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ABSTRACT

The photosensitized phosphorescence lifetime of biacetyl in the vapour phase has been determined using ortho, meta, and paraxylene, (Ist and 2nd singlet population) as donors of triplet energy, over several exciting wavelengths and various pressures of donor and acceptor. In each case, the sensitized lifetimes were found to be equal, within experimental error, to the lifetime of biacetyl phosphorescence for direct irradiation of biacetyl at 435.8 nm. Attempts to detect the triplet of biacetyl by its absorption spectrum were unsucsesful, due primarily, it is believed, to the low extinction coefficient of the triplet.

INTRODUCTION

The vapour sensitization of biacetyl phosphorescence by several aromatic donors has been investigated in detail, in an attempt to validate the "biacetyl method" of triplet yield determinations used extensively by many authors since the initial publication by Ishikawa and Noyes[1,2]. A brief description of the biacetyl methods is as follows.

An aromatic donor (e.g.: benzene) will be raised to its first excited singlet state by absorption of ultra violet radiation. Among other processes which will subsequently occur, the triplet state will be populated. If a suitable acceptor molecule (e.g.: biacetyl) is present, the electronic energy of the donor can be transferred to the biacetyl, producing a biacetyl molecule in its triplet state. Triplet biacetyl molecules so produced will phosphoresce and this behaviour is labelled "Sensitized phosphorescence", since emission occurs without the emitting molecule initially absor-

bing light. Comparing the quantum yield of the sensitized phosphorescence with that produced in a separate experiment where biacetyl itself is excited affords a determination of the triplet yield of the aromatic donor. The triplet yield is, in essence a measure of the number of singlet donor molecules which eventually cross over into the triplet manifold. The following reaction mechanism is typical.

Scheme 1

$D + h\upsilon \rightarrow {}^1D$	(I_1)
${}^1D \rightarrow D + h\upsilon_f$	(k_1)
${}^1D \rightarrow D$	(k_2)
${}^1D \rightarrow {}^3D$	(k_3)
${}^3D \rightarrow D$	(k_4)
${}^3D + BiA \rightarrow D + {}^3BiA$	(k_5)
${}^3BiA \rightarrow BiA + h\upsilon_p$	(k_6)
${}^3BiA \rightarrow BiA$	(k_7)

Here, D represents the donor and BiA represents biacetyl. The superscripts[1] and [3]denote multiplicities, being singlet and triplet respectively.

One of the basic assumptions in the method centres around reaction (5). The assumption is that process (k_5) subsequently behaves in an identical fashion to ${}^3BiA$ produced by the direct absorption of light by biacetyl e.g.:

Scheme 2

$BiA + h\upsilon \rightarrow {}^1BiA$	(I_2)
${}^1BiA \rightarrow {}^3BiA$	(k'_5)
${}^3BiA \rightarrow BiA + h\upsilon_p$	(k'_6)
${}^3BiA \rightarrow BiA$	(k'_7)

However, if for example, the sensitization process produces not ${}^3BiA$ but an exciplex (excited state complex between triplet donor and ground state biacetyl) then phosphorescence quantum yields and lifetimes will almost certainly be quite different.

Also, in the sensitized process, considerable excess vibrational energy will also be imported to the biacetyl, for in general triplet aromatic states lie at higher energies than ^{3}BiA. It is possible that ^{3}BiA could decompose under these conditions and thus change the phosphorescence quantum yield markedly from that obtained in the direct process. Any of the above complications would completely vitiate the biacetyl method for the determination of triplet yields.

EXPERIMENTAL

For the first series of experiments, a mercury-free vacuum line for handling and storing the various compounds is used, and modified a conventional microsecond flash apparatus for photographically detecting transient species.

The argon flashlamps had pulse widths of typically 20μ sec. The photolysis flash had an energy of 1800 Joules, and after suitable filtering to provide excitation at 435.8nm. (the maximum absorption wavelength for biacetyl), approximately 400 Joules were available.

The spectrographic flash could be delayed from 10μsec. to several seconds after the photolysis flash.

Although any transient absorption was carefully looked for on the photographic plates, none was ever found. The usual problems concerning scattered flash light, temperature effects caused by the photolysis flash etc. had all been eliminated.

