197. Triplet Lifetime Determination of Molecules in the Gas Phase by T-T Energy Transfer

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Summary

It has been demonstrated that the triplet lifetime of nonemitting molecules in the dilute vapor phase - even for complex triplet decays - can be accurately determined by means of time-resolved triplet-triplet (T-T) energy transfer to a strong emitter molecule. Besides the test molecules 1-butyne-3-one and benzaldehyde the lifetime of the vibrationally relaxed nonemitting $T_1(n\pi^*)$ state of cycloheptanone, $\tau = 63 \pm 5$ µs at ~0.5 Torr, together with its energy transfer rate constant to biacetyl, $k_{ET} = (1.80 \pm 0.08) \times 10^6$ s^{-1} Torr^{-1}, have been measured.

Introduction. - The lifetime of triplet molecules in the vapor phase is difficult to measure. Owing to the low phosphorescence quantum yield of most polyatomic molecules in the gas phase, emission measurements often fail and time-resolved triplet-triplet absorption is seldom sensitive or unambiguous enough [1]. Because of these experimental difficulties the indirect method of triplet-triplet (T-T) energy transfer to a strongly emitting acceptor molecule is frequently used to probe triplet molecules and to measure or estimate triplet lifetimes and intersystem crossing quantum yields [2] [3].

The aim of the present study is to evaluate the time-resolved T-T energy transfer method as a way to determine triplet lifetimes in dilute vapor phase where the triplet decay is complex. By monitoring the acceptor phosphorescence throughout its entire kinetics, *i.e.* from the grow-in to the decay, an accurate triplet lifetime determination of the donor molecules is obtained. The method has been tested for two strongly phosphorescing molecules, thus allowing a comparison between directly and indirectly measured triplet lifetimes. As an acceptor molecule, the well investigated biacetyl [4] was used. Furthermore by means of this energy transfer method, the lifetime of the nonemitting $T_1(n\pi^*)$ triplet of cycloheptanone [3] has been obtained at a pressure below 1 Torr.

Experimental Part. - *Materials.* Biacetyl (*Merck, puriss.*), benzaldehyde (*Merck,* analytic grade), butinone (1-butyne-3-one, *EGA-Chemie.*, analytic grade) and cycloheptanone (*Fluka, purum*) were purified by vacuum distillation and vapor-phase chromatography. Prior to use the samples were degassed (< 10^{-5} Torr) by several freeze-pump-thaw cycles.

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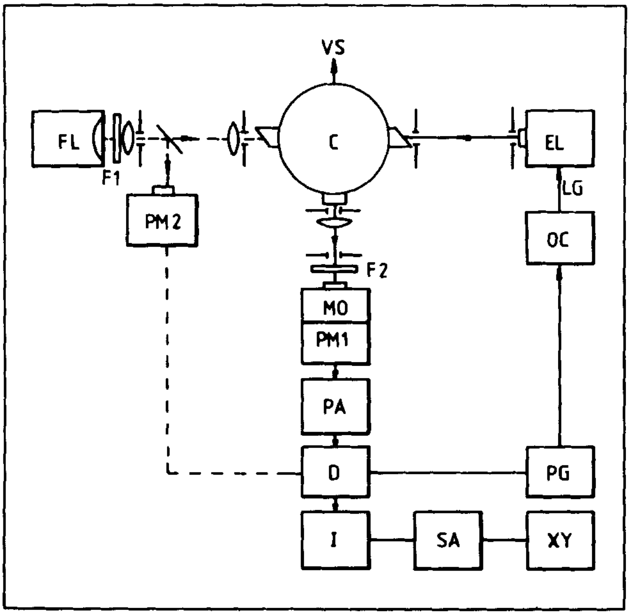

Fig. 1. *Block diagram of the experimental set-up* (The apparatus consists of vacuum system (VS), sample cell (C), multigas laser (EL), flash lamp (FL), cut-off filters (F), monochromator (MO), photomultipliers (PM), preamplifier (PA), transient digitizer (D), interface (I), signal averager (SA), plotter (XY), pulse generator (PG), opto-coupler (OC), and light guide (LG))

