Short Communication

## On the excited state kinetics between molecules linked by an inert chain

A. R. WATKINS

Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600 (Australia)

(Received February 13, 1980)

In recent years considerable interest has developed regarding the excited state reactions of bifunctional compounds, where two distinct reactive parts are linked by an inert chain which is usually made up of methylene units. Upon excitation of one of the functional groups, reaction can occur between it and the other group to which it is linked by the chain. In this way excimer emission, proceeding from a complex between an excited functional group and (usually) the same group in the ground state, has been observed in a wide range of such compounds [1].

Several attempts have been made to analyse the kinetics of such excimer-forming reactions. However, all of these methods have inherent disadvantages, and in this note a new approach is described which is relatively simple and relies on a minimum number of assumptions. It is based on the time-resolved measurement of the excimer fluorescence in the presence of quenchers Q' and Q''. The excimer formation kinetics of a bifunctional compound Ar-$(CH_2)_n Ar$ can be represented under these conditions by the following scheme:

$$\tag{1}$$
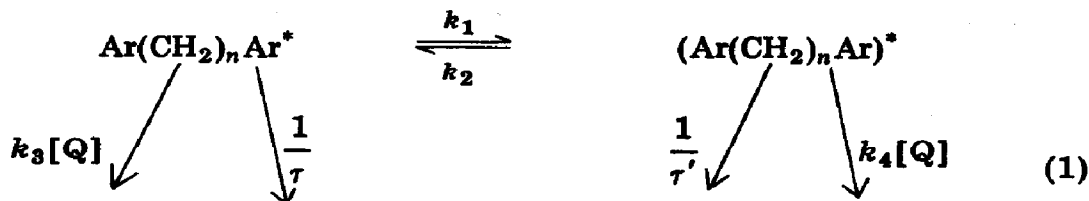
where τ and τ' are the lifetimes of the species in the absence of quencher Q. In general [2] the variation with time of the excimer fluorescence $I'(t)$ is given by

$$I'_e(t) = C\{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\} \tag{2}$$

where C, λ_1 and λ_2 are constants which can be readily obtained by fitting experimentally determined values of $I'(t)$ as a function of time to eqn. (2). In eqn. (2) λ_1 and λ_2 are given by

$$\lambda_{1,2} = \tfrac{1}{2}[1/\tau + k_1 + k_3[Q] + 1/\tau' + k_2 + k_4[Q] \mp$$
$$\mp \{(k_2 + 1/\tau' + k_4[Q] - k_1 - 1/\tau - k_3[Q])^2 + 4k_1k_2\}^{1/2}] \qquad (3)$$

from which the following relations can be derived:

$$\lambda_1 + \lambda_2 = 1/\tau + 1/\tau' + k_1 + k_2 + [Q](k_3 + k_4) \qquad (4)$$

and

$$\lambda_1\lambda_2 = (1/\tau + k_3[Q])(1/\tau' + k_4[Q] + k_2) + (1/\tau' + k_4[Q])k_1 \qquad (5)$$

Equation (5) can be further modified to give

$$\{\lambda_1\lambda_2 - (\lambda_1\lambda_2)_0\}/[Q] = k_4/\tau + k_3/\tau' + k_2k_3 + k_1k_4 + k_3k_4[Q] \qquad (6)$$

where $(\lambda_1\lambda_2)_0$, the value of $\lambda_1\lambda_2$ in the absence of any quencher, is given by

$$(\lambda_1\lambda_2)_0 = 1/\tau(1/\tau' + k_2) + k_1/\tau' \qquad (7)$$

In eqns. (4) and (6) all quantities on the left-hand sides are known; the right-hand sides are linear in $[Q]$. These equations will thus be expected to give straight lines of slopes and intercepts S_1 and I_1 (for eqn. (4)) and S_2 and I_2 (for eqn. (6)), where

$$I_1 = 1/\tau + 1/\tau' + k_1 + k_2 \qquad (8)$$
$$S_1 = k_3 + k_4 \qquad (9)$$
$$I_2 = k_4/\tau + k_3/\tau' + k_2k_3 + k_1k_4 \qquad (10)$$
$$S_2 = k_3k_4 \qquad (11)$$

