

COLLISIONAL EFFECTS ON THE PHOSPHORESCENCE OF 1,1,1-TRIFLUOROACETONE VAPOUR

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Summary

The effects of pressure of 1,1,1-trifluoroacetone (TFA) vapour on the phosphorescence quantum yield at a variety of excitation wavelengths have been analysed. A model has been proposed in which the initially prepared singlet state undergoes non-radiative decay in competition with single step collisional relaxation to produce a relaxed singlet from which only intersystem crossing to the phosphorescent state occurs. In the triplet manifold there exists a threshold energy for decomposition above which only decomposition occurs and below which phosphorescence results. The quantum yield for the formation of biacetyl from TFA subject to 302.5 nm excitation was shown to be 0.15 ± 0.03 . Relative rate constants for the quenching of TFA phosphorescence by biacetyl, *cis*-but-2-ene and buta-1,3-diene are also reported.

1. Introduction

1,1,1-trifluoroacetone (TFA) has been shown to produce a phosphorescent triplet state in the vapour phase upon excitation to the first excited singlet state with a relative phosphorescence quantum yield which is dependent upon the pressure of TFA and the wavelength of excitation [1], and some evidence is afforded of some excited-state-ground-state quenching interaction by the fact that a photodimer is formed on excitation of this compound. However, the quenching of TFA phosphorescence indicated by quantum yield measurements is in conflict with observations that the phosphorescence decay time of TFA vapour is 0.29 ms in the absence of mercury vapour, and is independent of TFA pressure and excitation wavelengths [2].

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The excited triplet state was shown to be quenched by mercury vapour [2, 3], and there are conflicting reports of photodecomposition mechanisms in the compound [4, 5]. The apparent conflict in the literature prompted the study of this molecule reported here.

2. Experimental

Relative quantum yields of phosphorescence of TFA were measured on a mercury-free and grease-free vacuum system with lamp, monochromator, optics and detection system which have been described adequately in earlier reports [6]. Relative quantum yields were made absolute by comparison with the limiting low pressure phosphorescence quantum yield reported for hexafluoroacetone of 0.11 [7]. The effects of various added gases upon the relative phosphorescence quantum yield of TFA were also measured using the above mercury-free system, and in some cases using a similar mercury-saturated apparatus.

Emission spectra were taken on a Farrand Mk 1 Spectrofluorimeter using a 6 cm long quartz emission cell and were uncorrected for the spectral response of the monochromators and detectors. The quantum yield of production of biacetyl from TFA was also measured. The photolysis was performed using a 200 W home-made medium pressure lamp and power supply, a Bausch and Lomb high intensity monochromator and a 6 cm quartz mercury-free T-cell (as described above) and the absorbed light was monitored using an RCA 935 photodiode that had previously been calibrated using potassium ferrioxalate as a primary actinometer. The resulting biacetyl phosphorescence was monitored using a single photon counting system described previously [8] and the Stern-Volmer slope of TFA sensitized biacetyl phosphorescence was obtained using the Farrand Mk 1 spectrofluorimeter and a mercury-free 3 cm × 1 cm cuvette. In both the photolysis and the sensitization experiments 120 Torr of TFA was employed and low conversions (about 1%) to biacetyl ensured uniformity of sensitization efficiency. In both experiments the sensitized biacetyl phosphorescence was monitored by excitation at 320 nm to ensure negligible absorption by the biacetyl.

3. Materials

All materials were distilled *in vacuo*, the middle fraction being retained. Quenchers were shown to be better than 99.5% pure by gas-liquid chromatography (GLC) analysis on a variety of columns.

1,1,1-Trifluoroacetone (TFA) was obtained from Bristol Organic Chemicals Ltd. Analysis on a dinonyl phthalate column showed there to be two impurities present in concentrations estimated to be less than 0.5%. Mass spectral analysis showed these to be diethyl ether and trifluoromethyl acetate ($\text{CH}_3\text{COOCF}_3$). The TFA was used with these impurities present, as their

removal by preparative GLC was shown to cause greater contamination by water. The presence of these impurities undoubtedly caused quenching of the triplet state, however. Biacetyl was obtained from British Drug Houses Ltd. and was fractionally distilled prior to use (purity, greater than 99.8%). *cis*-But-2-ene was obtained from Cambrian Chemicals Ltd. and contained only 0.07% of the *trans* isomer as impurity. Buta-1,3-diene was obtained from Cambrian Chemicals Ltd. and was shown to be free of impurities by GLC analysis. Perfluoromethylcyclohexane was obtained from Air Products Ltd. under the trade name of Flutec PP₂. It was purified by percolation through a 1 m neutral activated alumina column after which no proton resonances were detectable. Oxygen was manufactured on the vacuum line by heating Analar grade potassium permanganate.

4. Results

The vapour phase absorption spectra and uncorrected emission spectra of TFA are shown in Fig. 1, the dotted portion of the spectrum indicating that fraction of the total emission which is quenched by addition of a few Torr of molecular oxygen and which is considered here to represent phosphorescence. The effect upon the phosphorescence quantum yield of variation of the pressure of TFA for excitation at 280, 290, 300, 310 and 330 nm obtained in this work in the absence of mercury is shown in Fig. 2. Stern-Volmer plots for the quenching of phosphorescence from 120 Torr TFA by various additives are shown in Fig. 3.