Apparatus. Figure 1 shows a schematic diagram of the apparatus. The samples were excited by a multigas laser (*Lumonics TE-860,* fwhm ~15 ns, pulse energy employed 10-15 mJ). The collimated and baffled laser beam (~1 cm diameter) was directed into a spherical *Pyrex* cell (~30 cm diameter) with three suprasil windows mounted on 10 cm long side arms. The cell was connected to a vacuum line equipped with three pressure meters, a *Penning* pressure gauge (*Edwards,* accuracy 10^{-4} m Torr) for the background, an absolute capacitance pressure meter (*MKS Instr.*) for the sample, and a *Bourdon* gauge (*Leybold-Heraeus*) for the mixtures with a buffer gas.

The luminescence was observed at right angles to the excitation beam by means of a monochromator (*Bausch & Lomb,* High Intensity) fitted with an *EMI* 9781/R photomultiplier tube coupled to a preamplifier (*Burr-Brown* 3554). The signal was recorded with a *Biomation* 8100 transient recorder used in conjunction with a *Nicolet* 1070 multichannel averager for repetitive scans. Synchronization between laser pulse and signal detection was established with a *BNC* Mod. 7075 pulsegenerator.

Procedures. The accuracy of the rate constants obtained from an energy transfer experiment critically depends on the accuracy of the partial pressure measurement of the acceptor. Therefore, the biacetyl pressure was determined not only with a pressure meter but also by means of the biacetyl phosphorescence intensity using direct flash excitation (*Gen. Rad.* 1538-A and cut-off filters 400 nm) and an intensity-pressure calibration curve.

One data set consisted of four measurements: a) the partial pressure of biacetyl, b) the decay kinetics of the biacetyl phosphorescence to correct for pressure effects and impurity-quenching, c) the build-up of the acceptor phosphorescence upon energy transfer, and d) the stray-light and dc-base line drift. The latter effects were determined using the evacuated sample cell and the same number of repetitive scans as in c.

Results and Discussion. - *Figure 2* displays a typical set of emission intensity *vs.* time curves obtained with 1-butyne-3-one as donor and biacetyl as acceptor. The trace of *Figure 2a* represents the phosphorescence decay of the donor following

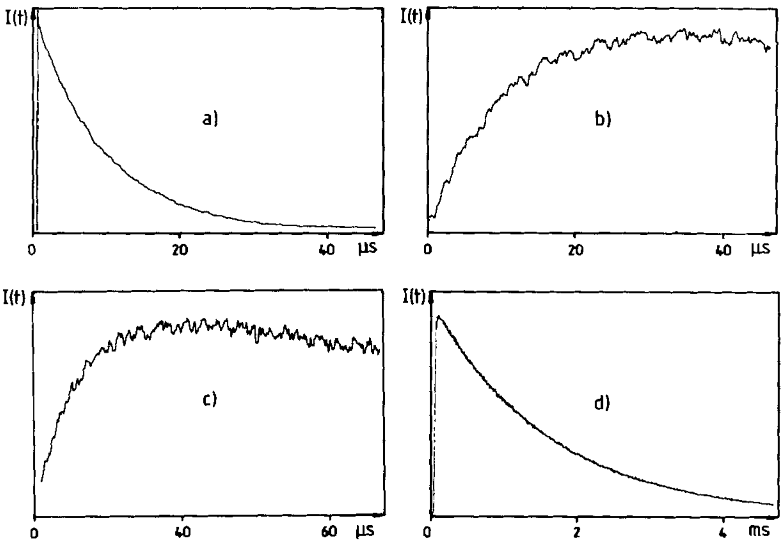

Fig. 2. *1-Butyne-3-one biacetyl system: a) Phosphorescence decay of the donor excited at 350 nm and monitored at 465 nm, b) and c) build-up of the acceptor phosphorescence monitored at 570 nm, d) Decay of the acceptor phosphorescence.* Total sample pressure ~ 1 Torr. (For details see the text)