Similar results had also been found earlier by Birks (3), who concluded that since plenty of triplets had been produced, the inability to detect the triplet by its absorption spectrum must be due to a very low extinction coefficient. A detected transient in the flash photolysis of biacetyl has been found by Bayrakçeken (4), but it is unlikely that this is the absorption spectrum of the triplet. The concentration of biacetyl triplet has dropped from $2\text{x}10^{-5}$M to $2\text{x}10^{-7}$M. Unfortunately, the extinction coefficient of the lowest triplet absorption is unknown, so it cannot be sta-

ted with certainly if this concentration is too low for a triplet absorption to be photographically recorded. However, the extinction coefficient for the first singlet absorption of biacetyl is 16 liter mole^{-1} cm^{-1}, and it is likely that the triplet extinction coefficient is similarly of a low value.

Normally, molecules with extinction coefficients of the order of 10.000 liter mole^{-1} cm^{-1} can be photographed at a concentration of 10^{-6} to 10^{-7}M.

The excitation light (provided by a spectroscopic flash lamp, 12 Joules output, 25 μ sec. duration) was passed through a monochromator and thence through a 1 cm. quartz cell containing the gaseous sample. Emission was detected at right angles via a photomultiplier and recorded photographically on a storage oscilloscope. Initially, excitation was at 435.9 nm. and the phosphorescence decay of pure biacetyl was recorded. Emission detected immediately on the tail of the flash lamp profile was markedly nonexponential, due possibly to triplet-triplet annhiliation caused by the initially high concentration of triplets produced. However, over 90 % of the decay profile was perfectly exponential from which the decay lifetime was obtained.

Experiments were then done on detecting the sensitized phosphorescence of biacetyl using a variety of aromatic donors. Here, excitation wavelengths were from 240 nm. to 320 nm. where absorption by biacetyl is either zero or less than 5 %. However, the slight absorption by biacetyl at these wavelengths if of no consequence since biacetyl under these conditions is excited to its second excited state from which there is no detectable emission. Pressures of donor ranged from 0.1 to 5 torr. Each mixture was flashed in the appropriate wavelength range for the donor at 10 nm. intervals, and the resulting sensitized phosphorescence decay recorded.

Figures 1, 2 and 3 show the sensitized phosphorescence of biacetyl and figure 4 shows direct phosphorescence of biacetyl. Results (5) are given in Table I.

TABLE I.

Substance	λ, nm	τ, sec
o-xylene+Biacetyl	243	1.360×10^{-3}
o-xylene+Biacetyl	247	1.255×10^{-3}
m-xylene+Biacetyl	252	1.357×10^{-3}
m-xylene+Biacetyl	264	1.437×10^{-3}
p-xylene+Biacetyl	244	1.372×10^{-3}
p-xylene+Biacetyl	256	1.367×10^{-3}
Biacetyl Direct Phosphorescence	435.8	1.259×10^{-3}

DISCUSSION

From the simple kinetic scheme proposed earlier (Scheme 2), we have:

$$\tau_p = \frac{1}{k'_6 + k'_7}$$

and from scheme 1:

$$\tau_{sp} = \frac{1}{k_6 + k_7}$$

Where τ_p and τ_{sp} are the phosphorescence and sensitized phosphorescence lifetimes respectively. For all the donors considered, the sensitized lifetimes are, within experimental error, independent of exciting wavelength and are equal to the lifetime of the phosphorescence produced by direct absorption of biacetyl.

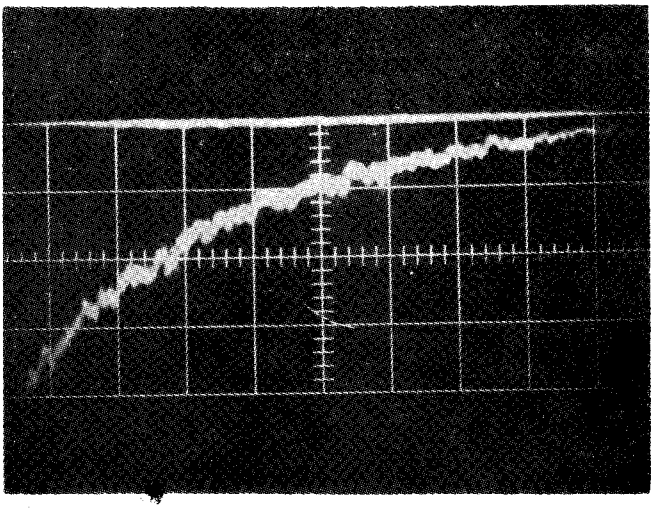
$$\text{Thus: } \tau_{sp} = \tau_p \tag{1}$$

From an analysis of the kinetic schemes presented, we get the following:

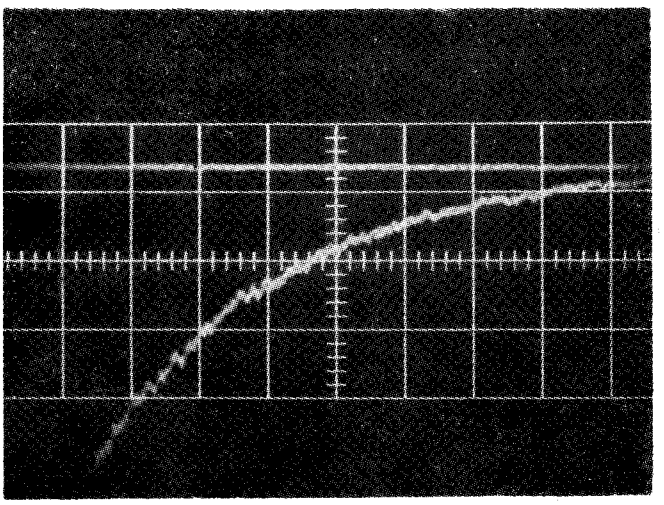
$$\varnothing_p = \varnothing_t^{BiA} \cdot \tau_p / \tau_o \tag{2}$$

$$\varnothing_{sp} = \varnothing_t^{D} \cdot \tau_{sp} / \tau_{oa} \tag{3}$$

Where $\varnothing_p$ and $\varnothing_{sp}$ are the quantum yields of direct and sensitized phosphorescence respectively, $\varnothing_t^{BiA}$ and $\varnothing_t^{D}$ are the triplet yields of biacetyl (1) and of donor respectively.

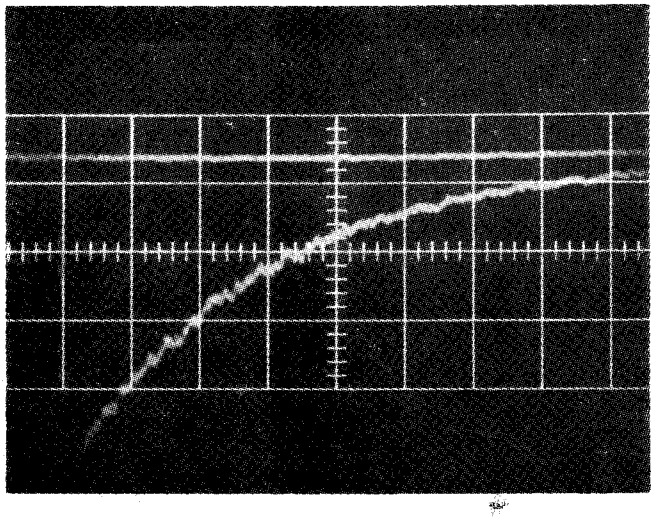


o-xylene (2.6 mm)	+	Biacetyl (0.8 mm)
Vertical voltage		0.01 volt/cm
Horizontal sweep		0.5 msec/cm
λexcitation		243 nm

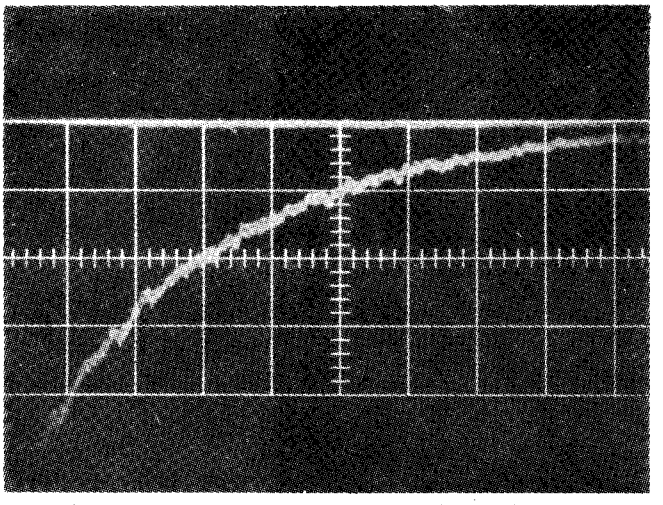


o-xylene (2.6 mm)	+	Biacetyl (0.8 mm)
Vertical voltage		0.02 volt/cm
Horizontal sweep		0.5 msec/cm
λexcitation		247 nm

