Preliminary Note

The phosphorescence of 1,1,1-trifluoroacetone*

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The phosphorescence of 1,1,1-trifluoroacetone (TFA) was first reported by Auloos and Murad [1]. It was shown that the relative phosphorescence yield increased with increasing pressure to a maximum value and thereafter decreased with increasing pressure. This behaviour was interpreted as evidence for competitition between collisional deactivation of the vibrationally-excited triplet state of TFA and self quenching of that state. These results were confirmed in a later study [2]; however, it was suggested that the "self-quenching" reaction could be ascribed to the presence of small amounts of a triplet-quenching impurity as the phosphorescence decay time of TFA had been shown to be pressure independent (τ_ρ = 292 ± 30 μs) [3].

A recent study of the phosphorescence of TFA excited by a nitrogen laser found that τ_ρ was pressure dependent ($\tau_\rho^{-1} = 1.7 \times 10^4$ s^{-1} + (4.6 ± 0.5) $\times 10^6$ $M^{-1} \times$ [TFA]) [4] and suggested that TFA excited triplet undergoes self quenching. The pressure-independent decay observed earlier [3] was attributed to emission from a dicarbonyl compound formed by photolysis of TFA. In order to clarify this qualitative difference in behaviour we have reinvestigated the phosphorescence lifetime of TFA as a function of TFA pressure.

Phosphorescence lifetimes were determined at 21 °C using the 2 mJ nitrogen laser flash apparatus previously described [5]. The results indicated a slight pressure dependence. The least-squares analysis of the data yields

$$\tau_\rho^{-1} = (3.80 \pm 0.02) \times 10^3 \text{ s}^{-1} + (2.67 \pm 0.1) \times 10^5 \, M^{-1} \, \text{s}^{-1} \times \text{[TFA]}$$

Identical results were obtained from single-pulse experiments and by signal averaging the results from 128 pulses. The phosphorescence decay was also independent of incident laser energy.

We have made a least-squares analysis of the data reported in the previous study [4], which shows the phosphorescence decay time of TFA at zero pressure to be 119 (+125, −30) μs. It would seem that since previously reported zero-pressure decay times [3, 4] and that obtained in the present study are within experimental error, the observed pressure quenching is

is due to an impurity. A calculation shows that 0.04% of an impurity able to quench triplet TFA with a rate constant of 2×10^{10} M^{-1} s^{-1} would account for the behaviour reported earlier [4].

This conclusion is supported by two further pieces of information. We have found that the quantum yield of phosphorescence measured by steady-state illumination at 335, 310 and 285 nm increases monotonically with increasing pressure up to 300 Torr of TFA. Also, the quantum yield of carbon monoxide production during 313 nm photolysis of TFA at 25 °C is quenched by mercury [6] to exactly the same degree as was the pressure-independent phosphorescence decay reported earlier [3].

It has been demonstrated that dicarbonyl compounds are formed during TFA photolysis [2, 7]. Since it has been suggested that such compounds accounted for the pressure-independent phosphorescence decay [4] we have further investigated their production using a rotating-can phosphorimeter. The phosphorimeter was designed to discriminate against TFA emission and to favour longer-lived emission. It was observed that a long-lived emission was produced during TFA photolysis ($\tau_\rho \cong 1.5$ ms) and that the rate of increase in the intensity of this emission, normalized for the number of photons absorbed, increased dramatically at wavelengths below 310 nm. This behaviour may account for the qualitative differences in the photolysis products observed by Sieger and Calvert [8] and Davidowicz and Patrick [7]. We are currently investigating these phenomena further in order to elucidate the photophysical and photochemical behaviour of TFA, and the nature of the excited-state potential-energy surfaces of this molecule.

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