The Effect of a Non-uniform Concentration Profile on the Kinetic Interpretation of Flash Photolysis Experiments, with Particular Reference to Time-dependent Electron Spin Resonance Signals

Shamol Basu and Keith A. McLauchlan *
Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ

It is shown that non-uniform concentrations of free radicals produced in light pulses in solution affect the kinetic behaviour which is observed. Effects due to variation of detection sensitivity over an e.s.r. sample can be ignored.

In chemistry, excited states or free radicals are commonly produced by intermittent illumination techniques so as to obtain their decay kinetics from a suitable concentration measurement as a function of time. Most often the excited species are created with a non-uniform spatial distribution, for example as a result of the Beer–Lambert law of light absorption, and this can lead to false impressions of reaction orders and erroneous values of rate constants. Departure from anticipated rate laws may be difficult to recognise within the noise limitations of the observations. Here the problem is considered in the general case [1] but then particular attention is paid to e.s.r. methods of radical detection. These imply fairly strict limitations on optical cell dimensions since the sample sits in a microwave cavity, and also the sensitivity of detection of a radical varies with its position within the cavity. It is assumed that this sensitivity and the general instrument response are independent of time. Diffusion is taken to be too slow to affect the initial non-uniform distribution within the radical's lifetime.[2]

A train of light pulses is often used experimentally with signal averaging of successive decay curves to improve the signal-to-noise ratio of the observations. It is assumed that the experiment is designed sufficiently well that either the radical concentration decays to zero between pulses or that a pre-pulse signal is subtracted from the post-pulse one; failure to meet this requirement leads to large errors in interpretation.[3] It is further assumed that the observed species is formed within a time short compared with the pulse length and then decays. This neglects the time profile of the light flash and is reasonable when the pulse length is much shorter than the period over which this species is formed. This condition is usually met in flash experiments, but not in chopped beam ones.

Theory

A sample cell of dimension $2\delta x \times 2\delta y \times 2\delta z$ is considered with the origin at its centre; a uniform uni-directional beam of light pulses is applied along the z-direction. The concentration and molar absorption coefficient of the absorber are taken as c_A and ε_A respectively. Assuming the system obeys the Beer–Lambert law, the concentration of the active species produced in the absence of reaction is given by equation (1)

$$c(z,t) = c(-\delta z,t)\,\mathrm{e}^{-(z+\delta z)/\lambda} \qquad (1)$$

where $c(-\delta z,t)$ is the concentration at the front face of the cell at time t after the pulse and $\lambda = (2.303\varepsilon_A c_A)^{-1}$ is the ' optical length '.

From an nth order decay, equation (2) holds where k is the

$$c(z,t) = -kc^n(z,t) \qquad (2)$$

rate constant of the reaction. The time-dependent signal observed is simply expressed by equation (3) where α is a

$$S(t) = \frac{\alpha}{2\delta z}\int_{-\delta z}^{\delta z} c(z,t)\,\mathrm{d}z \qquad (3)$$

time-independent constant of proportionality of the apparatus and an expression for the concentration must be substituted from equation (1).

For a first-order reaction $c(z,t)$ is directly proportional to $c(z,0)$, the initial concentration following the pulse, and so the effect of substitution from equation (1) leaves the time-dependence of $S(t)$ unchanged. The reaction is observed to be first-order with its true rate constant [equation (4)] where

$$S(t) = \frac{\alpha}{\beta}(\mathrm{e}^{\beta} - 1)\,c(-\delta z,0)\,\mathrm{e}^{-kt} \qquad (4)$$

$\beta = 2\,\delta z/\lambda$, 2.303 times the absorbance. For other orders of reaction, from equation (2) we have equations (5) and (6).

$$c(z,t) = [c^{(1-n)}(z,0) - (1-n)kt]^{(1-n)^{-1}} \qquad (5)$$

$$S(t) = \frac{\alpha}{2\delta z}\int_{-\delta z}^{\delta z} \{[c(-\delta z,0)\,e^{-(z+\delta z)/\lambda}]^{(1-n)} - (1-n)kt\}^{(1-n)^{-1}}\,\mathrm{d}z \qquad (6)$$

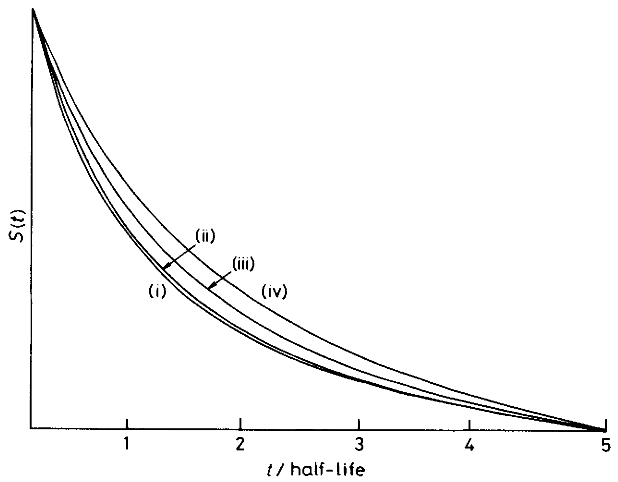
For a second-order reaction this yields equations (7) and (8) with $\tau = ktc(-\delta z,0) = t/t_{\frac{1}{2}}$, where $t_{\frac{1}{2}}$ is the half-life at the front of the cell.