Figure 1. Decay Curves Showing the Sensitized Phosphorescence of Biacetyl

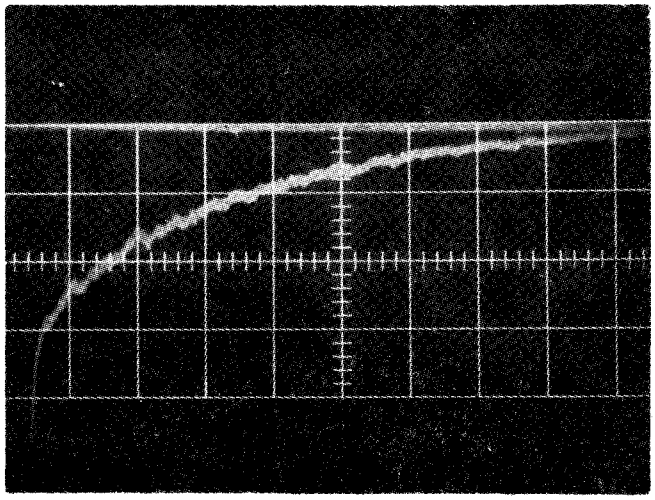


m-xylene (3.3 mm)	+	Biacetyl (0.8 mm)
Vertical voltage		0.05 volt/cm
Horizontal sweep		0.5 msec/cm
λexcitation		252 nm

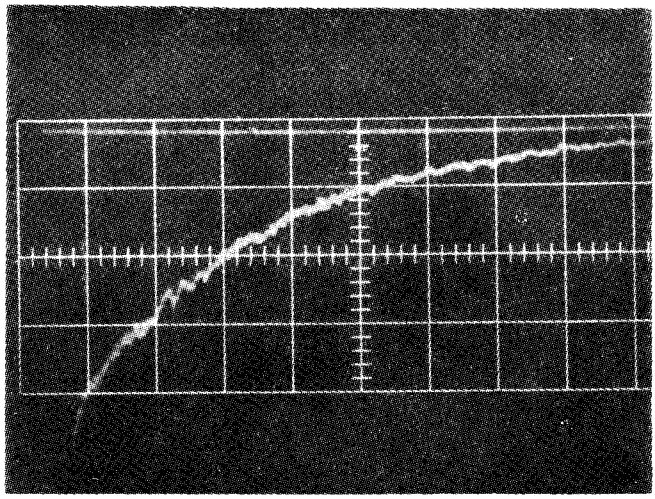


m-xylene (3.3 mm)	+	Biacetyl (0.8 mm)
Vertical voltage		0.1 volt/cm
Horizontal sweep		0.5 msec/cm
λexcitation		264 nm

Figure 2. Decay Curves Showing the Sensitized Phosphorescence of Biacetyl

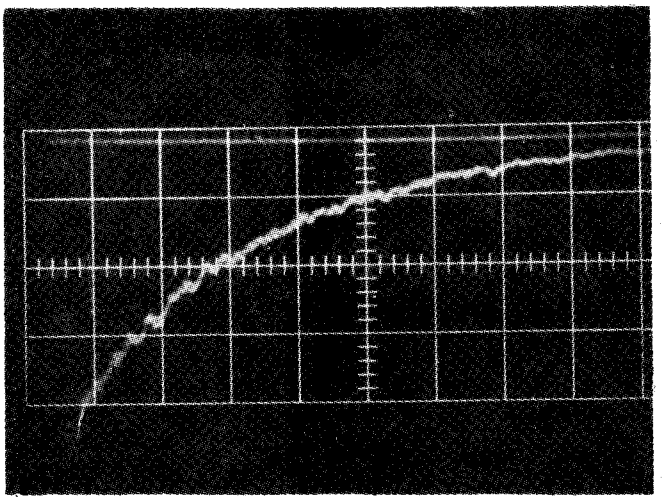


p-xylene (3.8 mm)	+	Biacetyl (1.1 mm)
Vertical voltage		0.02 volt/cm
Horizontal sweep		0.5 msec/cm
λexcitation		244 nm



p-xylene (3.8 mm)	+	Biacetyl (1.1 mm)
Vertical voltage		0.1 volt/cm
Horizontal sweep		0.5 msec/cm
λexcitation		256 nm

Figure 3. Decay Curves Showing the Sensitized Phosphorescence of Biacetyl



Biacetyl (20 mm)	Direct Phosphorescence
Vertical voltage	0.1 volt/cm
Horizontal sweep	0.5 msec/cm
λexcitation	435.8 nm

Figure 4. Decay Curve Showing the Phosphorescence of Biacetyl

$$\text{Thus if } \tau_p/\tau_o = \tau_{sp}/\tau_{oa} \tag{4}$$

$$\text{we have } \varnothing_t^D = \varnothing_{sp}/\varnothing_p \tag{5}$$

and equation 5 is the general result which is used in determining triplet yields by the biacetyl method.

