LASER PHOTOLYSIS OF ACETONE AT 308 NM

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Summary

Acetone was excited by an XeCl laser pulse at 308 nm. Using pressures in the range 1 - 50 Torr, at room temperature, the pressure dependence of various decay components of the emission was examined, and the rate constants for quenching of these components with acetone itself and with O_2 were determined. A simple model that accounts satisfactorily for the experimental data was developed.

1. Introduction

Acetone is one of the most thoroughly studied molecules of the past several decades. In particular, the photochemistry of acetone has been extensively studied [1 - 4], and its mechanism of decomposition is well established. At room temperature the $\pi^* \leftarrow n$ absorption spectrum has no discernible structure. Baba and Hanazaki [5] obtained the jet-cooled spectrum of acetone vibrationally resolved, and they determined the origin of the $S_1(n, \pi^*)$ state. The energy of the 0-0 band was determined to be 30 435 cm^{-1}. The fluorescence dynamics of acetone in the vapour phase and in the pressure range 10^{-4} - 1 Torr have been studied by Greenblatt *et al.* [6] and Copeland and Crosley [7] at room temperature, and by Anner *et al.* [8] after cooling by supersonic expansion. These studies in the low pressure regime showed several interesting and unexpected emission and collisional phenomena. In particular, Greenblatt *et al.* observed the existence of up to four decay components in the fluorescence emission of acetone at pressures above 0.5 mTorr. They assigned these four components as follows. The fastest component is due to dephasing of the initially excited state, forming a quasi-stationary eigenstate. The second component is due to the radiative decay of the eigenstates, the third to decay of triplet states not directly coupled to the initially excited singlet states, and the last to the vibrationally thermalized triplet state. Copeland and Crosley [7] observed the same components and examined in more detail the third decay component or

"hot" triplet component. They gave an alternative interpretation to that of Greenblatt *et al.* with respect to the radiative mechanism involving these hot triplet states.

We have studied the emission characteristics of acetone in the pressure range 1 - 50 Torr, at room temperature, following pulsed laser excitation at 308 nm. Our aim was to study the above-cited new emission phenomena in the medium pressure range in order to obtain experimental data that could clarify the above controversy and give some new insight into the complicated relaxation mechanism of acetone. A deeper understanding of acetone photolysis is of great interest not only for its own sake but also in connection with studies on the decomposition of tetramethyldioxetane [9], a compound that generates electronically excited acetone upon decomposition and which has received thorough attention in the last few years.

2. Experimental details

Acetone vapour was irradiated by the output of a home-made XeCl laser of the "automatic" pre-ionization type, similar to that described by Kearsley *et al.* [10]. The maximum laser energy was 26 mJ per pulse, the repetition rate was 1 Hz and the pulse length was about 15 ns. The laser beam was focused by a Spectrosil lens of focal length 50 cm into a horned fluorescence cell 150 mm long and 50 mm in diameter equipped with a Spectrosil input window.

The fluorescence emitted at right angles to the laser beam was imaged by an $f/2$ BK-7 lens onto the entrance slit of a 0.2 m Applied Photophysics monochromator and was viewed by an EMI 9816QB photomultiplier. The photomultiplier signals were collected and displayed by a Tektronix 468 digital storage oscilloscope. The signal was averaged until an acceptable signal-to-noise ratio was observed.

The BK-7 lens acts as a filter for the 308 nm scattered laser radiation. Further discrimination against scattered light was provided by the monochromator, which is usually set to pass a bandwidth of about 10 nm. The level of the stray light was obtained by evacuating the cell and using the same excitation and observation parameters. The scattered light signal was orders of magnitude weaker than that obtained with acetone in the cell.

Pressures were measured using an MKS Baratron type 221A capacitance manometer. The acetone was used pure, or mixed with different gases in the quenching experiments. Repeated irradiation of the same sample with several hundred shots results in no observable effect on the signal intensity or lifetime. Because of this, all the experiments were performed without employing a gas flow.

Spectroscopic grade chemicals were used. Acetone was obtained from Scharbau. Liquids were degassed prior to use. Gases were used as received, all with a stated purity exceeding 99.9%.

