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Short Communication

Laser-induced time-resolved phosphorescence of oxalyl fluoride ^3A_u molecules

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1. *Introduction*

There has been considerable interest recently in the dynamics of electronically excited dicarbonyls [1 - 8]. We have been interested in the photochemistry and photophysics of several different dicarbonyls, and have recently reported on our work with the dynamics of ^3A_u biacetyl [4] and ^3A_u 2,4-pentadione [5]. We have also been investigating the dynamics of electronically excited halogenated carbonyls (COF_2 and COFCl) and the dicarbonyl $(COF)_2$. We report here our preliminary findings for the laser-induced time-resolved quenching of the ^3A_u state of $(COF)_2$.

2. *Experimental*

A CMX-4 flashlamp-pumped dye laser operating with rhodamine 6-G was frequency doubled to yield 298 nm radiation having a bandwidth of 5.4 cm^{-1}. The pulsed output energy was about 0.1 mJ and had a pulse duration of about 1 μs. The fundamental frequency was filtered out before the laser beam entered the Pyrex fluorescence cell of radius 4 cm which was fitted with Suprasil windows. A RCA C31034A photomultiplier tube was positioned perpendicular to the laser beam and appropriate beam apertures were positioned in the cell to discriminate against scattered light. A Corning 5-59 filter was placed in the $f/1.5$ collection optics and phosphorescence in the 340 - 520 nm spectral region was monitored. A Pacific Photometric model 2A44 preamplifier in the tube housing fed the signal into a Tektronix 7844 oscilloscope and the resulting phosphorescence intensities were photographed. The decays were found to be single exponentials.

The oxalyl fluoride from PCR Research Chemicals Inc. was frozen at liquid nitrogen temperature and was pumped on to remove volatile impurities. The argon and oxygen were both the Matheson ultrahigh purity products and were used without further purification. Gas mixtures were circulated for 2 min prior to observation to ensure mixing with a Metal Bellows pump. A grease-free mercury-free vacuum system was fitted with MKS Baratron 10 and 1000 Torr pressure gauges. The laser was blocked between observations to prevent photolysis and was attenuated at higher pressures to prevent photomultiplier saturation.

3. Results and discussion

The phosphorescence decay in pure oxalyl fluoride for excitation at 298 nm and 22 °C was recorded from 0.014 to 400 Torr and the observed pressure dependence (0.3 - 8.0 Torr) is shown in Fig. 1. Many of the low pressure data points have been omitted to facilitate clarity in graphical display. From the low pressure data (0.3 - 8.0 Torr) the collision-free lifetime was found to be τ_0 = 1.43 ± 0.21 ms. All error limits for our data are for 95% confidence limits. This compares very closely with literature measurements for the collision-free lifetime of biacetyl: 1.70 ± 0.08 ms [4]; 1.52 ± 0.17 ms [1]; 1.65 ± 0.2 ms [9]; 1.40 ms [10]; 1.8 ms [2]; 1.7 ms [11]; 1.8 ms [12]; and 1.87 ± 0.1 ms [3]. This is also comparable with our recent measurement of 1.8 ms [5] for 1,4-pentadione but is significantly shorter than the literature value of 3.29 ± 0.1 ms for *trans*-glyoxal [13]. It should be noted here that oxalyl fluoride is the perfluorinated analog of glyoxal. Further work on the spectroscopy and zero pressure quantum yield of $(COF)_2$ will be necessary to evaluate the relative importance of the first order radiative and non-radiative decay constants.

A least squares fit of the 0.3 - 114 Torr data yields a self-quenching rate constant $k\{(COF)_2\} = (1.05 \pm 0.05) \times 10^7$ l mol^{-1} s^{-1}. No curvature was observed up to 400 Torr. The Stern–Volmer plots at 22 °C for O_2 and Ar are depicted graphically in Fig. 2. The $(COF)_2$ pressure was held constant at 5.00 Torr. The rate constants determined by least square fits were $k(Ar) = (2.71 \pm 1.28) \times 10^4$ l mol^{-1} s^{-1} and $k(O_2) = (1.40 \pm 0.03) \times 10^8$ l mol^{-1} s^{-1} and are representative of the high efficiency of $O_2(^3\Sigma^-)$ as a triplet quencher. Extreme care was taken to avoid any O_2 contamination in the Ar experiments because of the large differences in the O_2 and Ar quenching

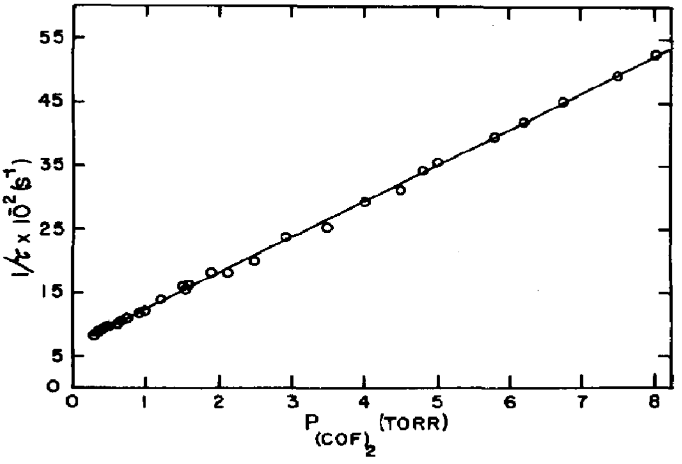

Fig. 1. Stern–Volmer plot for $(COF)_2$ self-quenching at 22 °C. Excitation λ = 298 nm.

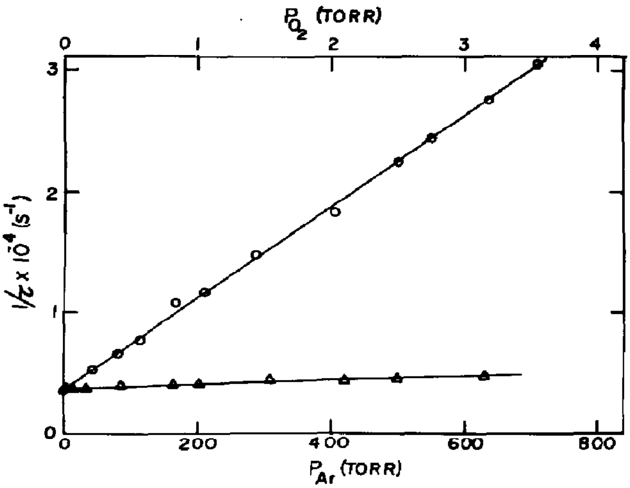

Fig. 2. Stern–Volmer plots at 22 °C for O_2 (circles) and Ar (triangles). $P\{(COF)_2\}$ = 5.00 Torr. Excitation λ = 298 nm.

efficiencies. For the Ar quenching data we have gone to very high pressures (633 Torr) and over this pressure range one can detect quenching by Ar. Our measurement for the quenching rate constant $k(O_2)$ of $(COF)_2$ ^3A_u molecules by O_2 of $(1.40 \pm 0.05) \times 10^8$ l mol^{-1} s^{-1} compares as follows with literature values for other dicarbonyls: 2,4-pentadione, 6.6×10^8 [5]; biacetyl, 5.2×10^8 [4]; and glyoxal, 5.59×10^7 l mol^{-1} s^{-1} [13]. Further work will be needed to characterize the quenching dynamics of ^3A_u oxalyl fluoride molecules properly.

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