From eqns. (9) and (11) k_3 and k_4 can be immediately obtained for any quencher Q:

$$k_4 = \tfrac{1}{2}\{S_1 \pm (S_1{}^2 - 4S_2)^{1/2}\} \qquad (12)$$
$$k_3 = \tfrac{1}{2}\{S_1 \mp (S_1{}^2 - 4S_2)^{1/2}\} \qquad (13)$$

If the experiment is carried out with two quenchers Q' and Q'', then application of eqn. (10) in both cases leads to

$$(I_2'k_4'' - I_2''k_4')/(k_3'k_4'' - k_3''k_4') = 1/\tau' + k_2 \qquad (14)$$

where the primed and double-primed quantities are derived from experiments with one or other of the two quenchers Q' or Q''. Since, from eqns. (9) and (11), k_3' and k_4' and k_3'' and k_4'' for these two quenchers are known, eqn. (14) provides a direct relation between τ' and k_2. This, together with eqns. (7), (8) and (10), allows a complete solution to be made for the four quantities k_1, k_2, τ and τ'.

This procedure, which might at first sight appear rather cumbersome, is in fact experimentally quite feasible. Work in this laboratory has shown that λ_1 and λ_2 can be determined with a high degree of accuracy using single-photon counting equipment, and that relations such as those outlined in this work can be used successfully to obtain the rate parameters for excimer formation between unlinked molecules [3, 4]. A wide range of choice is

available for the quenchers Q' and Q'', among them heavy atom quenchers [5] and free radical quenchers [6]. The methods derived earlier can be extended to exciplex formation in linked molecules [7], and to excimer formation of linked compounds in aqueous micelles [8] provided that the quenching species (which in this case could be metal ions) are located in the bulk aqueous phase and not in the micellar phase where they would give rise to undesirable statistical effects [9].

Perhaps the most useful aspect of this procedure is that, unlike other methods [10 - 12], it does not rely on measurements on the unlinked molecule ArH or $ArCH_3$, or on the linked molcule at very low temperatures [13], to provide a value of τ. While it may seem not unreasonable that the properties of the excited monomer part of the linked molecule will closely resemble those of its unlinked analogue, this is an untested and untestable assumption about which nothing is known with certainty. In addition, our procedure does not rely on being able to resolve two distinct decay modes in the monomer emission [11, 13] nor does it necessitate a suitable temperature region (apparently difficult to obtain) in the steady state fluorescence behaviour of the linked compound from which $\ln(1 + k_2\tau')$ or $\ln(1 + 1/k_2\tau')$ can be determined [12].

1 F. C. De Schryver, N. Boens and J. Put, *Adv. Photochem.*, *10* (1977) 359.
2 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley–Interscience, New York, 1970, p. 307.
3 A. R. Watkins and B. K. Selinger, *Chem. Phys. Lett.*, *64* (1979) 250.
4 A. R. Watkins and B. K. Selinger, to be published.
5 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley–Interscience, New York, 1970, p. 338.
6 J. A. Green and L. A. Singer, *J. Am. Chem. Soc.*, *96* (1974) 2730.
7 J. B. Birks, in J. B. Birks (ed.), *Organic Molecular Photophysics*, Vol. 2, Wiley, New York, 1975, p. 530.
8 C. N. Henderson, B. K. Selinger and A. R. Watkins, to be published.
9 B. K. Selinger and A. R. Watkins, *Chem. Phys. Lett.*, *56* (1978) 99.
10 W. Klöpffer and W. Liptay, *Z. Naturforsch., Teil A*, *25* (1970) 1091.
11 P. Avouris, J. Kordas and M. A. El-Bayoumi, *Chem. Phys. Lett.*, *26* (1974) 373.
12 K. A. Zachariasse, W. Kühnle and A. Weller, *Chem. Phys. Lett.*, *59* (1978) 375.
13 G. E. Johnson, *J. Chem. Phys.*, *61* (1974) 3002; *63* (1975) 4047.