3. Results

Prior to the study of the fluorescence dynamics of acetone we obtained the spectral distribution of the emission intensity. The emission spectra were taken with 196 mTorr acetone. The intensity distribution peaks at about 430 nm. In agreement with previous studies (see, for instance, Fig. 4 of ref. 11) the emission maximum is shifted to about 400 nm when up to 250 Torr O_2 are added to suppress the phosphorescence emission. This shorter wavelength emission, which is very weak compared with the total emission, is
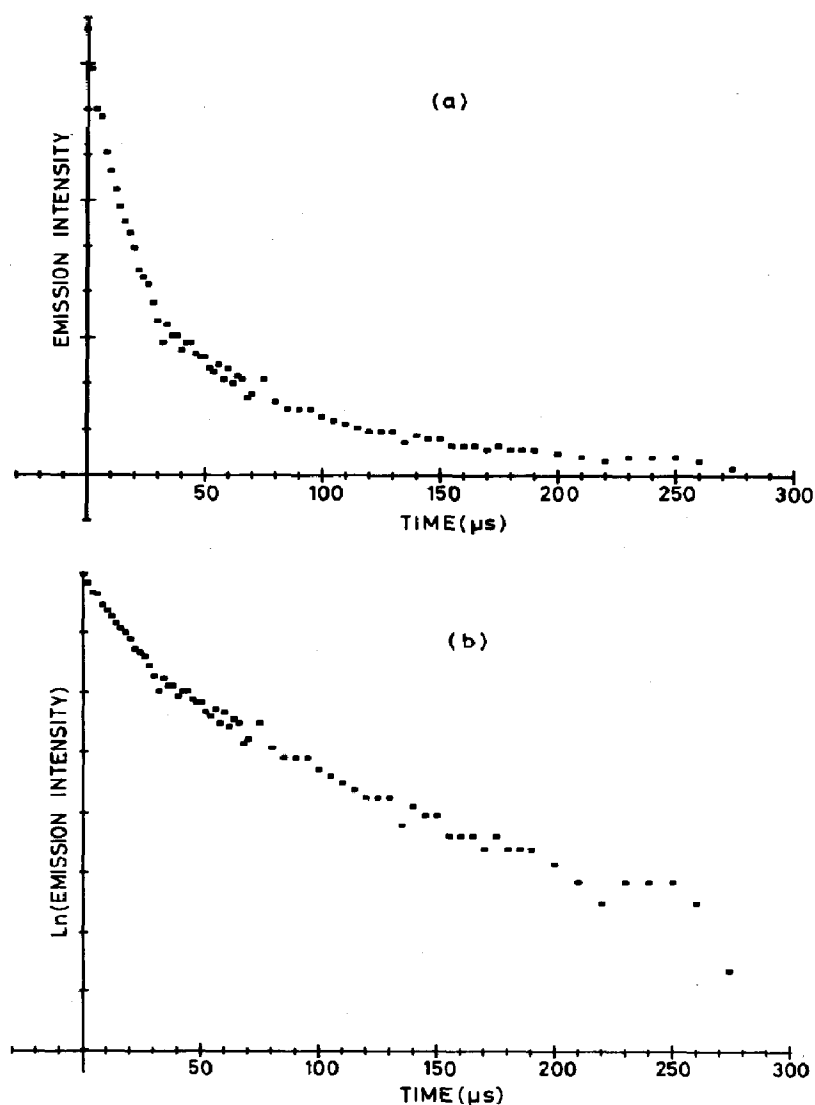

Fig. 1. Typical decay plots for 2 Torr acetone: (a) experimental signal; (b) logarithm of the signal (used to determine decay times). The points are taken from oscilloscope traces of the output of the photomultiplier.

ascribed to fluorescence emitted from the first excited singlet with a lifetime of a few nanoseconds [12]. In the light of these results our real-time studies of the emission dynamics of acetone were performed with the monochromator set at 430 nm with a bandpass of about 10 nm. Our detection system did not have sufficient time resolution for studying the dynamics of the fast component of the emission, so we limited ourselves to the study of the slower components.