It was noticed that upon irradiation of a pure sample of TFA in the Farrand Mk 1 spectrofluorimeter the emission spectrum was dependent upon the time of irradiation, developing a structured emission to the red of the TFA phosphorescence (Fig. 4). The phosphorescence spectra of biacetyl and hexafluorobiacetyl are also given in Fig. 4 for comparison. The build-up of

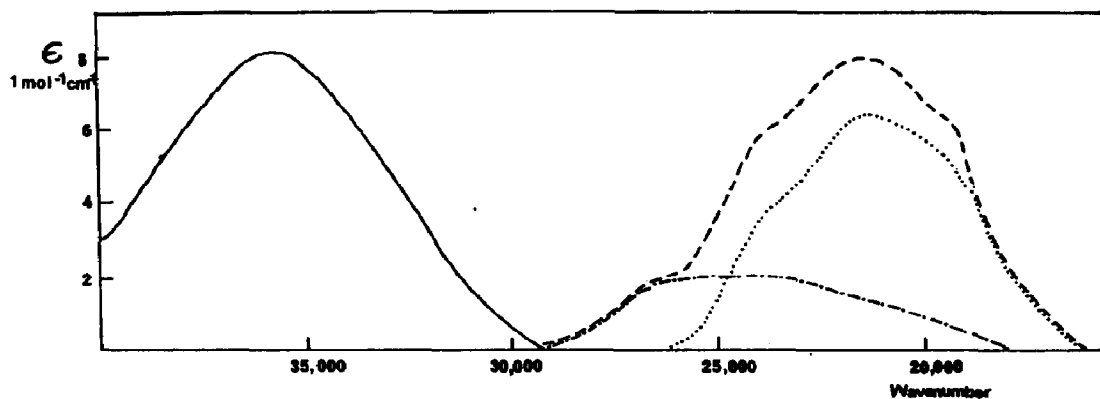


Fig. 1. Absorption (—), total emission (---), fluorescence (-·-·-) and phosphorescence (·····) spectra of 120 Torr of 1,1,1-trifluoroacetone at 298 K. Emission spectra are uncorrected.

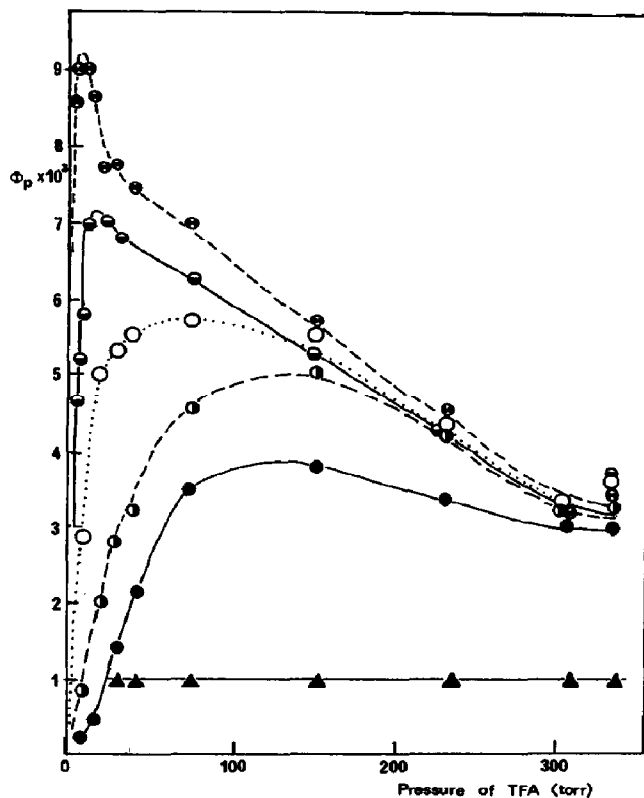


Fig. 2. Emission quantum yields of TFA: (a) fluorescence excited at 330 nm (Δ); (b) phosphorescence excited at 330 (\bullet), 310 (\circ), 300 (\circ), 290 (\bullet) and 280 nm (\bullet).

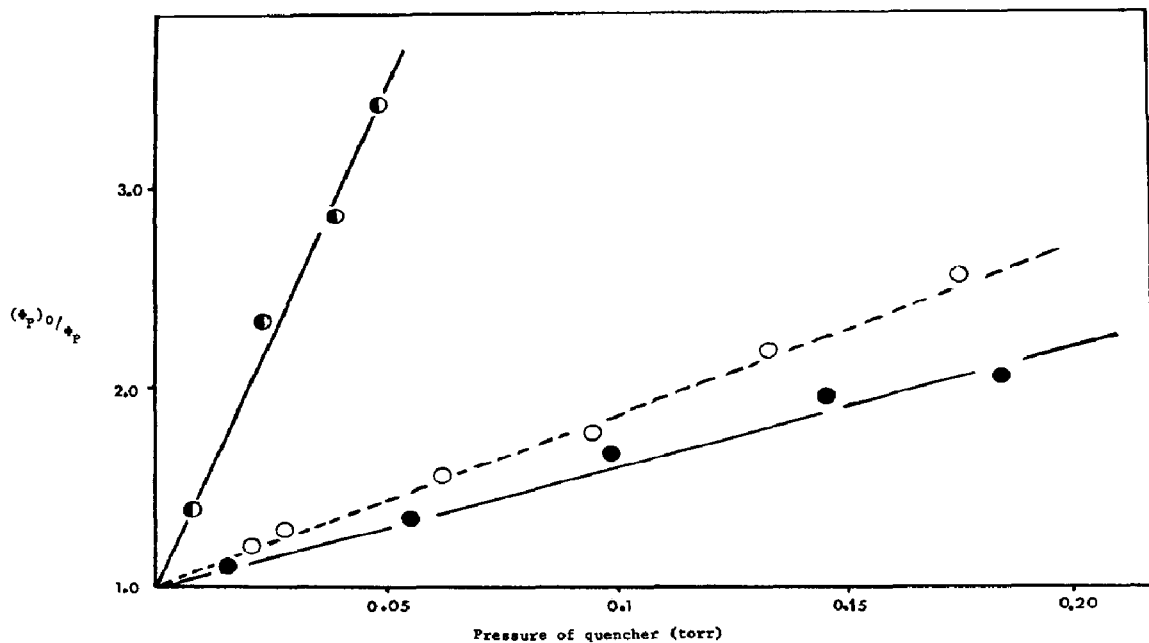


Fig. 3. Stern-Volmer plots obtained from the quenching of the phosphorescence of 120 Torr of TFA (excited at 312 nm) by but-1,3-diene (\circ), oxygen (\circ) and but-2-ene (\bullet) in the presence of mercury.

