

method of Somogyi⁹; the nature of this product is under investigation and will be the subject of a future communication.

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(9) M. Somogyi, *J. Biol. Chem.*, **160**, 69 (1945).

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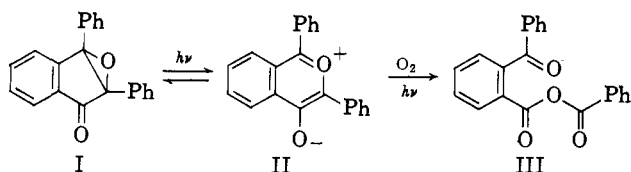
RECEIVED SEPTEMBER 23, 1964

The Use of 2,3-Diphenylindenone Oxide as a Triplet-State Indicator

Sir:

Triplet excited states of many substances have been studied by phosphorescence,^{1a,b} triplet-triplet absorption,^{1c,d} and singlet-triplet absorption induced by oxygen or heavy atoms.^{1e,f} However, some compounds do not lend themselves to these measurements, presumably because of rapid rearrangement or inter-system crossing of the initially formed "spectroscopic" triplet. In our studies of the photochemistry of 2,3-diphenylindenone oxide² (I) we have found that this compound can serve as an indicator for certain short-lived triplets when employed in simple color tests performed without the exclusion of oxygen. A description of the method as applied to a study of *trans*-stilbene follows.

Benzene solutions of colorless I undergo reversible photochemical rearrangement to the red pyrylium oxide II. The forward reaction (I → II) is photosensitized by sensitizers of triplet energy $E_T > 68$ kcal.² In the presence of oxygen using acetophenone ($E_T = 73.9$ kcal.)³ or benzophenone ($E_T = 68.7$ kcal.)³ as sensitizers, irradiation (365 mμ) produces a steady-state concentration of II controlled by photosensitized interconversion of II and I and simultaneous thermal and



photosensitized oxidation of II to give the anhydride III.⁴ The use of sensitizers of $E_T < 68$ kcal. in sufficient quantity to absorb nearly all of the light produces complete bleaching since reaction I → II is no longer sensitized. Lesser amounts of sensitizer produce low (weakly colored) steady-state concentrations of II by competing direct photochemical conversion of I to II. Under these latter conditions addition of *trans*-stilbene (10^{-3} to 10^{-1} M) to the solution produced, with some sensitizers, an increase in color on irradiation

(1) (a) A. Jablonski, *Z. Physik*, **94**, 38 (1935); (b) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944); (c) G. N. Lewis, D. Lipkin, and T. T. Magel, *ibid.*, **63**, 3005 (1941); (d) G. Porter and M. W. Windsor, *J. Chem. Phys.*, **21**, 2088 (1953); (e) M. Kasha, *ibid.*, **20**, 71 (1952); (f) D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

(2) E. F. Ullman and Wm. A. Henderson, Jr., *J. Am. Chem. Soc.*, **86**, 5050 (1964).

(3) G. S. Hammond and J. Saltiel, *ibid.*, **84**, 4983 (1962).

(4) Wm. A. Henderson, Jr., and E. F. Ullman, unpublished observation.

relative to a simultaneously irradiated portion of the solution with no *trans*-stilbene added. The effect was found to be directly related to the triplet energy of the sensitizer used. Thus stilbene produced shifts in the photostationary state only when using sensitizers with $E_T > 44$ kcal. (Table I).

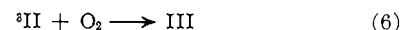
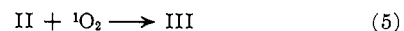
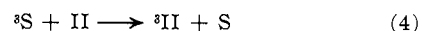
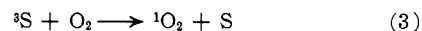
TABLE I
QUENCHING BY *trans*-STILBENE^a

Sensitizer	E_T , kcal.	Increase in concn. of II
1,2,3,4-Dibenzanthracene	51 ^{1f}	+
Pyrene	48 ^{1f}	+
1,2-Benzanthracene	47 ^b	+
Acridine	45 ^{1f}	+
Phenazine	44 ^{1b}	+
Anthracene	42 ^{1d}	—
9,10-Dichloroanthracene	40 ^c	—
Perylene	36(?) ^d	—
Naphthacene	29 ^c	—

^a Experiments carried out using sufficient sensitizer in benzene solutions of I to produce only weak color (absorptivity at λ_{max} 544 mμ of ~0.05) with 365 mμ light. Several stilbene concentrations (up to $\sim 10^{-1}$ M) were used with each sensitizer to detect difficultly observable color changes with low energy sensitizers. ^b D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949). ^c S. P. McGlynn, T. Azumi, and M. Kasha, *ibid.*, **40**, 507 (1964). ^d G. G. Hall, *Proc. Roy. Soc. (London)*, **A213**, 113 (1952).

