \rightleftharpoons C_2H_5^+ + C_2H_6 \qquad (4)$$

Experimental details will be reported elsewhere.[4] For each of the reactions (2–4) it was observed that $k_f/k_r \gg 1$. The identity of the product ion ($m/e = 31$) in reactions 2 and 3 was established as $C_2H_7^+$ by isotope analysis. Values of $PA(N_2O) = 134^{+5}_{-2}$ kcal mol^{-1} and $PA(CO) = 138^{+5}_{-2}$ have both been determined in our laboratory,[5a] from equilibrium studies of proton transfer involving CH_4, N_2O, and CO and the value of $PA(CH_4) = 126^{+5}_{-1}$ of Chupka and Berkowitz.[5b] Our value for PA(CO) is in good agreement with Harrison's value[6] of 137^{+12}_{-3}. $PA(C_2H_4)$ has been calculated to be 159 kcal mol^{-1} from the known heats of formation[7] of $C_2H_5^+$, H^+, and C_2H_4. Our observations of reactions 2–4 therefore imply $136 < PA(C_2H_6) < 159$ kcal mol^{-1}. The lower limit is 9 kcal mol^{-1} higher than the value reported by Chong and Franklin,[2] which implies a value for the equilibrium constant of reaction 1 of at least 8×10^5 compared with their observation of 4.9.

One theoretical value is available for comparison. Lathan, Hehre, and Pople[8] have made *ab initio* molecular orbital calculations of the geometry and energy of $C_2H_7^+$. Their theoretical value of $PA(C_2H_6) = 140.1$ kcal mol^{-1} at 0°K (not corrected for zero point vibrations) lies within our limits. Thus it appears that, although the high-pressure, ion source technique has correctly assigned the order of the proton affinities, *viz.* $PA(C_2H_6) > PA(CH_4)$, it has not provided the correct value for the proton affinity difference. There are several possible reasons for this. (1) Mass discrimination in the ion detection system. Chong and Franklin do not comment on this possible source of error. (2) Thermodynamic equilibrium may not have been established. The range in $p_{C_2H_6}$ of less than a factor of 3 may have been insufficient to test this. (3) Probably the most important possibility is the failure to achieve thermalization of the protonated species prior to reaction in either direction. This can lead to steady-state conditions which do not reflect true thermodynamic equilibrium. Since the rate in the forward direction is close to the collision rate, while the rate in the reverse direction is much ($\sim 10^6$) slower, the latter is likely to be affected by ion excitation to a greater extent than will the forward rate. This will result in a measured equilibrium constant lower than the true value. Such effects may also have led to a low value for the equilibrium constant reported by Kasper and Franklin[9] for the reaction

$$CO_2H^+ + CH_4 \rightleftharpoons CH_5^+ + CO_2 \qquad (5)$$

although the disagreement with our flowing afterglow studies[10] in this case was less severe, perhaps because the rate constants of the forward and reverse reactions do not differ to so large an extent.

---

(1) This work was supported in part by the National Research Council of Canada.

(2) S. L. Chong and J. L. Franklin, *J. Amer. Chem. Soc.*, **94**, 6347 (1972).

(3) D. K. Bohme, R. S. Hemsworth, H. W. Rundle, and H. I. Schiff, *J. Chem. Phys.*, **58**, 3504 (1973).

(4) R. S. Hemsworth, J. D. Payzant, H. I. Schiff, and D. K. Bohme, *J. Amer. Chem. Soc.*, to be submitted for publication.

(5) (a) D. K. Bohme, R. S. Hemsworth, H. W. Rundle, P. F. Fennelly, A. E. Roche, and H. I. Schiff, *J. Chem. Phys.*, to be submitted for publication; (b) W. A. Chupka and J. Berkowitz, *ibid.*, **54**, 4256 (1971).

(6) A. G. Harrison, *J. Chem. Phys.*, **50**, 1043 (1969).

(7) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, 26 (1969).

(8) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971).

(9) S. F. Kasper and J. L. Franklin, *J. Chem. Phys.*, **56**, 1156 (1972).

(10) R. S. Hemsworth, H. W. Rundle, D. K. Bohme, H. I. Schiff, D. B. Dunkin, and F. C. Fehsenfeld, *J. Chem. Phys.*, **59**, 61 (1973).