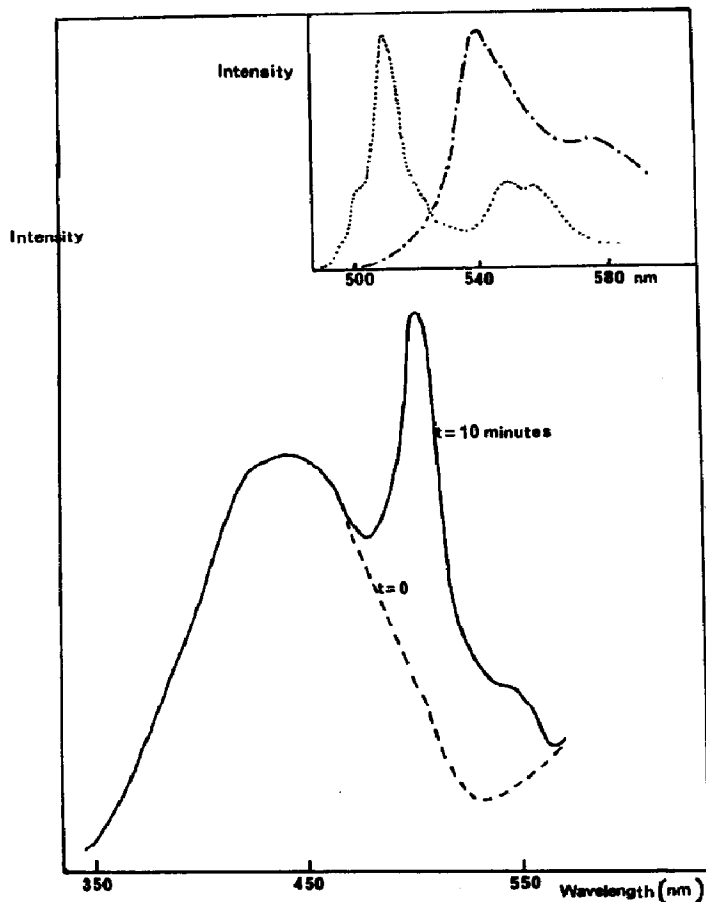


Fig. 4. Time dependence of the emission spectrum of TFA. Inset, phosphorescence spectra of biacetyl (.....) and hexafluorobiacetyl (-----).

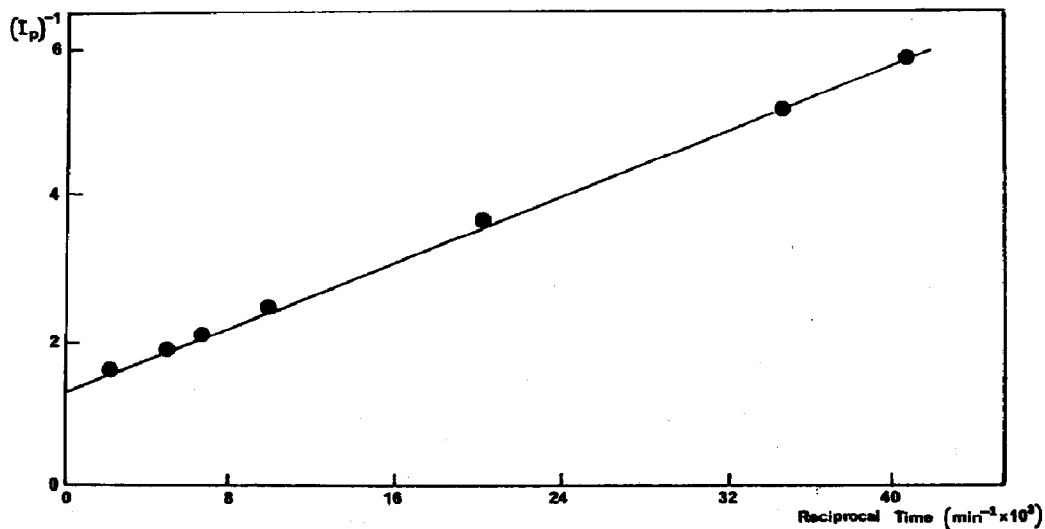


Fig. 5. Reciprocal phosphorescence intensity $1/I_p$ vs. time observed from biacetyl produced following photolysis of 120 Torr of TFA at 300 nm.