The increase in the steady-state concentration of II on addition of *trans*-stilbene must arise by inhibition of a bleaching process. As *trans*-stilbene had little effect on unsensitized photochemical bleaching of II and produced no increase in the stability of II in the dark, it must be acting as an inhibitor of photosensitized oxidation of II and/or photosensitized isomerization of II to I. Since photosensitized bleaching of II was 10–100 times more efficient with oxygen present than in degassed solution, the observed shifts in the steady-state concentrations are due to inhibition of the oxidation process.

The following reactions may be involved in photosensitized oxidation of II.



Inhibition of photosensitized oxidation by *trans*-stilbene might occur either by trapping of singlet oxygen (1O_2)⁵ with *trans*-stilbene or by quenching of sensitizer triplet (3S), of triplet II (3II), or of 1O_2 . However, of these possibilities only quenching of 3S can explain the variation in inhibition of reaction II → III with sensitizer energy.⁶

The formation of *trans*-stilbene triplets by energy transfer from sensitizer triplets was demonstrated by the weak bleaching effect of *trans*-stilbene on solutions containing sufficient benzophenone to absorb most of the light. Since benzophenone sensitizes both reactions I → II and II → III, quenching of sensitizer

(5) We need not differentiate here between 1O_2 and a possible oxygen-sensitizer complex; cf. C. S. Foote and S. Wexler, *J. Am. Chem. Soc.*, **86**, 3879, 3880 (1964).

(6) The significance of the observed fall-off in quenching efficiency at 44 kcal. (Table I) will be discussed in the full paper.

triplets by some process that did not produce *trans*-stilbene triplets would proportionally inhibit both reactions causing no net color change under these conditions. The observed bleaching must therefore be due to selective sensitization of reaction II \rightarrow III by *trans*-stilbene triplets. However, *trans*-stilbene triplets must be much less efficient in sensitizing this bleaching process than sensitizer triplets, for otherwise *trans*-stilbene inhibition of sensitized bleaching would not occur with the lower energy sensitizers. This low sensitization efficiency strongly suggests that *trans*-stilbene triplets have a substantially shorter lifetime than sensitizer triplets. Since quenching of sensitizer triplets by dissolved atmospheric oxygen ($[O_2] = 4 \times 10^{-4} M$) is close to diffusionally controlled ($k \sim 3 \times 10^9 l. \text{ mole}^{-1} \text{ sec.}^{-1}$),⁷ the sensitizer triplet lifetimes must be about $8 \times 10^{-7} \text{ sec.}$ ($1/k[O_2]$) and the *trans*-stilbene triplet lifetime must be even shorter.⁸

The method thus appears to be a simple sensitive test for compounds having exceptionally short-lived triplet states. Its use in the demonstration of exceptionally short lifetimes for, *inter alia*, the tetraphenylallene, diphenylacetylene, stilbene, and tetraphenylethylene triplets will be discussed in a future publication.

(7) (a) R. Livingston and D. W. Tanner, *Trans. Faraday Soc.*, **54**, 765 (1958); (b) G. Porter and M. W. Windsor, *Proc. Roy. Soc. (London)*, **A245**, 238 (1958).

(8) This is in accord with the maximum *trans*-stilbene triplet lifetime of $7.7 \times 10^{-1} \text{ sec.}$ estimated by G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

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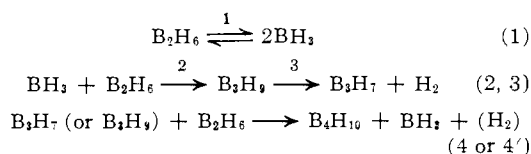
EDWIN F. ULLMAN

RECEIVED AUGUST 24, 1964

Mass Spectrometric Investigation of the Pyrolysis of Diborane. Triborane and Tetraborane Intermediates¹

Sir:

The results of many investigations on the pyrolysis mechanism of diborane have been published since the pioneering work of Stock.^{2a} The present state of affairs has been adequately summarized by Lipscomb.^{2b} The initial stages of the polymerization are believed to proceed by the following mechanism.



The postulation of reactions 1 and 2 as the most probable initial steps is based on kinetic evidence. Thus, the initial stages of the B_2H_6 pyrolysis reaction³⁻⁵ and the B_2H_6 - B_2D_6 ⁶ and B_2H_6 - $^{10}B_2H_6$ ⁷ exchange reactions

(1) Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1, 1964.