At pressures below 5 Torr the emission consisted mainly of two clearly distinct components, each with a characteristic lifetime and pressure dependence. The fastest component has a lifetime of about 30 μs, and we shall designate this component I. The slow component, component II, has a lifetime of about 200 μs. At pressures above 5 Torr only component II is observed. Figure 1 shows a typical decay plot for 2 Torr acetone.

Each component has a distinctive pressure dependence. Component I is quenched by acetone itself with a rate constant of $(5.2 \pm 0.5) \times 10^{-3} \mu s^{-1}$ Torr^{-1} (obtained from a plot of inverse lifetime *versus* acetone pressure with only three experimental points but with a correlation coefficient of 0.995). The lifetime of component II decreases with increasing pressure below 5 Torr acetone, to reach an almost constant value of about 150 μs at higher pressures.

In addition to acetone self-quenching the effect of O_2, helium and N_2 quenching was studied for 2 Torr acetone and different amounts of added quencher. Figure 2 shows Stern–Volmer plots of the decay rate *versus* O_2 pressure for both component I and component II. For 2 Torr acetone, O_2 pressures higher than 0.03 Torr completely quenched component II. From these plots we calculated the quenching rate constant to be (0.48 ± 0.02) μs^{-1} Torr^{-1} for component I and $(2.4 \pm 0.1) \times 10^{-2} \mu s^{-1}$ Torr^{-1} for component II.

Addition of helium up to a pressure of 250 Torr had no effect on the decay rates of either component I or component II. Addition of N_2 up to pressures of 303 Torr had a small effect on both components. This effect, however, could be attributed to a small amount of O_2 present as an impurity in the N_2. In fact, a rough calculation shows that 0.05 mol.% O_2 in the gas used would suffice to account for the observed effect.

4. Discussion

Our longer lived component (component II) is easily identified as acetone thermal triplet phosphorescence, and its lifetime and pressure dependence agree well with previous measurements [1].

Component I can be identified with component III of Greenblatt *et al.* as originating from a hot triplet. In the investigation carried out in refs. 6 and 7 in the millitorr range a component with a typical decay time of about 5 μs was also observed. At the acetone pressures used in this work the decay time of this component is in the nanosecond range [5]. As stated previously,
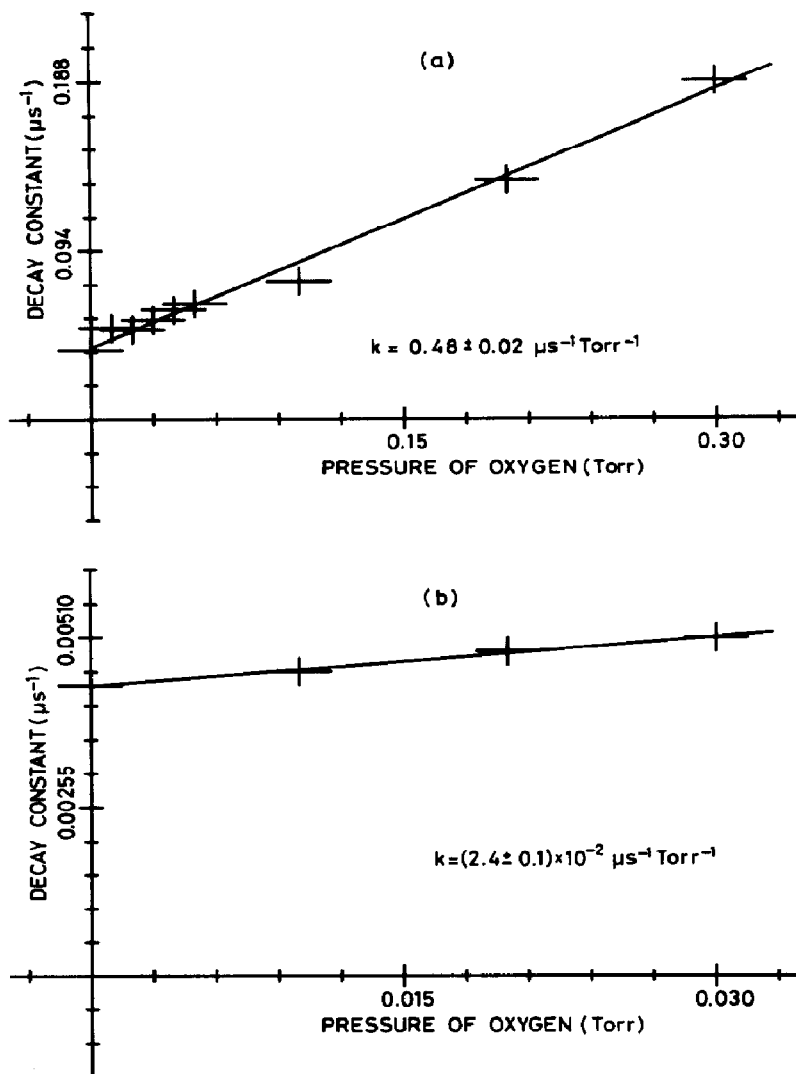
Fig. 2. Stern–Volmer plots of the decay rate *vs.* O_2 pressure: (a) component I; (b) component II. The error bars represent the standard deviation.