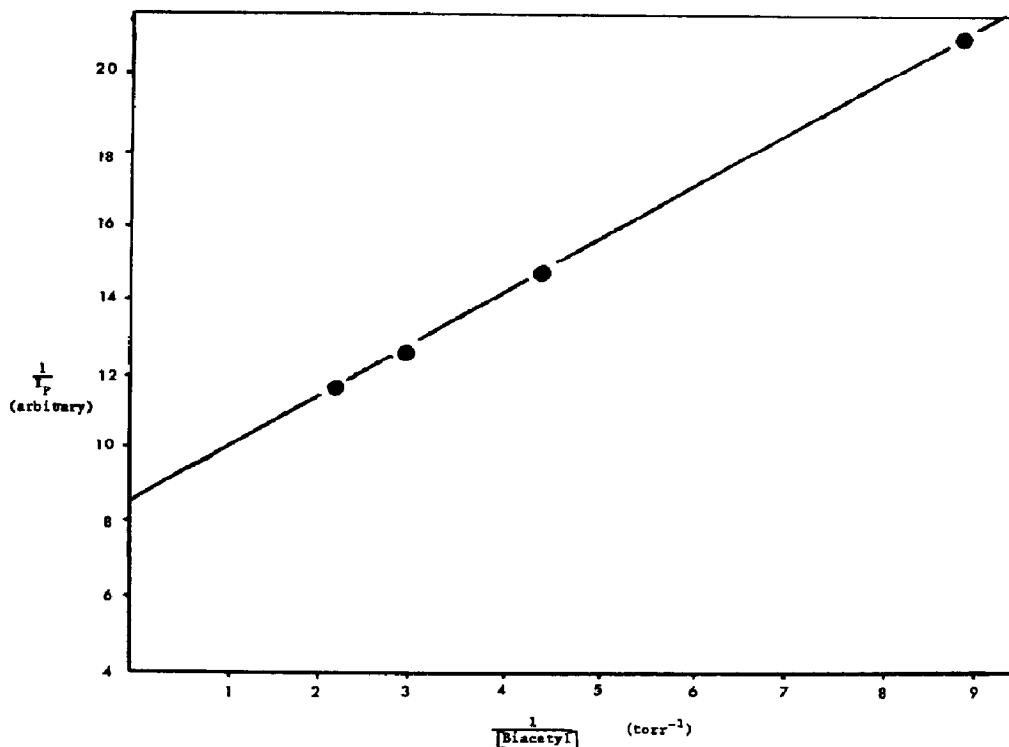


Fig. 6. Plots of reciprocal phosphorescence yield of biacetyl sensitized by 120 Torr of TFA excited at 320 nm against the reciprocal of biacetyl pressure.

the intensity of the emission band at 510 nm with time of irradiation is shown in Fig. 5. The results of experiments in which successive concentrations of biacetyl were added to TFA and the measured quantum yield of sensitized emission from biacetyl are shown in Fig. 6 as plots of reciprocal yield of sensitized phosphorescence of biacetyl against the reciprocal concentration of biacetyl added.

5. Discussion

5.1. Vibrational relaxation

The curves depicted in Fig. 2 are consistent with the earlier report [1] on the variation in phosphorescence quantum yield with pressure of TFA and can be explained on the basis of a state from which a non-radiative decay process occurs in competition with collisional relaxation to form immediately or ultimately the phosphorescent state which is also quenched (probably by impurity). That collisional stabilization does occur is shown in Fig. 7 in which it can be seen that addition of the inert gas perfluoromethylcyclohexane to 20 Torr TFA excited at 280 nm causes the phosphorescence quantum yield to increase to an asymptotic value. The question of whether the vibrational relaxation occurs predominantly in the singlet state of TFA, or the triplet state or both now arises.

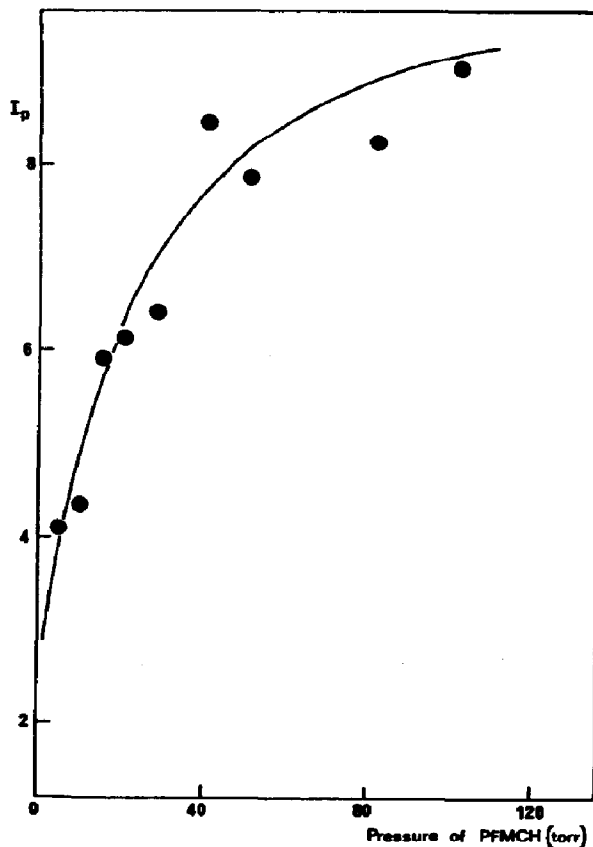


Fig. 7. Phosphorescence intensity I_p observed from 20 Torr of TFA excited at 289 nm following addition of pressures of perfluoromethylcyclohexane (PFMCH).

Whatever kinetic scheme is chosen must be compatible with the data in Fig. 2 and also with the information which exists concerning triplet state formation, namely that the use of the method of sensitization of phosphorescence from biacetyl gives values for the quantum yield Φ_{ISC} of $S_1 \rightarrow T_1$ intersystem crossing to the scavengeable triplet for TFA shown in Table 1.

TABLE 1

Phosphorescence yields Φ_P and Φ_S of TFA and biacetyl sensitized by TFA

Excitation wavelength (nm)	$(\Phi_P)_{rel}^a$	Φ_S	Φ_{ISC}^b	$(\Phi_{ISC})_{rel}^c$
330	(1.00)	0.148	0.97	(1.00)
300	0.75	0.128	0.85	0.85
280	0.28	0.045	0.30	0.30

TFA pressure, 35 Torr; temperature, 20°C.

^a Relative to value at 330 nm excitation. Data from Fig. 2.