(2) (a) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933; (b) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

(3) J. K. Bragg, L. V. McCarty, and F. J. Norton, *J. Am. Chem. Soc.*, **73**, 2134 (1951).

(4) R. P. Clarke and R. N. Pease, *ibid.*, **73**, 2132 (1951).

(5) S. H. Bauer, *ibid.*, **78**, 5775 (1956).

(6) P. C. Maybury and W. S. Koski, *J. Chem. Phys.*, **21**, 742 (1953).

(7) I. Shapiro and B. Keilin, *J. Am. Chem. Soc.*, **77**, 2663 (1955).

are all observed to be kinetically of three-halves order with respect to the diborane concentration. This agrees with eq. 1 and 2 if one assumes that a steady-state concentration of BH_3 is obtained. The recently reported detection of both BH_3 and BH_2^8 is not necessarily in contradiction to this mechanism. This aspect, however, has to be discussed further elsewhere.

Although a triborane species, B_3H_9 or B_3H_7 , is the most readily imagined product formed in the propagation step, direct observation of either has so far not been accomplished.

Another important question in the B_2H_6 pyrolysis reaction is the "first stable intermediate" problem discussed by Schaeffer⁹ and by Enrione and Schaeffer.¹⁰ These authors conclude that reaction 3 is rate determining and that the very reactive triborane-7 reacts with B_2H_6 to give the "first stable intermediate," B_4H_{10} , plus BH_3 . Under conventional experimental conditions, this B_4H_{10} is too reactive to be isolated prior to decomposition to a postulated B_4H_8 , which in turn reacts with B_2H_6 to produce the observed³ B_5H_{11} .

Using a mass spectrometric technique, we have investigated the B_2H_6 pyrolysis reaction in an endeavor to observe directly any mono-, tri-, or tetraborane species.

An Inghram-type mass spectrometer¹¹⁻¹³ was used. Diborane was introduced into a baffled¹⁴ $3/4$ in. i.d. stainless steel crucible. Contact time for diborane was 0.04 sec. and did not necessarily correspond to attainment of equilibrium at the higher pressures. A movable beam defining slit ("shutter")¹¹ provided unambiguous identification of species emerging directly from the crucible orifice. This arrangement is a general method for investigation of gas-phase reaction intermediates over wide temperature and pressure ranges. The mass analyzer could detect 10^{-9} atm. of diborane in the crucible. Furthermore, it could resolve boranes from background; *e.g.*, the triplet at mass peak 36 ($H^{35}Cl$, $^{12}C_3$, and $^{10}B_3H_6$) was resolved to the base line. This is most important, since, even with a base pressure of 3×10^{-8} torr, large "background" peaks, not readily eliminated by reducing the ionizing electron voltage, are always present between mass peaks 28 and 45.

Differential pumping was provided between the furnace (500 l./sec in the compartment), ion-source (20 l./sec), and analyzer (20 l./sec) chambers. Pressure drops of 5000:1:^{1/20} were maintained between the furnace, furnace chamber, and ion source. Temperature was measured with three thermocouples spotwelded to the furnace.

Only species whose ions and neutral progenitors were identified by mass spectrum, mass defect, dependence on inlet valve setting, temperature dependence, and "shutter" profile¹¹ are considered. In all experiments, all peaks up to at least mass 130 were scrutinized.

(8) (a) T. P. Fehlner and W. S. Koski, *ibid.*, **86**, 2733 (1964); (b) G. Herzberg and J. W. C. Johns (National Research Council, Ottawa, private communication) report a rotational analysis of the BH_2 spectrum; (c) R. W. Diesen (private communication) reports a mass spectrometric identification of BH_2 in a shocktube (*cf.* R. W. Diesen, *J. Chem. Phys.*, **39**, 2115, 2121 (1964)).

(9) R. Schaeffer, *J. Inorg. Nucl. Chem.*, **15**, 190 (1960).

(10) R. E. Enrione and R. Schaeffer, *ibid.*, **18**, 10377 (1961).

(11) M. G. Inghram and J. Drowart, in "High Temperature Technology," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

(12) W. A. Chupka and M. G. Inghram, *J. Phys. Chem.*, **59**, 100 (1955).

(13) Nuclide Analysis Associates, State College, Pa., Model-12-60 H. T.

(14) J. Berkowitz, *J. Chem. Phys.*, **36**, 2533 (1962).