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Short Communication

Oscillatory reactions observed in flash photolysis — an artefact?

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A strongly damped oscillatory decay curve in a flash photolysis experiment has recently been reported by Kemp and Martins [1] who were unable to give a mechanistic explanation of this behaviour. We have also frequently observed such damped oscillations in flash photolysis and we have been able to show unequivocally that these were artefacts. Although other workers have also observed this phenomenon [2], to the best of our knowledge no reports have been published. Micheau *et al.* [3] have shown that damped oscillations can be explained as a consequence of biphotonic consecutive photoreactions under steady irradiation. Since artificial oscillations may lead to serious misinterpretations of experimental data, it seems worthwhile to describe this phenomenon in some detail.

In classical flash photolysis cylindrical cells are usually used with broad band excitation perpendicular to the analysing beam. If the absorbance of the cell is not uniformly low at all wavelengths of the exciting light, then the concentration of the photoexcited species will not be uniformly distributed across the cell diameter and fast radiationless processes will produce a spatial non-equilibrium state with respect to temperature and pressure. This may result in the production of a sound wave which will make the cell act like a lens with an oscillating focal length.

Figure 1 shows an example of this effect. The sample was a solution of 6.7×10^{-4} M *o*-naphthoquinone diazide in methanol. The experimental

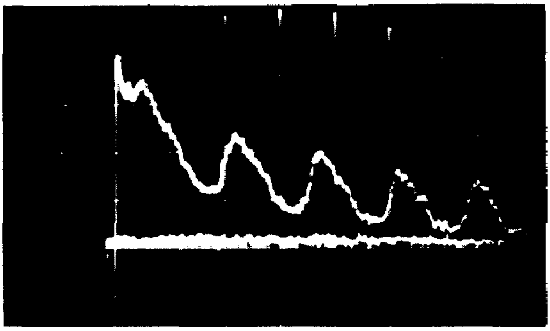

Fig. 1. Damped oscillatory flash photolysis signal from *o*-naphthoquinone diazide (see text).

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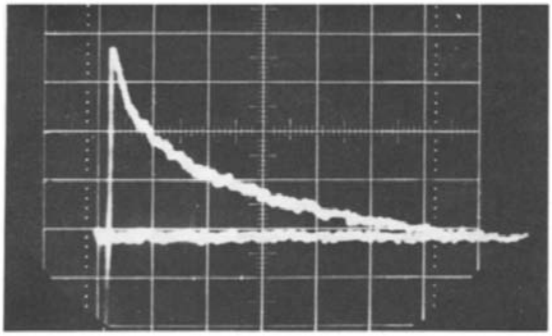
conditions were as follows. 1 kJ of electrical energy was discharged in two xenon flash tubes of length 15 cm arranged in series in a double elliptical reflector with semiaxes 60 and 25 mm long. A 10 cm cell of diameter 1 cm was used and the time base was 200 μs per major division. Figure 2 shows a trace obtained from a sample of the same compound at half the concentration but using a filtered excitation flash (Schott filter UG 2) and enhanced ordinate sensitivity to obtain approximately the same signal height.

Figure 3 shows a trace recorded by a piezoelectric detector mounted at the end of the cell. The conditions were the same as those for Fig. 1. Very similar curves were recorded on knocking on the other cell window. When the piezoelectric detector was attached to the side wall of the photolysis cell the signal was more than tenfold weaker and even more irregular showing that a longitudinal vibration was responsible for the light modulation. This is a little surprising because the initial pressure profile (the quinone diazide produces nitrogen) created by the absorbed flash light must be perpendicular to the cell axis. The shock wave generated in the flash tubes by the rapid electrical discharge was shown not to be responsible for the vibration of the cell by mechanically decoupling the cell from the reflector and recording the vibrations of the housing. The frequency of the damped oscillation depended on the cell length as well as on the solvent used. However, a simple relation between the oscillation frequency and the velocity of sound or the compressibility of the solvents could not be established. Although we did not perform a quantitative investigation of the complicated vibrational behaviour of the solvent-filled cylindrical cells, it seems clear that the light-induced initial transverse pressure profile is responsible for the generation of a sound wave which has the major component of its amplitude parallel to the cell axis.

Since light modulation by a vibrating cell can be observed at any wavelength it can easily be distinguished from a real oscillatory reaction. However, it is also possible, as we have observed, that only the first member of the pulse train has an easily detectable amplitude. If a real transient absorption



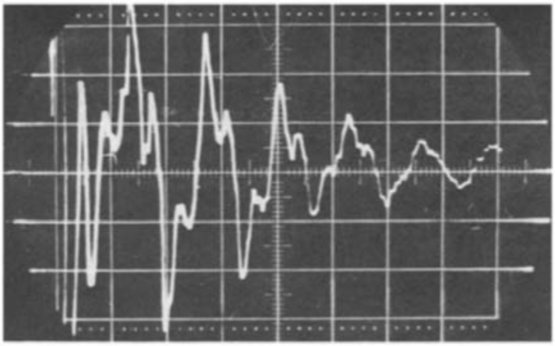


Fig. 2. Unperturbed signal from the same sample as in Fig. 1.

Fig. 3. Cell vibrations recorded using a piezoelectric detector after flash excitation under conditions identical with those in Fig. 1.

signal which has a decay rate of the same order of magnitude as the decay time of the first vibrational pulse is to be recorded, a spectral dependence of the signal amplitude will be observed but the apparent rate constant will be erroneous and will become a function of the cell length. Finally, if the lifetime of the transient is large compared with the inverse modulation frequency and if the modulation amplitude is small then it might be assumed to be noise. In this case the mean value of the recorded signal would not be the correct measure of the light intensity and erroneous rate constants would again be obtained. If the optical path is correctly adjusted any inhomogeneity of the sample can only decrease the observed light intensity, *i.e.* the lowest points of the pulse train should represent the kinetic curve (see Figs. 1 and 2) otherwise an apparent depletion may be observed.

In conclusion it should be noted that in order to avoid signal distortion as a result of mechanical vibration of the photolysis cell both the excitation energy and the sample absorbance should be kept as low as possible. A repetition of the experiments with a cell of a different length is recommended if perturbations by sound waves are suspected.

1 T. J. Kemp and L. J. A. Martins, in W. J. Gettins and E. Wyn-Jones (eds.), *Techniques and Applications of Fast Reactions in Solution*, Reidel, Dordrecht, 1979, p. 549.
2 V. Řehák and K.-P. Schumacher, personal communication, 1975.
3 J.-C. Micheau, S. Boué and E. Vander Donckt, *J. Chem. Soc., Faraday Trans. II*, *78* (1982) 39.