^b Assuming biacetyl phosphorescence yield to be 0.15.

^c Relative to value at 330 nm.

Clearly, a complete reaction scheme may be written in which initially formed excited singlet state TFA molecules undergo intersystem crossing, internal conversion and fluorescence in competition with collisional deactivation to lower lying levels which suffer similar fates until equilibration is achieved. If the triplet levels formed on each intersystem crossing step are also allowed to be collisionally relaxed by a multistep mechanism in competition with decomposition it should be evident that the resulting scheme will be of such complexity that analytical expressions for the behaviour of the phosphorescence quantum yield as a function of excitation energy and pressure will be insoluble. Thus the approach adopted here is to seek the simplest possible kinetic scheme which is compatible with the observations.

5.2. Triplet state relaxation

Recently Hackett and Kutschke [9] have shown that for hexafluoroacetone (HFA) vapour, as in acetone itself, there exists a triplet state threshold energy above which only decomposition of the isolated molecule occurs. Below this threshold, triplet state HFA molecules phosphoresce. For excitation energies near 313 nm intersystem crossing of excited singlet state molecules to a triplet state just above the threshold energy occurs and thus collisional relaxation in the singlet manifold results in formation of a phosphorescent triplet state. A one-step collisional relaxation was shown to be sufficient to explain decomposition data [9, 10].

It is easily demonstrated that the following similar scheme is compatible with the TFA data reported here.

	Rate constant	Process	
$A + h\nu \rightarrow {}^1A_n$		absorption	(1)
${}^1A_n \rightarrow A + h\nu_F$	k_{RF}	resonance fluorescence	(2)
${}^1A_n \rightarrow A_k$	k_{NR}	non-radiative decay	(3)
${}^1A_n \rightarrow {}^3A_m$			(4)
${}^1A_n + A \rightarrow {}^1A_0 + A_n$	k_S	collisional stabilization	(5)
${}^1A_0 \rightarrow A + h\nu_F$	k_F	fluorescence	(6)
${}^1A_0 \rightarrow {}^3A_0$	k_{ISC}	intersystem crossing	(7)
${}^3A_m \rightarrow \text{decomposition}$	k'_D	decomposition	(8)
${}^3A_0 \rightarrow A + h\nu_P$	k'_P	phosphorescence	(9)
${}^3A_0 \rightarrow A$	k'_{ISC}	intersystem crossing	(10)
${}^3A_0 + A \rightarrow \text{quenching}$	k'_Q	impurity quenching	(11)

where A is the trifluoroacetone molecule, the superscripts refer to the multiplicity, and the subscripts to the vibrational energy content. In the triplet manifold subscript m refers to triplet molecules above the threshold for decomposition [8] and subscript zero to those triplets with insufficient energy to decompose. Step (11) represents electronic impurity quenching. Since the concentration of the impurity is proportional to [A], the rate is $k'_Q[A][{}^3A_0]$. Principal features on this scheme are that vibrational relaxation occurs in the singlet manifold and that vibrational relaxation in the triplet manifold can be ignored because of the threshold requirement for

decomposition. The arguments here follow closely those of Hackett and Kutschke [9].

The complete expression for the quantum yield of TFA phosphorescence from the above scheme is

$$\Phi_P = \frac{k_S[A]}{k_S[A] + k_{NR} + k_{RF}} \Phi''_{ISC} \frac{k'_P}{k'_P + k'_{ISC} + k'_Q[A]} \quad (12)$$

where $\Phi''_{ISC} = k_{ISC}/(k_{ISC} + k_F)$, *i.e.* the quantum yield of the phosphorescent triplet state formation neglecting k_{RF} . Expression (12) can be rewritten as expression (13), where $k_R = k_{NR}/k_S$. $(\Phi_P)_0$ is the phosphorescence quantum yield for a fully relaxed system (all ${}^1A_n \rightarrow {}^1A_0$) in which no electronic quenching occurs (*i.e.* $k_Q[A] [{}^3A_0] = 0$) and is given by $k'_P/(k'_P + k'_{ISC})$ where K'_Q is the usual Stern-Volmer quenching parameter:

$$\Phi_P = \Phi''_{ISC} \frac{[A]}{[A] + k_R} \frac{(\Phi_P)_0}{1 + K'_Q[A]} \quad (13)$$

Differentiation of expression (12) yields

$$\begin{aligned} \frac{d[\Phi_P]}{d[A]} = & (k_S[A] + k_{NR})(k'_{ISC} + k'_Q[A])k'_Pk_S - \\ & - k'_Pk_S[A] \{ (k_S[A] + k_{NR})k'_Q + (k'_P + k'_{ISC} + k'_Q[A])k_S \} \times \\ & \times \frac{\Phi_{ISC}}{(k_S[A] + k_{NR})^2(k'_P + k'_{ISC} + k'_Q[A])^2} \end{aligned} \quad (14)$$

At the maximum in Φ_P expression (14) can be set equal to zero, yielding

$$\frac{k_{NR}}{k_S} = [A]_{\max}^2 \frac{k'_Q}{k'_P + k'_{ISC}} \quad (15)$$

or

$$k_R = [A]_{\max}^2 K'_Q \quad (16)$$

where $[A]_{\max}$ is the concentration of TFA required to give the maximum value of Φ_P for each particular excitation wavelength. Expression (16) was thus used to evaluate the approximate values for the ratios k_{NR}/k_S at each wavelength using the values of $[A]_{\max}$ and K'_Q obtained from Fig. 2. K'_Q was evaluated roughly for pressures above 20 Torr using the 330 nm results by plotting Φ_P^{-1} against $[A]$ in the usual Stern-Volmer fashion. The approximate values of k_R thus obtained were then employed in a computer fit of the experimental results to expression (13). The program devised allowed k_R to vary considerably about the mean value evaluated as described above and also permitted values of Φ''_{ISC} and k_Q to be varied. Typical best fit curves are shown for excitation at 280 nm (Fig. 8), 300 nm (Fig. 9) and 310 nm (Fig. 10) together with the experimental data points from this study and those of Ausloos and Murad [1] normalized to the present results. Best fit parameters were $K'_Q = 94.3 \text{ l mol}^{-1}$, $(\Phi_P)_0 = 0.01$ and $\Phi''_{ISC} = 1.00$. The K'_Q parameter is