our detection system does not have sufficient temporal resolution to resolve this component.

We have elaborated a simple model that accounts satisfactorily for the photophysical behaviour of acetone in the pressure range employed in this work. The origins of the n, π^* singlet (S_1) and triplet (T_1) states of acetone are at 30 435 cm^{-1} and 27 300 cm^{-1} respectively [5, 13] above the ground electronic state S_0. As the average energy of acetone at room temperature is about 650 cm^{-1} [8], our 308 nm (32 468 cm^{-1}) photons excite the acetone to vibrational states of S_1 of energy 2600 cm^{-1}. These initially formed states are not pure singlet, but can be thought of as a superposition of zero-order states belonging to the singlet and triplet manifolds [13]. The mixed states

which contain a large degree of triplet character return to the ground state by light emission (giving rise to component II of Greenblatt *et al.*) or lose a small amount of energy by a weak collision transferring the system out of the mixed state into a hot triplet state. These levels either emit light (our component I) or are deactivated by collisions with other acetone molecules to the thermalized triplet (T_1) from which the phosphorescence (our component II) is emitted.

Our kinetic model consists of three levels (T_1^*, T_1 and S_0) including appropriate rate constants (radiative, decomposition and quenching) for each level (Fig. 3). In accordance with the mechanism discussed above for the appearance of the T_1^* state, this assumption seems to be justified because of the microsecond temporal range in which our experiments are performed.
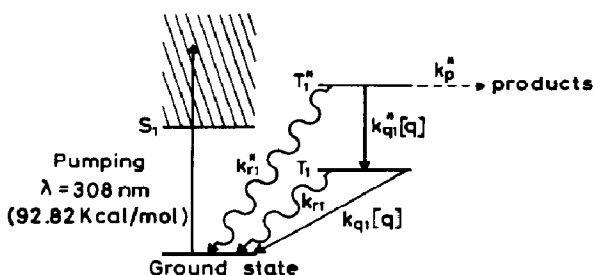

Fig. 3. Schematic diagram of the acetone energy levels relevant to our kinetic model. Wavy lines, radiative processes; full lines, non-radiative quenching processes; broken line, dissociation process.

As shown by Copeland and Crosley [7], at 91.5 ± 0.5 kcal mol^{-1} above the acetone ground state a rapid dissociation channel opens up. As the energy of the 308 nm excitation photons is 92.82 kcal mol^{-1}, in the model we have taken into account the decomposition of acetone from the hot triplet state. We have not considered the decomposition from the thermalized triplet state T_1 as there appears to be a barrier. The height of the barrier is not yet known for certain but it has been suggested that the Arrhenius activation energy is 5.7 kcal mol^{-1} for T_1 [3]. Dissociation of acetone has not been experimentally observed below 30 000 cm^{-1} [13].

The temporal evolution of the populations of the T_1^* and T_1 states is given by the equations

$$\frac{d[N_1^*]}{dt} = -k_{r1}^*[N_1^*] - k_p^*[N_1^*] - k_{q1}^*[q][N_1^*]$$

$$\frac{d[N_1]}{dt} = k_{q1}^*[q][N_1^*] - k_{r1}[N_1] - k_{q1}[q][N_1]$$

(1)

where $[N_1^*]$ and $[N_1]$ are the concentrations of the T_1^* and T_1 states respectively, k_{r1}^* and k_{r1} are their radiative rate constants, k_{q1}^* and k_{q1} are their

quenching rate constants, k_p^* is the decomposition rate constant of the T_1^* state and [q] is the concentration of the quencher.