$$S(t) = \frac{\alpha}{2\delta z}\int_{-\delta z}^{\delta z} \frac{c(-\delta z,0)\,e^{-(z+\delta z)/\lambda}}{1 + ktc(-\delta z,0)\,e^{-(z+\delta z)/\lambda}}\,\mathrm{d}z \qquad (7)$$

$$= -\frac{\alpha}{\beta}\frac{1}{\tau}\ln\left(\frac{1+\tau\,e^{-\beta}}{1+\tau}\right) \qquad (8)$$

Expanding the exponential in equation (8), neglecting terms higher than first-order in β and expanding the logarithm yields $S(t) = \alpha/(1+\tau)$ provided $\beta \ll 1$. This has the same functional dependence on time as is obtained from a simple second-order analysis.

Second-order behaviour is consequently observed provided that the z dimension of the cell is small compared with its optical length. The effect of changing the ratio of the two is shown in the Figure: the decay appears to be slower as the fraction of light absorbed is increased. Once more than a few percent of the incident light is absorbed a significant deviation from true second-order behaviour is observed. Both the shape and the apparent rate change, with the fit of the decays to pure $(1+\tau)^{-1}$ behaviour growing progressively worse as more light is absorbed. Physically this is simply due to the initially high concentration of reactive species at the front of the cell making reaction there faster than at the back.



The dependence of the observed signal on time for (i) pure second-order behaviour, $\beta = 0$, (ii) $\beta = 0.1$, (iii) $\beta = 0.7$, and (iv) $\beta = 2.3$, corresponding to 0, 10, 50, and 90% of the incident light being absorbed respectively. The curves have been normalised to emphasise the shape changes

Although e.s.r. sample cells are narrow, the conditions required to distort second-order behaviour are easily reached in practice. In this laboratory, an observation was made of the decay of durosemiquinone anion radicals formed upon irradiation of a 0.05M solution of duroquinone in 4 : 1 (v/v) propan-2-ol–triethylamine with a nitrogen laser at room temperature. Simple analysis gave an apparently good statistical fit for a conventional second-order decay curve with a radical first half-life of 2.56 ms. However with $\varepsilon_A = 27.6 \times 10^3$ m^2 mol^{-1} and a cell width of 3 mm, $\beta = 9.5$ and the experiment was well within the non-uniform concentration region; a proper full analysis gave a half-life of 0.72 ms. It cannot be stressed too strongly that apparent fit to assumed kinetic behaviour is not a sufficient test to justify simple analysis. Contributions to the literature which have neglected or underestimated the effect of light absorption on second-order decays are common and recent,[4] although proper consideration has sometimes been given to it.[5] Methods for dealing with the problem in the gas phase have long been known.[6,7]

Spatial Dependence of Sensitivity.—The foregoing analysis has assumed no dependence of the sensitivity of detection of the radicals on their position in the sample cell although this is a known characteristic of a microwave cavity. *A priori*, the spatial dependence of the sensitivity will affect the apparent time dependence of the signal *via* the *z*-dependence of concentration. Below saturation, the signal from an e.s.r. spectrometer is proportional to the ratio of the power dissipated in the sample to the power stored in the overall cavity volume [equation (9) where B_1 is the microwave field, V is the volume of the sample, and γ is a constant].

$$S(t) = \frac{\gamma}{V}\iiint_{\text{sample}} c(z,t) \cdot \frac{B_1^2(x,y,z)}{\langle B_1^2 \rangle_{\text{cavity}}}\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \qquad (9)$$

Consider the commonly used TE_{102} cavity with dimensions $a \times b \times c$ and let $c = 2a$, as is approximately the usual case. The cavity is centred at the origin. The components of the B_1 field are given by equation (10)[8] where $B_1(0,0,0)$ is (within a normalization factor) the microwave field at the centre of the cavity. Note that the axis system is shifted with respect to that employed in ref. 8. Consequently, we have equation (11).

$$B_1(x,y,z) = B_1(0,0,0)/2 \left[\cos\left(\frac{\pi x}{a}\right)\cos\left(\frac{\pi z}{a}\right), 0, \sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{\pi z}{a}\right)\right] \qquad (10)$$

$$\begin{aligned}\frac{1}{\langle B_1^2\rangle_{\text{cavity}}}\iint_{\text{sample}} B_1^2(x,y,z)\,\mathrm{d}x\,\mathrm{d}y &= \frac{4}{B_1^2{}_{(0,0,0)}} \cdot \frac{1}{2\delta x}\int_{-\delta x}^{\delta x} B_1^2(x,y,z)\,\mathrm{d}x \\ &= 1 + \left(\frac{a}{2\pi\delta x}\right)\sin\left(\frac{2\pi\delta x}{a}\right)\cos\left(\frac{2\pi z}{a}\right) \qquad (11)\end{aligned}$$