excitation at 350 nm. With respect to the unperturbed phosphorescence this decay is accelerated by the T-T energy transfer to the acceptor. Using the same time scale, the build-up of the acceptor phosphorescence at 570 nm is shown in *Figure 2b*. Since the acceptor triplet molecule is an intermediate species in a consecutive reaction, its emission intensity passes through a maximum demonstrated in *Figure 2c*. The relatively slow decay of the acceptor phosphorescence has been monitored on a much longer time scale *(Fig. 2d)*.

These decay curves have been analysed considering a kinetics based on the following scheme from which the excitation process has been omitted.

$$ {}^3D^* + M \xrightarrow{k_{vv}} {}^3D + M \qquad (1)$$

$$ {}^3D^* + D_0 \xrightarrow{k^*_{SQ}} 2\, D_0 \qquad (2)$$

$$ {}^3D^* \xrightarrow{k_T^{D^*}} D_0 + (h\nu_p) \qquad (3)$$

$$ {}^3D \xrightarrow{k_T^{D}} D_0 + (h\nu_p) \qquad (4)$$

$$ {}^3D^* + A_0 \xrightarrow{k^*_{ET}} {}^3A + D_0 \qquad (5)$$

$$^3\mathrm{D} + \mathrm{A}_0 \xrightarrow{k_{\mathrm{ET}}} {}^3\mathrm{A} + \mathrm{D}_0 \tag{6}$$

$$^3\mathrm{D} + \mathrm{D}_0 \xrightarrow{k_{\mathrm{SQ}}} 2\ \mathrm{D}_0 \tag{7}$$

$$^3\mathrm{A} \xrightarrow{k_{\mathrm{T}}^{\mathrm{A}}} \mathrm{A}_0 + h\nu_{\mathrm{p}} \tag{8}$$

Here $^3\mathrm{D}, {}^3\mathrm{A}$, and $\mathrm{D}_0, \mathrm{A}_0$ denote the donor and acceptor molecules in the triplet and ground states and M that of the buffer gas (or D_0 molecule). The rate coefficients k_{T}, k_{ET}, k_{vv}, and k_{SQ} refer to the triplet decay (radiative as well as non-radiative), the electronic energy transfer, the vibrational energy transfer and the self-quenching (SQ), respectively.

Following excitation into the $\mathrm{S}_1 \leftarrow \mathrm{S}_0$ transition and intersystem crossing $\mathrm{S}_1 \rightarrow \mathrm{T}_x$ $(x \geqslant 1)$, the donor triplet molecules T_1 are produced in a vibrationally excited state with an excess vibrational energy $\Delta E_{\mathrm{vib}} \geqslant \Delta E(\mathrm{S}_1 - \mathrm{T}_1)$. The hot triplet molecules are then either bath-equilibrated (equ. 1), quenched by collisions with D_0 molecules (equ. 2), deactivated by intramolecular processes (equ. 3), or deactivated by electronic energy transfer to A_0 (equ. 5). The bath-equilibrated $^3\mathrm{D}$ molecules undergo the same decay processes (equ. 4, 6, and 7). Since the donnors examined are relatively large molecules and under our excitation conditions ΔE_{vib} is small, it was expected that $k_{\mathrm{T}} = k_{\mathrm{T}}^{*}$. Furthermore, results of a previous study suggested [5] that k_{ET} and k_{SQ} are not significantly dependent on ΔE_{vib}. These assumptions proved to be correct. With the addition of a buffer gas which assures all donor triplet molecules to be bath-equilibrated prior to any electronic decay, the same results were obtained.

