Phosphorescence Quenching by Triethylborane

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IN a previous paper[1] we have pointed out that it might be of interest to measure the biacetyl phosphorescence yield in the presence of triethylborane (TEB). We now can show that triethylborane is a strong quencher of biacetyl triplets.

Results were obtained with a Hilger and Watts fluorimeter. Light of 3660 or 4350 Å with a green secondary filter was employed.

The biacetyl was charged first under high vacuum conditions in a Pyrex cell coupled to a greaseless stopcock. After measurement of its phosphorescence, small amounts of triethylborane were added, the resulting phosphorescence being recorded (Figure 1; phosphorescence yield in arbitrary units). It appears that triethylborane is a strong phosphorescence quencher. The results are practically independent of the wavelength employed.

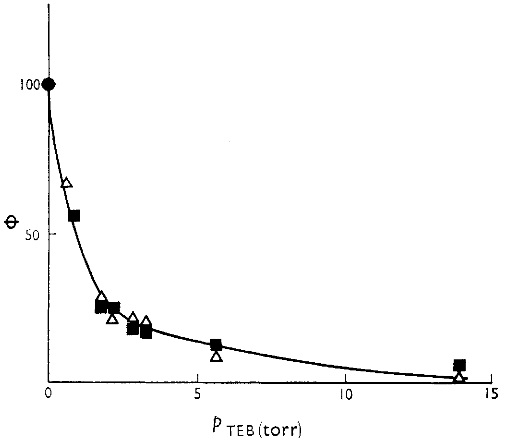

FIGURE 1. *Biacetyl phosphorescence as a function of triethylborane pressure.* ■ 3660 Å *radiation*; △ 4350 Å *radiation.*

On the assumption that at long wavelengths the triplet imput is proportional to the absorbed intensity (for a given initial biacetyl pressure and with a small amount of added gas), the following reactions account for the main features of the photolysis of biacetyl (B) in the presence of strong triplet quenchers[2]

$$\mathrm{B} + h\nu \rightarrow {}^3\mathrm{B} \qquad (1)$$

$$^3\mathrm{B} \rightarrow \mathrm{B} + h\nu' \qquad (2)$$

$$^3\mathrm{B} \rightarrow \mathrm{B} \qquad (3)$$

$$^3\mathrm{B} + \mathrm{B} \rightarrow \mathrm{B} + \mathrm{B} \qquad (4)$$

$$^3\mathrm{B} + \mathrm{M} \rightarrow \text{non-radiative products} \qquad (5)$$

This set of equations leads to equation (6)

$$\frac{\Phi_0}{\Phi_p} = 1 + \frac{k_5}{k_2 + k_3 + k_4 p_\mathrm{B}}\, p_\mathrm{M} \qquad (6)$$

where Φ_0 is the phosphorescence yield of pure biacetyl at a pressure p_B and Φ_p is the phosphorescence yield with a pressure p_M of quencher.

In Figure 2 the data are presented as Φ_0/Φ_p against p_TEB. It can be seen from this Figure that equations (1) to (5) account for the main features of the experimental results, and that reaction (4) is playing a less important role, as can be concluded

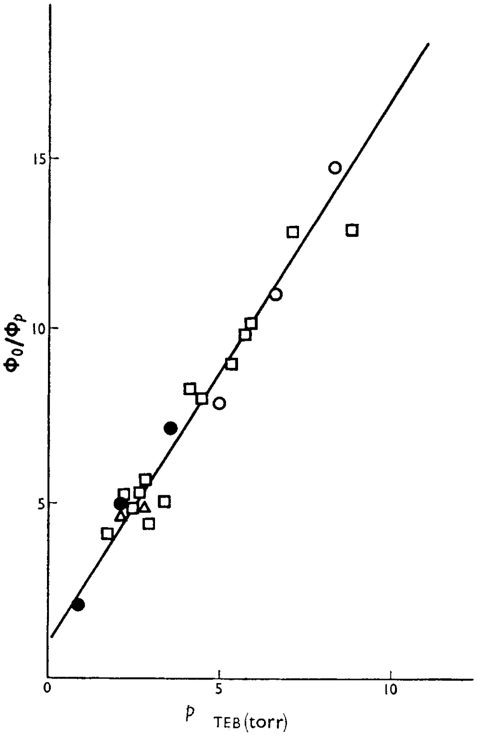

FIGURE 2. $(\Phi)_0/(\Phi)_\mathrm{TEB}$ *as a function of triethylborane pressure. Biacetyl pressure* 17 *torr*: □ *"Bulk"*; ● *"Purified"*; ▲ *"Head"*; △ *"Tail"*; ○ *"Pretreated" biacetyl; biacetyl pressure* 31 *torr*: ■ *"Bulk"*.

from the independence of the data from the biacetyl pressure.

From the slope of Figure (2) it can be concluded that, with triethylborane as quencher,

$$\frac{k_5}{k_2 + k_3 + k_4 p_B} = 1{\cdot}55\ \text{torr}^{-1}\ (20°,\ p_B\ ca.\ 20\ \text{torr})$$

For the sake of comparison, data were obtained for oxygen and acetylene. With oxygen, the results resembled those obtained with triethylborane, with $(k_5)_{O_2}/(k_5)_{TEB} = 40$, but with acetylene, the results were sensitive to the primary filter employed. With the shorter wavelength, an enhancement of the phosphorescence was observed. This can be due to the fact that with the 3660 Å radiation, reaction (7) is competing with reaction (8)

$$^1B^* + M = {}^1B + M \qquad (7)$$

$$^1B^* = \text{products} \qquad (8)$$

where $^1B^*$ is a molecule in the excited singlet state with excess of vibrational energy.[3] This effect is not noted either with triethylborane or with oxygen owing to the low pressures required to quench the phosphorescence.

From the slope of Φ_0/Φ_p obtained with the 4350 Å radiation, a value of

$$\frac{(k_5)_{C_2H_2}}{k_2 + k_3 + k_4 p_B} = 3{\cdot}10^{-3}\ \text{torr}^{-1}$$

could be obtained. This value is quite similar to those obtained by Garabedian and Dows[2] for several quenchers.

The high quenching efficiency of the triethylborane might arise from impurities in the triethylborane or in the biacetyl that may be able to react with triethylborane giving compounds with high quenching efficiencies.

The first possibility was checked in the following way: in Figure 2 results are presented for "bulk" triethylborane, "purified" by trap–to–trap fractioning and degassing from a bath at −90°, and "head" or "tail" fractions. It was expected that, if an impurity was present, one of these fractions would be enriched or depleted in it. However, the results of Figure 2 show that all the fractions have practically indistinguishable efficiencies.

To test the second possibility, biacetyl was mixed with an excess of triethylborane and the fraction condensable at −40° was retained. This fraction, "pretreated" biacetyl, displayed normal phosphorescence and normal behaviour when mixed with fresh triethylborane (Figure 2).

We conclude that reaction (9)

$$^3B + \text{TEB} \rightarrow \text{non-radiative products} \qquad (9)$$

represents the quenching process. Triethylborane has no low electronic levels that could be excited by the amount of energy involved in the biacetyl excitation. In this sense, triethylborane is a quencher of the same kind as acetylene and those discussed by Garabedian and Dows,[2] but is more than 200 times more efficient as a quencher than any of these. Hence reaction (9) must involve a particularly efficient triplet–singlet crossing or, more probably, a reactive quenching.

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