The fluorescence intensity is given by

$$I \propto k_{r1}^* [N_1^*] + k_{r1}[N_1] \tag{2}$$

Integration of eqns. (1) and substitution into eqn. (2) yields

$$I \propto \frac{[N_1^*]_0}{k^* - k} [k_{r1}^*(k^* - k) \exp(-k^*t) + k_{r1}k_{q1}^*[q]\{\exp(-k^*t) - \exp(-kt)\}] \tag{3}$$

where

$$k^* = k_{r1}^* + k_p^* + k_{q1}^*[q]$$
$$k = k_{r1} + k_{q1}[q] \tag{4}$$

and $[N_1^*]_0$ is the initial concentration of T_1^* (it is assumed that initially $[N_1] = 0$).

This model reproduces satisfactorily our experimental results under the following conditions.

(1) The quenching rate constant k_{q1}^* is the experimental value of $5.2 \times 10^{-3} \, \mu s^{-1} \, Torr^{-1}$.

(2) The experimental "zero-pressure" extrapolated values for the lifetimes of the T_1 and T_1^* states yield

$$k_{r1} = 5 \times 10^{-3} \, \mu s^{-1}$$

$$k_{r1}^* + k_p^* = 3.2 \times 10^{-2} \, \mu s^{-1}$$

(3) The quenching rate constant k_{q1} for the T_1 state and the radiative rate constant k_{r1}^* for the T_1^* state are the adjustable parameters of this model. The values for these constants that produce the best fitting are $k_{q1} = 1 \times 10^{-4} \, \mu s^{-1} \, Torr^{-1}$ and $k_{r1}^* = 1 \times 10^{-2} \, \mu s^{-1}$. Changes in these values of 10% or more result in a lack of agreement between the calculated curves and the experimental curves.

(4) The T_1^* and T_1 radiative rate constants are different, the T_1^* rate constant being shorter. It is not possible to fit the experimental results satisfactorily with the assumption that these constants are equal. This is in agreement with the interpretation suggested by Greenblatt et al. [6] and contrary to the suggestion of Copeland and Crosley [7] that the hot triplet has the same radiative lifetime as T_1, the measured shorter T_1^* lifetime being caused by collisional transfer back into the strongly coupled triplet levels.

Figure 4 shows a typical theoretical curve and its comparison with experiment. In spite of the simplicity of the model, the agreement with experiment is quite acceptable.