For the kinetic analysis a distinction between $^3\mathrm{D}^*$ and $^3\mathrm{D}$ is thus no longer necessary reducing the above scheme to equ. 4, 6, 7, and 8. Accordingly, the rate equations of the triplet states of D and A become

$$\frac{\mathrm{d}[^3\mathrm{D}]}{\mathrm{dT}} = -\gamma\,[^3\mathrm{D}] \tag{9}$$

$$\frac{\mathrm{d}[^3\mathrm{A}]}{\mathrm{dT}} = k_{\mathrm{ET}}[\mathrm{A}_0][^3\mathrm{D}] - k_{\mathrm{T}}^{\mathrm{A}}[^3\mathrm{A}] \tag{10}$$

where $\gamma = k_{\mathrm{T}}^{\mathrm{D}} + k_{\mathrm{ET}}[\mathrm{A}_0] + k_{\mathrm{SQ}}[\mathrm{D}_0]$. Under our excitation conditions $[^3\mathrm{D}] \ll [\mathrm{D}_0], [^3\mathrm{D}] \ll [\mathrm{A}_0]$ and $[^3\mathrm{A}] \ll [\mathrm{A}_0]$ at all times. Integration of these equations leads to

$$[^3\mathrm{D}] = [^3\mathrm{D}]_0\,\mathrm{e}^{-\gamma t} \tag{11}$$

$$[^3\mathrm{A}] = \frac{k_{\mathrm{ET}}[\mathrm{A}_0][^3\mathrm{D}]_0}{\gamma - k_{\mathrm{T}}^{\mathrm{A}}}\left\{\mathrm{e}^{-k_{\mathrm{T}}^{\mathrm{A}} t} - \mathrm{e}^{-\gamma t}\right\} \tag{12}$$

The energy transfer is measured by monitoring the phosphorescence intensity of the acceptor I_{ET}, where

$$I_{ET}(t) = G \cdot k_p^A [^3A] \tag{13}$$

Here G is a geometrical factor and k_p^A denotes the phosphorescence rate constant of the acceptor. Substitution of equ. 12 into equ. 13 gives

$$I_{ET}(t) = G \cdot k_p^A \frac{k_{ET}[A_0][^3D]_0}{\gamma - k_T^A} \left\{ e^{-k_T^A t} - e^{-\gamma t} \right\} \tag{14}$$

Depending on the absorption and fluorescence properties of the donor it is often unavoidable that acceptor triplet molecules are produced prior to energy transfer ($[^3A]_d$) by either direct laser excitation or absorption of donor fluorescence. Including this component in equ. 14, the total intensity $I = I_{ET} + I_A$, normalized by setting $G \cdot k_p^A = 1$, becomes

$$I(t) = \frac{k_{ET}[A_0][^3D]_0}{\gamma - k_T^A} \left\{ e^{-k_T^A t} - e^{-\gamma t} \right\} + [^3A]_d \, e^{-k_T^A t} \tag{15}$$

(In the above equation the concentrations, used for notational clarity, can simply be replaced by the appropriate partial pressures.)

For the data evaluation it is convenient to rewrite equ. 15 as

$$I' = e^{-k_T^A t} - \rho e^{-\gamma t} \tag{16}$$

where the parameter ρ scales the intensity such that the 'preexponential factor' of the first term is one. Using an iterative method the parameter ρ and γ are varied till the best fit on the basis of a χ^2-test is reached between the calculated and the experimental curves [6]. The values of $\gamma = k_T^D + k_{SQ} p_{D_0} + k_{ET} p_{A_0}$ obtained from experiments with different acceptor pressures are then plotted *vs.* p_{A_0}, as shown in *Figures 3-5,* resulting in k_{ET} and $k_T^D + k_{SQ} p_{D_0}$. At low donor pressures and for large k_T^D the self-quenching term can be neglected. Otherwise, additional measurements at various donor pressures but at a constant acceptor pressure would be performed to determine k_{SQ}.