Thus, from 4 if $\tau_o = \tau_{oa}$, (if the radiative lifetimes in the direct and sensitized processes are equal) then from these results equation 5 is validated at least for the sensitizers considered in this research.

APPENDIX (Computer Outputs)

SENSITIZED PHOSPHORESCENCE
ORTHO-XYLENE + BIACETYL
WAVELENGTH 2430A
I INFINITY (10) 26.40D 00

TIME (SEC)	I
5.00D–04	18.40D–00
1.00D–03	12.00D–00
1.50D–03	85.00D–01
2.00D–03	61.00D–01
2.50D–03	42.00D–01
3.00D–03	30.00D–01

B 7.34902D–02 1/SEC
LIFE TIME ..... 1.36073D–03 SEC
HALF-LIFE ..... 9.43183D–04 SEC
SENSITIZED PHOSPHORESCENCE
ORTHO–XYLENE + BIACETYL
WAVELENGTH 2470A
I INFINITY (10) 74.00D 00

TIME (SEC)	I
5.00D–04	47.00D–00
1.00D–03	31.60D–00
1.50D–03	21.00D–00
2.00D–03	14.00D–00
2.50D–03	10.00D–00
3.00D–03	76.00D–01

B 7.96864D–02 1/SEC
LIFE TIME ..... 1.25492D–03 SEC
HALF-LIFE ..... 8.69844D–04 SEC
SENSITIZED PHOSPHORESCENCE
META–XYLENE + BIACETYL
WAVELENGTH 2520A
I INFINITY (10) 14.00D 01

TIME (SEC)	I
5.00D–04	98.00D–00
1.00D–03	67.50D–00
1.50D–03	45.00D–00
2.00D–03	35.00D–00
2.50D–03	23.50D–00
3.00D–03	15.00D–00
3.50D–03	10.00D–00

B 7.36628D–02 1/SEC
LIFE TIME ..... 1.35754D–03 SEC
HALF-LIFE ..... 9.40973D–04 SEC
SENSITIZED PHOSPHORESCENCE
META-XYLENE + BIACETYL
WAVELENGTH 2640A
I INFINITY (10) 41.00D 01

TIME (SEC)	I
5.00D–04	28.80D–01
1.00D–03	20.00D–01
1.50D–03	14.00D–01
2.00D–03	10.00D–01
2.50D–03	71.00D–00
3.00D–03	50.00D–00
3.50D–03	38.00D–00

B 6.95694D–02 1/SEC
LIFE TIME ..... 1.43741D–03 SEC
HALF-LIFE ..... 9.96340D–04 SEC
SENSITIZED PHOSPHORESCENCE
PARA-XYLENE + BIACETYL
WAVELENGTH 2440A
I INFINITY (10) 59.00D 00

TIME (SEC)	I
5.00D–04	40.00D–00
1.00D–03	27.00D–00
1.50D–03	18.00D–00
2.00D–03	13.00D–00
2.50D–03	86.00D–01
3.00D–03	64.00D–01
3.50D–03	56.00D–01

B 7.28623D–02 1/SEC
LIFE TIME ..... 1.37245D–03 SEC
HALF-LIFE ..... 9.51311D–04 SEC
SENSITIZED PHOSPHORESCENCE
PARA-XYLENE + BIACETYL
WAVELENGTH 2560A
I INFINITY (10) 32.00D 01

TIME (SEC)	I
5.00D–04	21.50D–01
1.00D–03	15.50D–01
1.50D–03	10.20D–01
2.00D–03	75.00D–00
2.50D–03	51.00D–00
3.00D–03	36.00D–00
3.50D–03	25.00D–00

B 7.31689D–02 1/SEC
LIFE TIME ..... 1.36670D–03 SEC
HALF-LIFE ..... 9.47324D–04 SEC

ACKNOWLEDGEMENTS

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ÖZET

"Orto, Meta ve Para Xylene" molekülleri kullanılarak "biacetyl" molekülünün gaz halinde fotosensitize fosforesans emisyonunun bozunması zamanın fonksiyonu olarak osiloskopta kayıt edilmiş ve hayat süresi ölçülmüştür. Değişik basınçlar ve değişik uyarma enerjileri kullanılmış hayat süresinin değişmediği (deneysel hata sınırında kaldığı) ve "biacetyl" in 435.8 nm. irradyasyonu ile verdiği direk fosforesans spektrumu ile elde edilen hayat süresine eşit olduğu görüldü. Triplet-triplet soğurma spektrumu T_1 seviyesi için ε değerinin küçük olması nedeni ile kayıt edilemedi.

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