Substitution into equation (9) gives (12) where $\varphi = [a\sin(2\pi\delta x/a)]/2\pi\delta x$, a constant for a given sample cell in a given cavity.

$$S(t) = \frac{\gamma}{2\delta z}\int_{-\delta z}^{\delta z} c(z,t)\left[1 + \varphi\cos\left(\frac{2\pi z}{a}\right)\right]\mathrm{d}z \qquad (12)$$

The shape of $S(t)$ is affected by sensitivity considerations only in so far as the cosine term is involved. Expanding the cosine and excluding terms second order or higher in $(2\pi z)/a$ yields equation (13) which is isomorphic with equation (3), showing that any distortions of the shape are due to the higher order terms.

$$S(t) = \frac{\gamma}{2\delta z}\int_{-\delta z}^{\delta z} (1 + \varphi)\,c(z,t)\,\mathrm{d}z \qquad (13)$$

$S(t)$ in equation (12) was evaluated numerically, using Romberg's algorithm,[9] for a second-order reaction. Analytical solution, employed to check the numerical calculation, is straightforward except for the integral [equations (14)—(16)].

$$I = \int_{-\delta z}^{\delta z} \frac{\cos(2\pi z/a)}{\tau + \mathrm{e}^{(z+\delta z)/\lambda}}\,\mathrm{d}z \qquad (14)$$

$$= \tau^{-1}\int_{-\delta z}^{\delta z}\left[1 + \frac{\mathrm{e}^{(z+\delta z)/\lambda}}{\tau}\right]^{-1}\cos(2\pi z/a)\,\mathrm{d}z \qquad (15)$$

$$= \int_{-\delta z}^{\delta z} [1 + \tau\,\mathrm{e}^{-(z+\delta z)/\lambda}]^{-1}\,\mathrm{e}^{-(z+\delta z)/\lambda}\cos(2\pi z/a)\,\mathrm{d}z \qquad (16)$$

Expansion of the term in brackets in equation (15) for $\tau > \mathrm{e}^{(z+\delta z)/\lambda}$, or in equation (16) for $\tau < \mathrm{e}^{(z+\delta z)/\lambda}$ then yields solvable integrals of the form $\int \mathrm{e}^{\pm n(z+\delta z)/\lambda}\cos(2\pi z/a)\,\mathrm{d}z$.

For typical cavity (a 23 mm) and sample cell (δx 10 mm, $\delta z \leqslant 5$ mm) dimensions, the contribution from the higher order terms is a few percent of that due to equation (13). More importantly, the shape of the decay due to these terms is different from the uncorrected solution of equation (13) by well under 1% and the net effect on the shape of $S(t)$ is negligible.

Irradiation down the long axis of the sample tube, *i.e.* the x-axis, would yield identical results (since the field distribution is the same) while direction of the light along the y-axis would allow the spatial dependence of the sensitivity to be truly neglected, since $B_1(y) = 0$.

Conclusions.—In this analysis of the time dependence of the e.s.r. signals observed from radicals produced in a light pulse it has been shown that unless a few percent of the incident light only is absorbed the non-uniform distribution of reactive species affects the observed kinetics. A possible further effect on the observed signal arising in the non-uniform sensitivity of the detection method over the sample is negligible for a TE_{102} cavity using sample cells of typical dimensions.

References

1 The special case of a chain reaction is considered in J. C. Andre, A. Tournier, M. Nicleuse, and X. Daglise, *React. Kin. Catal. Lett.*, 1981, **16**, 177.

2 J. C. Andrew, A. Tournier, M. Nicleuse, and X. Dablise, *React. Kin. Catal. Lett.*, 1981, **16**, 171.

3 R. P. Grant, D.Phil. Thesis, Oxford, 1981.

4 For example, S. K. Wong, *Int. J. Chem. Kin.*, 1981, **13**, 433; H. Paul, *Chem. Phys.*, 1979, **40**, 265.

5 For example, P. B. Ayscough and R. C. Sealy, *J. Chem. Soc., Perkin Trans. 2*, 1973, 543.

6 P. B. Ayscough, A. J. Cocker, F. S. Dainton, and S. Hirst, *Trans. Faraday Soc.*, 1962, **58**, 295.

7 W. G. Burns and F. S. Dainton, *Trans. Faraday Soc.*, 1950, **46**, 411.

8 C. P. Poole, ' Electron Spin Resonance,' Interscience, New York, 1967.

9 F. L. Bauer, *Commun. Ass. Comp. Machines*, 1961, **4**, 255.

Received 20*th August* 1982; *Paper* 2/1459