For the butinone/biacetyl system, the plots γ *vs.* p_{A_0} obtained by monitoring the butinone (1-butyne-3-one) phosphorescence or by T-T energy transfer *(Fig. 3)* are identical, within experimental error. Benzaldehyde *(Fig. 4)* as well as butinone were excited into the $S_1(n\pi^*) \leftarrow S_0$ absorption at 337 nm (N_2 laser) while cycloheptanone *(Fig. 5)* was excited at 308 nm (XeCl laser). Moreover, the T-T energy transfer between cycloheptanone and biacetyl measured with and without a buffer gas (200 Torr N_2) gave exactly the same results. The reciprocal lifetimes of the triplet decay $1/\tau = k_T^D$ and the energy transfer rate constants to biacetyl are

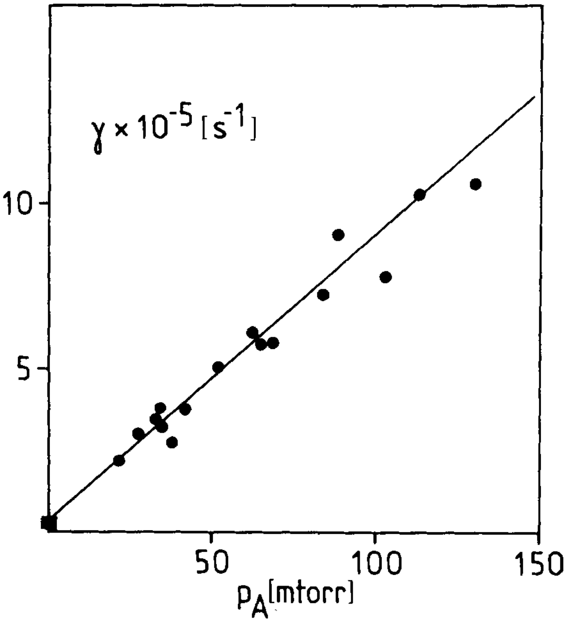

Fig. 3. Stern-Volmer *type plot* γ vs. p_{A_0} *of the 1-butyne-3-one/biacetyl system* (Partial pressure of the donor 400-500 mTorr. In this pressure range the self-quenching term $k_{SQ} \cdot p_{D_0}$ can be neglected [k_{SQ}(Butinone) = 1.5×10^3 s^{-1} Torr^{-1}])

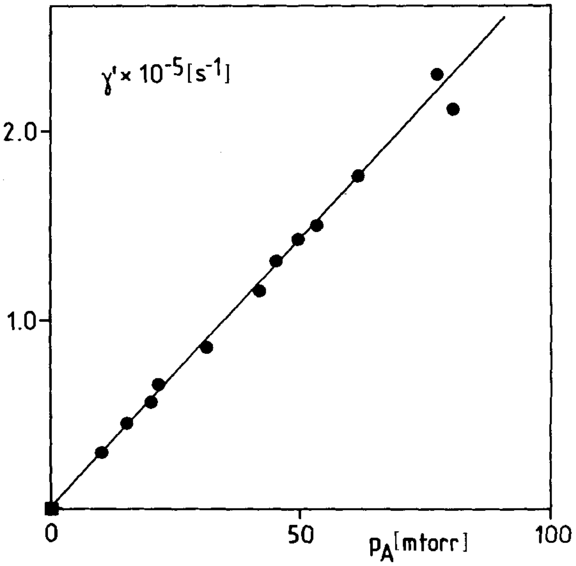

Fig. 4. Stern-Volmer *type plot* γ' vs. p_{A_0} *of the benzaldehyde/biacetyl system* (Partial pressure of the donor 200-300 mTorr. $\gamma' = \gamma - k_{SQ}\, p_{D_0}$ is corrected for self-quenching using $k_{SQ} = 2.4 \times 10^4$ s^{-1} Torr^{-1} [5])