One interesting aspect of our experimental results is the different quenching effect of O_2 on the T_1^* and T_1 states, because, in principle, there
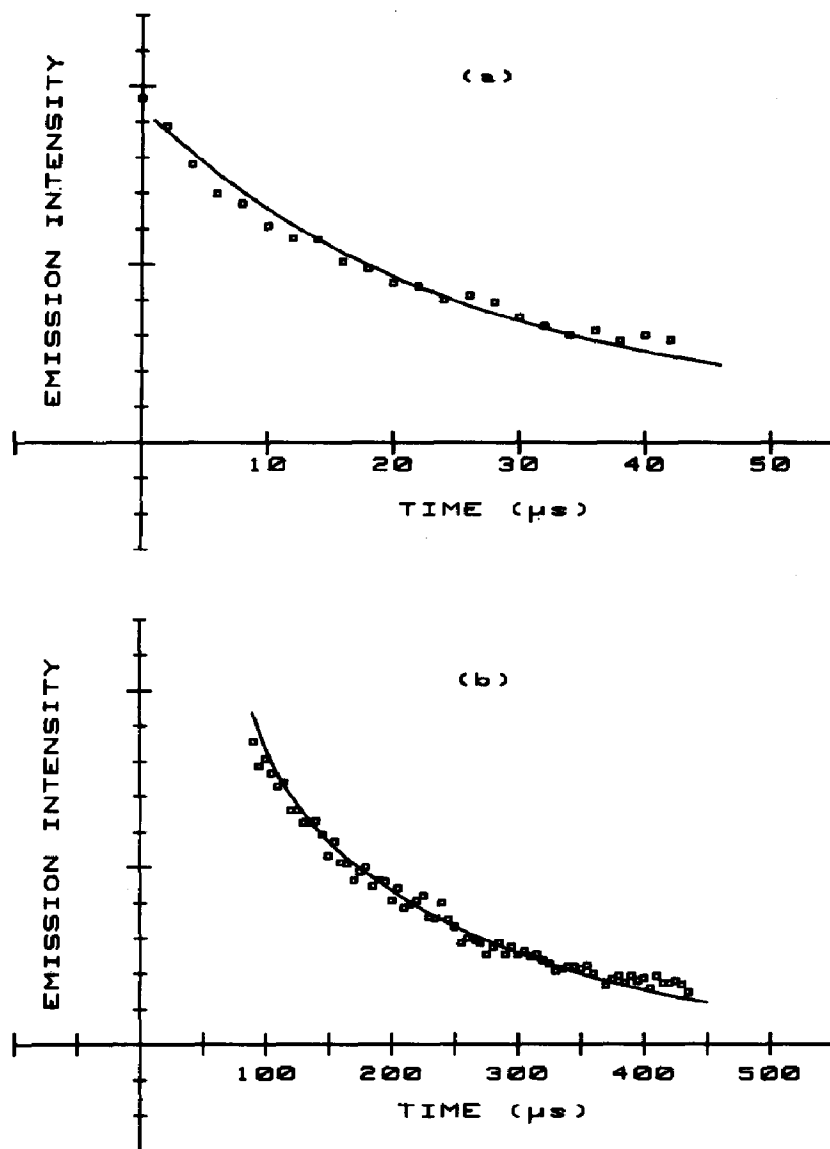
Fig. 4. Theoretical decay curve and its comparison with experiment: (a) expanded initial part; (b) long-time behaviour. The acetone pressure is 2 Torr. Open squares, experimental points; full curve, theoretical calculation.

is no reason to believe that O_2, with its ground triplet state, will distinguish between a thermalized triplet and its vibrationally excited counterpart. Furthermore, N_2 does not seem to have any noticeable effect on either the T_1^* or the T_1 state, whereas one would expect some effect on T_1^* if this were a vibrationally excited state of T_1. Both results taken together could be a further indication that the T_1^* state is not pure triplet but is a mixed state having a partial singlet–partial triplet character, as suggested by Haas et al. [14].

References

1 H. E. O'Neal and C. W. Larson, *J. Phys. Chem.*, *73* (1969) 1011.
2 R. B. Cundall and A. S. Davied, *Proc. R. Soc. London, Ser. A*, *290* (1966) 563.
3 A. J. C. Nicholson, *Can. J. Chem.*, *61* (1983) 1831.
4 E. K. C. Lee and R. S. Lewis, *Adv. Photochem.*, *12* (1981) 1.
5 M. Baba and J. Hanazaki, *Chem. Phys. Lett.*, *103* (1983) 93.
6 G. D. Greenblatt, S. Ruhman and Y. Haas, *Chem. Phys. Lett.*, *112* (1984) 200.
7 R. A. Copeland and D. R. Crosley, *Chem. Phys. Lett.*, *115* (1985) 362.
8 O. Anner, H. Zuckermann and Y. Haas, *J. Phys. Chem.*, *89* (1985) 1336.
9 S. Ruhman, O. Anner and Y. Haas, *Faraday Discuss. Chem. Soc.*, *75* (1983) 239.
10 A. J. Kearsley, A. J. Andrews and C. E. Webb, *Opt. Commun.*, *31* (1979) 181.
11 P. Lechtken and H.-Ch. Steinmetzer, *Chem. Ber.*, *108* (1975) 3159.
12 D. A. Hansen and E. K. C. Lee, *J. Chem. Phys.*, *62* (1975) 183.
13 Y. Haas, *Adv. Chem. Phys.*, *47* (1981) 713.
14 Y. Haas, S. Ruhman, G. D. Greenblatt and O. Anner, *J. Am. Chem. Soc.*, *107* (1985) 5068.