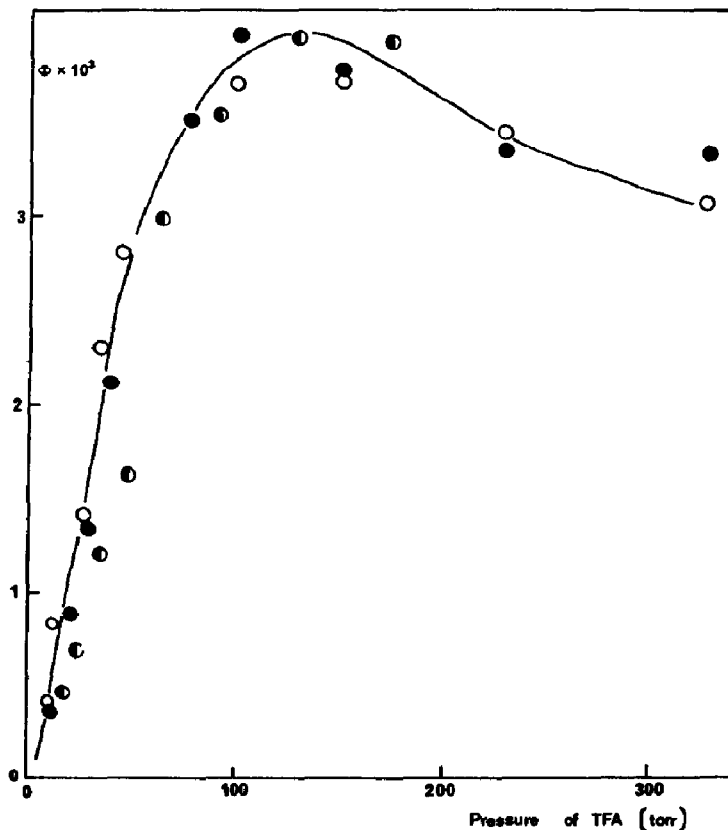


Fig. 8. Pressure dependence of the phosphorescence quantum yield of TFA: this work (●); Ausloos and Murad [1] (○); curve fitting procedure (○). Excitation wavelength, 280 nm.

due to the impurity and will not be discussed further. It can be seen that a very reasonable fit of the data to this scheme is possible and it should be stressed that the relaxation is assumed to be a single step process. Hackett and Kutschke [9] have provided a plausible explanation of this in which a single collision suffices to relax the singlet state molecule from that with an internal energy such that upon intersystem crossing (step (4)) the triplet formed is above the energy threshold for decomposition to that with an energy below threshold. While subsequent collisions which remove energy to relax the triplet state fully must occur physically they do not contribute to any increase in phosphorescence and may thus be omitted from the scheme. The requirement that Φ_{ISC} must be unity for fitting of data to the scheme above (defined earlier as intersystem crossing from the relaxed singlet state) is compatible with biacetyl sensitization data which show a value of the triplet state quantum yield varying from unity at 330 nm down to 0.30 at 280 nm (see above) if it is recognized that the biacetyl may only scavenge non-dissociative triplet states. The values obtained by the biacetyl method should thus correlate with values of Φ_P at a TFA pressure of 35 Torr taken from Fig. 2. The results given in Table 1 show this to be the case.

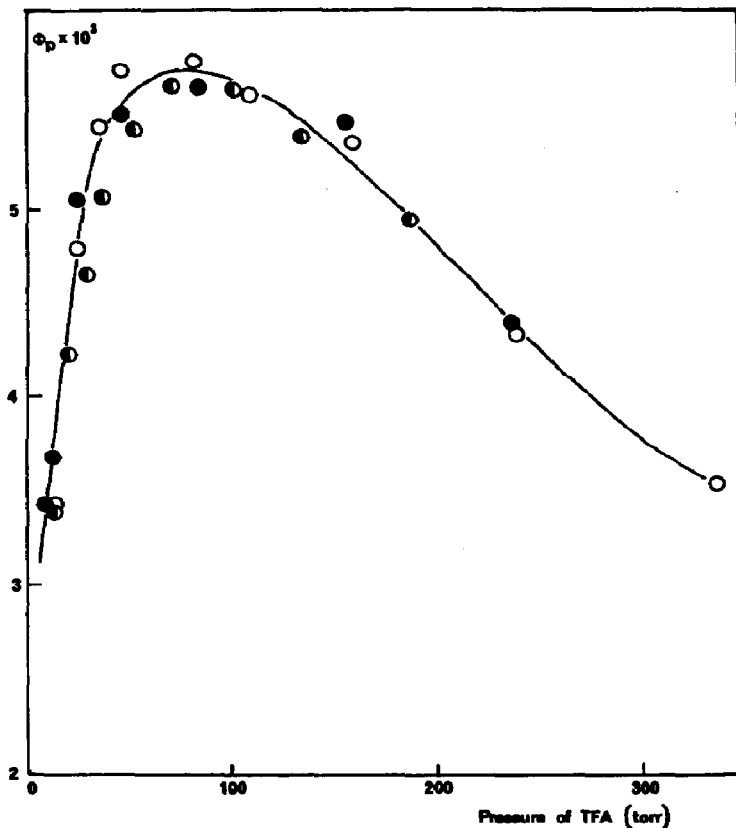


Fig. 9. Pressure dependence of the phosphorescence quantum yield of TFA: this work (\bullet); Ausloos and Murad [1] (\circ); curve fitting procedure (\circ). Excitation wavelength, 300 nm.