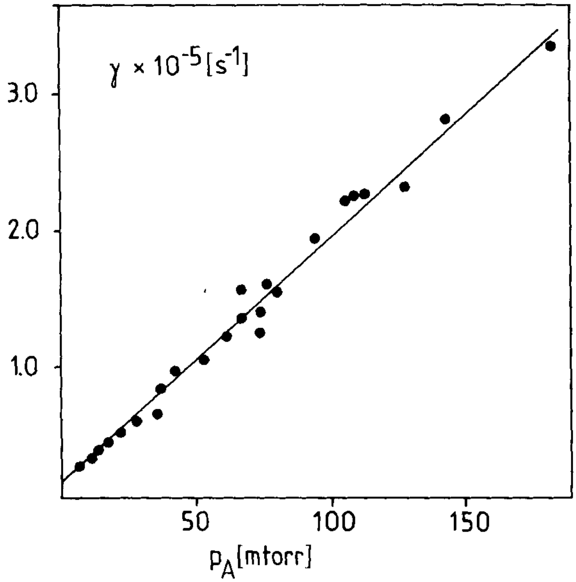

Fig. 5. Stern-Volmer *type plot* γ vs. p_{D_0} *of the cycloheptanone biacetyl system* (Partial pressure of the donor 300-700 mTorr. The donor triplet self-quenching was found to be negligible)

listed in the *Table.* A recent measurement [3] under stationary conditions of the biacetyl phosphorescence intensity I_p sensitized by cycloheptanone $[I_p^{-1} = 1 + (k_T^D/k_{ET}) p_A^{-1}]$ led to a ratio $k_T^D/k_{ET} = 8.8 \times 10^{-3}$ Torr. From the values given in the *Table* this ratio is 9.1×10^{-3} Torr.

The excellent agreement between the triplet of butinone and benzaldehyde obtained by their phosphorescence decay and by T-T energy transfer demonstrates the reliability of this indirect method. The larger standard deviation in k_T and k_{ET} of the latter method is ascribed to the detector system. With a more appropriate detector, *i.e.* a more sensitive photomultiplier, a better S/N ratio would be obtained, allowing a higher accuracy of the fit and thus an even more accurate γ. We estimate that triplet lifetimes $\leqslant 1$ ms can be determined with this method within a relative error limit of ±5%. For longer lifetimes a larger error has to be considered, which is strongly dependent on the accuracy of the partial pressure

Table. *Rate constants of the triplet decay* (k_T^D) *and the triplet-triplet energy transfer to biacetyl* (k_{ET})

Molecule	Direct method[a])		T-T energy-transfer method[b])	
	k_T^D $[s^{-1}]$	k_{ET} $[s^{-1} \cdot Torr^{-1}]$	k_T^D $[s^{-1}]$	k_{ET} $[s^{-1} \cdot Torr^{-1}]$
Butinone	6.07×10^3	7.70×10^5	6.86×10^3	7.89×10^5
Benzaldehyde	0.44×10^3	2.80×10^6	0.42×10^3	2.80×10^6
Cycloheptanone	-	-	1.63×10^4	1.80×10^6

[a]) Error $\leqslant \pm 5\%$. [b]) Error $< \pm 10\%$.

measurement of the acceptor. In any case, using biacetyl as the acceptor, the energy of the probed triplet must be $\geqslant 20000$ cm^{-1} [4].

Finally it is noted that the above described procedure is also applicable when the energy transfer partially or entirely occurs from hot triplet molecules (equ. 5). In this case experiments performed with and without buffer gas result in different k_T and probably different k_{ET} values. To insure the dominance of reaction 5 over 6 the donor gas pressure has to be appropriately reduced.

In view of the fact that most molecules in the gas phase practically do not phosphoresce and that triplet lifetimes are important parameters in photochemical and photophysical studies, the T-T energy transfer method applied to triplet lifetime measurements is certainly a useful tool. By monitoring and analyzing the acceptor kinetics throughout its entire course the method's range of application can be broadened and its accuracy significantly improved.

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