

Short Communication

Laser-induced time-resolved phosphorescence of 2,4-pentadione (a tautomeric system)*

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(Received November 4, 1977)

The quenching reactions of electronically excited α -diketones have been reported frequently in the literature. In particular biacetyl has been studied by numerous workers because of its utility in photosensitized emission studies. However, there has not been much attention given to the quenching of excited β -diketones. Tautomerism can occur easily with β -diketones and thus the self-quenching reaction of the triplet state of these molecules may be enhanced by the participation of the unsaturated enolic form as a quencher. For biacetyl it should be noted that at 25 °C there is no observable self-quenching of the 3A_u state [1 - 4]. Thus, we have undertaken the present investigation to see whether 2,4-pentadione (PD) exhibits self-quenching and to compare its dynamical properties with other diketones.

1. Experimental

A Phase-R Model 2100B coaxial flashlamp-pumped dye laser was operated with Pilot "386" dye in a flat-flat cavity. The lasing wavelength was 3891 Å with an FWHM of 40 Å. The laser beam was passed through an appropriate arrangement of spatial filters and neutral density filters before entering the 20 cm diameter and 30 cm length cylindrical quartz photolysis cell. Emission was viewed at right angles to the cell with an RCA 7265 photomultiplier tube. A filter transmitting at λ greater than 4500 Å was placed in front of the photomultiplier tube to discriminate against scattered laser light. Neutral density filters were used to reduce the intense laser beam to ensure that the concentration of triplet PD molecules was low enough to avoid triplet-triplet annihilation reactions such as those noted for intense laser irradiation of biacetyl [1]. All decays noted were single exponentials. The output from the photomultiplier tube was properly terminated at the input of a Tektronix Model 556 oscilloscope and the displayed decay trace was photographed using high speed Polaroid film. A mercury-free grease-free

*Work performed under the auspices of the United States Energy Research and Development Administration.

vacuum system fitted with the appropriate pressure gauges was used to handle the gaseous components. The PD was the high purity product of the Eastman Kodak Company and the O₂ and Ar were the high purity products of Matheson and Airco, respectively. The PD was bulb-to-bulb distilled and the middle fraction was retained for experiments. The other gases were used without further purification.

2. Results and discussion

Figure 1 displays a Stern–Volmer plot for PD self-quenching. Figure 2 depicts the Stern–Volmer plots for O₂ and Ar quenching. Note in Fig. 1 that PD does exhibit self-quenching and the quenching rate constant is estimated to be $2.2 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$. The collision-free lifetime for the emission is 1.8 ms. In Fig. 2 it is noted that Ar does not have a noticeable quenching effect at all on the emission from electronically excited 2,4-pentadione (*PD). However, *PD is quenched by O₂ relatively efficiently and its quenching constant is estimated to be $6.6 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$. The relative quenching rates by Ar and O₂ would support the emission as being phosphorescence.

Biacetyl ³A_u molecules do not exhibit self-quenching at room temperature as do the ³PD molecules. One possibility which would tend to lead to an increased self-quenching efficiency for ³PD is that PD displays tautomerism in which 91 - 93% of PD is present in the enolic form in the gas phase at 25 °C [5]. Even though the ³PD may conceivably have a lower triplet level than enolic PD, the formation of a charge-transfer complex between the π systems of enolic PD and ³PD could still facilitate a reasonable quenching efficiency, as has been noted in other triplet quenching reactions [6, 7].

The magnitude of the quenching constant of ³PD by O₂, $6.6 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$, compares closely with rate constant values of $5.6 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ [8] and $5.4 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ [9] reported for quenching of biacetyl ³A_u molecules. It may be that the detailed mechanistic quenching reaction

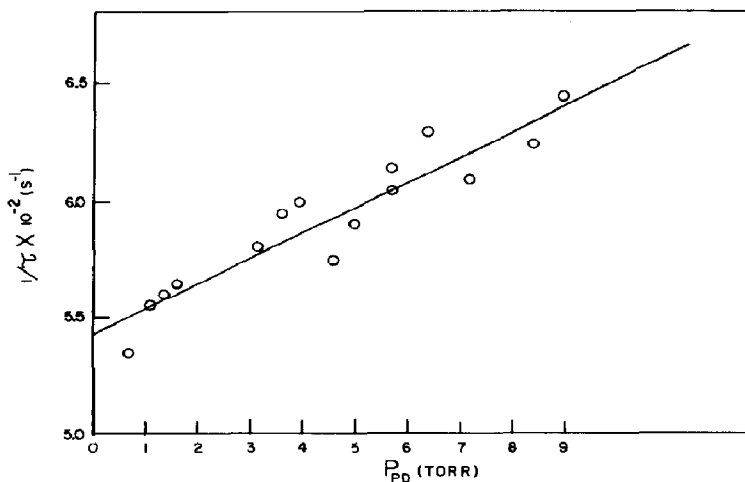


Fig. 1. A Stern–Volmer plot at 25 °C and $\lambda = 3891 \text{ \AA}$ for PD self-quenching.

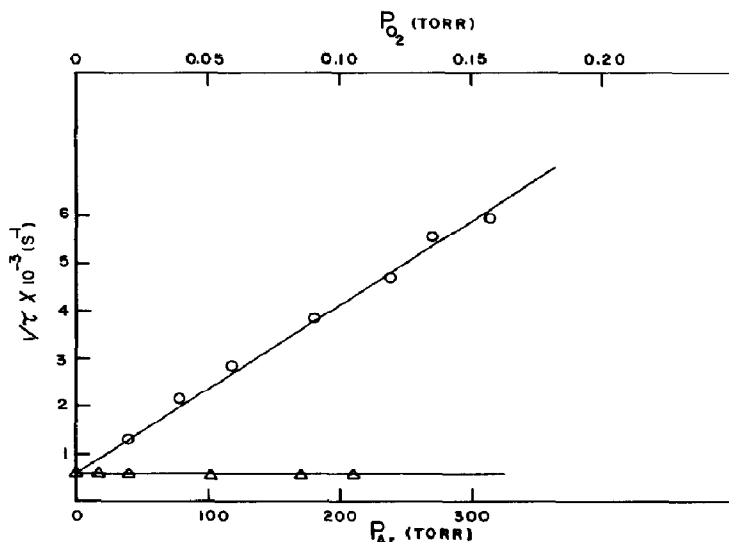


Fig. 2. A Stern-Volmer plot at 25 °C and $\lambda = 3891 \text{ \AA}$ for quenching of electronically excited PD by O_2 (circles) and Ar (triangles); $P_{PD} = 5.70 \text{ Torr}$.

by O_2 is quite similar for 3PD and 3A_u biacetyl molecules. There are no known chemical quenching routes involving Ar, and the quenching rate by a physical energy-transfer mechanism generally correlates with the energy level separation of the collision partners. The fact that Ar collisions are ineffective in relaxing triplet PD indicates that this triplet energy level is relatively low-lying. Further work is needed in the gas phase to understand properly the excited state dynamics of compounds that can undergo tautomerism.

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