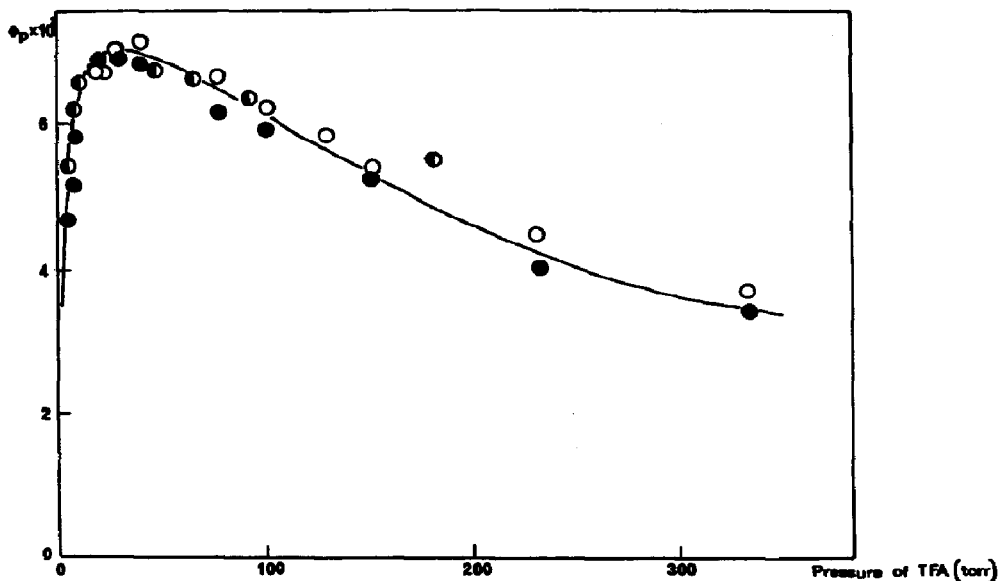


Fig. 10. Pressure dependence of the phosphorescence quantum yield of TFA: this work (\bullet); Ausloos and Murad [1] (\circ); curve fitting procedure (\circ). Excitation wavelength, 310 nm.

The values obtained in this study for k_{NR}/k_S are shown in Table 2 and compared with those for hexafluoroacetone [11] and acetone [12]. The somewhat larger values of k_{NR}/k_S obtained for acetone may be partially explained by the increased temperature at which those experiments were performed. The value of k_{NR}/k_S for TFA at 310 nm is also in good accord with decomposition results [4]. The quantum yields of formation of the products of decomposition of TFA have been shown to be lowered by a factor of approximately 4.0 when the pressure of TFA employed is increased from 40 to 120 Torr at 45 °C and irradiated at 313 nm. Use of these concentrations and the value of k_{NR}/k_S from Table 1 at 310 nm and 25 °C shows that the ratio of decomposition yields should be 2.7, in reasonable agreement considering the temperature differences.

TABLE 2

Values of k_{NR}/k_S for vibrational relaxation of TFA^a, HFA^b and acetone^c

	Temperature (°C)	Wavelength (nm)	k_{NR}/k_S (mol l ⁻¹ × 10 ³)
TFA	25	280	4.4
	25	290	3.13
	25	300	1.00
	25	310	0.39
	25	330	0.01
HFA	25	313	0.26
Acetone	40	280	16.4
	40	289	5.63
	40	297	2.25
	40	302	1.92
	40	313	0.42
	44	314	0.28

^aThis work.

^bFrom ref. 11. Note that the mechanism used by these authors also involves singlet state decomposition and relaxation. The value quoted is that for a single step deactivation process.

^cFrom ref. 12.

5.3. Correlation with fluorescence measurements

The results show that in the singlet manifold increase in excitation energy results in an increase in the value of k_{NR} , which may have contributions from both intersystem crossing (step 4) and internal conversion (step 3). Recently, Gillespie and Lim [13] have computed Franck-Condon factors for $S_1 \rightarrow S_0$ internal conversion in simple aliphatic ketones as a function of excitation energy in S_1 and a typical result is shown in Fig. 11. This was calculated assuming that the ground-state-excited-singlet-state electronic energy separation $\Delta E_{S_0-S_1} = 30\,000\text{ cm}^{-1}$, $\omega''_{C-O} = 1800\text{ cm}^{-1}$, $\omega'_{C-O} = 1300\text{ cm}^{-1}$ and $\Delta R_{C-O} = 0.12\text{ \AA}$ and has been normalized to the highest energy data point for excess non-radiative decay over that for the zero point level of

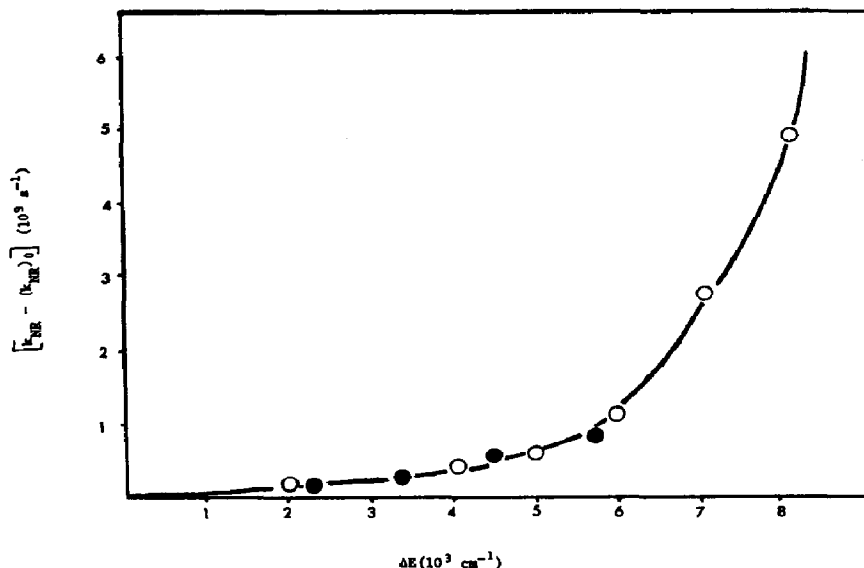


Fig. 11. Non-radiative decay of the singlet state of TFA as a function of excess vibrational energy in S_1 : ○ k_{NR} for initially excited singlet state from fluorescence excitation study [14]; ● values of k_D from this study assuming $k_S = 2 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$; solid curve, computed for internal conversion of ketone by Gillespie and Lim [13].

S_1 obtained from a recent fluorescence excitation study using very sensitive single photon counting techniques [14]. The plot shows that only for excess energies above 6000 cm^{-1} does internal conversion become the dominant mode of decay, and in the present study excess energies are below this. Moreover, the analysis in Fig. 11 is based upon the assumption that the rate constant for $S_1 \rightarrow T_1$ intersystem crossing is independent of excitation energy. In HFA Hackett and Kutschke [9] have shown that k_{ISC} may in fact increase substantially with excitation energy and thus the experimentally determined excess non-radiative decay shown in Fig. 11 may not be attributable solely to internal conversion. However, within the rather broad limits of experimental error, it can be seen from Fig. 11 that the present values of k_{NR} , those obtained from fluorescence excitation spectra and those obtained by calculation assuming excess non-radiative decay to be accounted for by internal conversion are in agreement.

5.4. Production of biacetyl

It is evident from Fig. 4 that biacetyl is produced in the photolysis of TFA and that, as the concentration of the diketone product increases, the triplet state of TFA is quenched leading to sensitized emission from the biacetyl. There is no spectral evidence for the formation of hexafluorobiacetyl, which would perhaps result from reaction (17) and is the decomposition mode favoured by Sieger and Calvert [5]. The present results indicate that reaction (18) is a much more likely decomposition step:



The quantum yield of biacetyl formation from 120 Torr TFA irradiated at 302.5 nm was found by monitoring the intensity I_S of the produced biacetyl phosphorescence (sensitized by TFA) with time t and relating I_S^{-1} versus t^{-1} (Fig. 5) to the Stern–Volmer slope obtained by the sensitization of added biacetyl phosphorescence by TFA, *i.e.* I_S^{-1} versus reciprocal biacetyl concentration (Fig. 6). In this manner the rate of production of biacetyl could be found. Knowing the rate of absorption of light, the quantum yield of biacetyl formation was thus found to be 0.15 ± 0.03 under these conditions.

5.5. Quenching rate constants

For quenching of TFA phosphorescence by buta-1,3-diene, *cis*-but-2-ene, and oxygen the usual Stern–Volmer relationship (19) is used, where $(\Phi_P)_0$ is the measured phosphorescence yield of TFA in the absence of additive, Φ_P that at any concentration $[Q]$ and K'_Q the usual parameter $k_Q\tau_0$:

$$(\Phi_P)_0/\Phi_P = 1 + K'_Q[Q] \quad (19)$$

From the results obtained in Fig. 3 the values of K'_Q shown in Table 3 were obtained. In the case of biacetyl as a quencher the weak TFA phosphorescence was masked by the much more efficient diketone luminescence, and the alternative approach of plotting reciprocal biacetyl phosphorescence yield Φ_S^{-1} against reciprocal biacetyl concentration $[\text{BiA}]$ (Fig. 6, eqn. (20)) was employed to obtain the value of K'_Q given in Table 3:

$$\Phi_S^{-1} = \frac{1}{\Phi_{\text{ISC}}} 0.15 \left(1 + \frac{1}{K'_Q[\text{BiA}]} \right) \quad (20)$$

TABLE 3

Quenching parameters for TFA phosphorescence

Quencher	K'_Q (l mol^{-1}) (= $k_Q\tau_0$)	Relative k'_Q ^a
<i>Mercury absent</i>		
Biacetyl	2.2×10^5	1.3
But-2-ene	1.70×10^5	(1.00)
<i>Mercury present</i>		
But-2-ene	1.14×10^5	(1.00)
Buta-1,3-diene	9.5×10^5	8.4
Oxygen	1.6×10^5	1.4

λ_{ex} , 312 nm; TFA pressure, 120 Torr; temperature, 20°C.

^a Relative to that for but-2-ene.

Here $\Phi_{ISC} = 1.00$ (see earlier) is the quantum yield for $S_1 \rightarrow T_1$ intersystem crossing in TFA, 0.15 is the quantum yield of phosphorescence from biacetyl vapour and vibrational relaxation is assumed to be complete at the pressure of TFA employed.

It can be seen from Table 3 that for the single additive investigated under mercury-free and mercury-saturated conditions the ratio of quenching parameters is as has been found in other studies [4, 5]:

$$\frac{K'_Q}{(K'_Q)_{Hg}} = 1.5$$

It can be seen from Table 3 that if buta-1,3-diene quenches TFA triplet with unit collision efficiency, the rate constant for quenching by O_2 is 1/9 of this within the limits of experimental error as expected on the basis of the spin statistical factor for the reaction



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