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STERN–VOLMER QUENCHING KINETICS FOR USE OF A DUALISTIC QUENCHER

TADASHI HASEGAWA* AND AYUMI MATSUHISA
Department of Chemistry, Tokyo Gakugei University, Nukuikitamachi, Koganei, Tokyo 184, Japan
AND
MICHIKAZU YOSHIOKA
Department of Chemistry, Saitama University, Shimookubo, Urawa, Saitama 338, Japan

The Stern–Volmer quenching equation for use of a dualistic quencher, which serves not only as the quencher for an excited starting molecule but also as the promoting agent for product formation, was obtained by applying the steady-state approximation to the photoreaction system. The equation was applied to the kinetic analysis of the Norrish type II photoreaction of valerophenone using triethylamine, which serves as the excited-state quencher and as the promoting agent for product formation.

INTRODUCTION

The lifetime of an excited organic molecule which undergoes measurable chemical change can, in principle, be determined by the employment of a suitable quencher which interacts with the excited molecule in an energy-transfer process. The normal Stern–Volmer equation, $\phi^0/\phi = 1 + kq\tau[\mathrm{Q}]$, can be applied for lifetime determination generally using dienes as quenchers.[1,2] The rate of the energy-transfer process is usually assumed to be diffusion controlled under given reaction conditions.[2] The Stern–Volmer equation is derived on the assumptions (i) that the intensity of radiation absorbed by the starting molecules is essentially unchanged, that is, no products are formed which act as internal filters,[3] over the period of reaction, (ii) that the quencher does not react and merely interacts only with the molecule in the reactive excited state involved in the product-formation process, and (iii) that the product is formed from only one excited state, which is the one quenched by a quencher.[1]

Much attention has recently been focused on synthetic and mechanistic problems related to reactions involving one-electron transfer from an amine nitrogen to an excited ketone carbonyl group to generate a radical ion pair.[4–7] Since amines with appropriately low ionization potentials quench triplet states of ketones,[8] they can be used as quenchers for the Norrish type II photoreaction of alkyl aryl ketones.[9] However, amines prevent the reverse hydrogen transfer to reproduce the starting ketone from 1,4-biradical intermediates because of intermolecular hydrogen bonding and so promote the product formation.[10] This process has the opposite effect to the quenching process. Therefore, the normal Stern–Vblmer equation cannot be applied straightforwardly to such systems involving an amine as a quencher. In order to develop a more thorough understanding of the chemical aspects and predictive capabilities of a system involving an excited-state electron-transfer process, it is necessary to probe more deeply the factors which influence the electron-transfer efficiency and its rate. We report here on a generalized Stern–Volmer equation which is applicable to such a system.

EXPERIMENTAL

Chemicals. Valerophenone and triethylamine were purified by fractional distillation with a Taika SM-NB spinning-band distillation apparatus. Benzene was washed with sulphuric acid and then water, dried and fractionally distilled over phosphorus pentoxide. Pyridine was dried over potassium hydroxide and then fractionally distilled.

Irradiation procedures. Benzene or benzene containing *ca* $0{\cdot}5\ \mathrm{mol\,l^{-1}}$ of pyridine, solutions of

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* Author for correspondence.

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valerophenone (*ca* 0·05 mol l^{-1}) containing a known concentration of heptadecane (*ca* 0·0025 mol l^{-1}) as a calibrant and appropriate concentrations of triethylamine were placed in 150 × 15 mm Pyrex culture tubes. The tubes were degassed by three freeze–pump–thaw cycles and then sealed. Irradiation was performed on a 'merry-go-round' apparatus with an Ushio 450 W high-pressure mercury lamp. Potassium chromate filter solution was used to isolate the 313 nm line.[11] Analyses were performed on a Shimadzu GC-8A gas chromatograph equipped with a flame ionization detector which was connected to a Shimadzu C-R6A Chromatopac integrator, using a 2 m column containing 15% propylene glycol succinate on Uniport B.

RESULTS AND DISCUSSION

Valerophenone undergoes the Norrish type II photoreaction to give acetophenone and 2-methyl-1-phenylcyclobutanol. The quantum yields are affected by the solvent properties.[9,12] The quantum yields of acetophenone formation and for total photoreaction increase from 0·33–0·44 and 0·45, respectively, in hydrocarbon solvents to 0·90 and 1·0 respectively in *tert*-butanol.[9,12] These solvent effects are attributable to the prevention of reverse hydrogen transfer to reproduce the starting ketone from a 1,4-biradical intermediate because of the presence of intermolecular hydrogen bonding between the intermediate and the alcohol.[12] The photoreaction of valerophenone is quenched with dienes or amines.[9] The Stern–Volmer plots using a diene as an energy-transfer quencher are straight lines with a slope of 40 in benzene.[9] However, the Stern–Volmer plots using triethylamine as an electron-transfer quencher did not show a linear relationship (Figure 1). It is notable that the ϕ^0/ϕ values are lower than unity at low quencher concentrations. A reaction-prompting process must be occurring when triethylamine is used as a quencher.

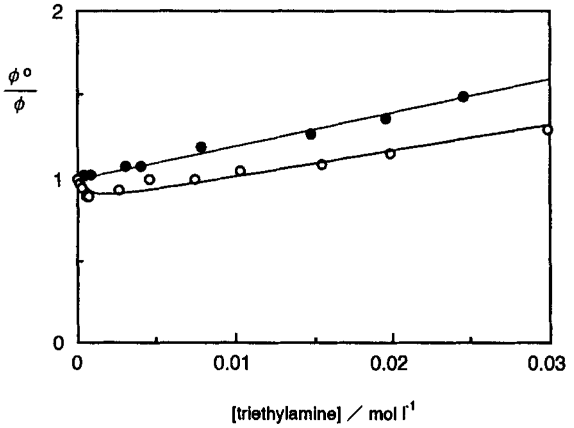
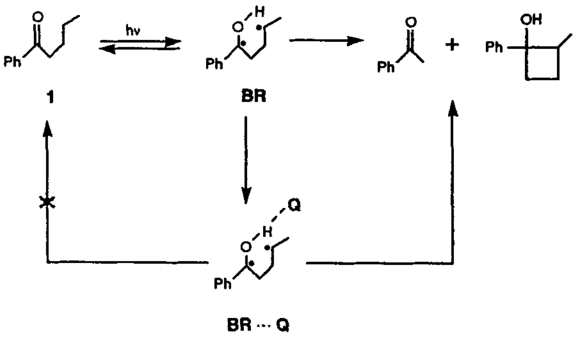


Figure 1. Stern–Volmer plots for quenching by triethylamine of acetophenone formation from valerophenone: (○) in benzene; (●) in benzene containing 0·5 M pyridine. The curved line was obtained from equation (10) by using $a = 18$, $b = -453$ and $c = 2966$



Scheme 1

The following equations can be written for the quenching of valerophenone (**1**) with triethylamine (Q), where BR is the 1,4-biradical intermediate (see Scheme 1):

$$1 \underset{k_d}{\overset{h\nu}{\rightleftarrows}} 1^{*1} \tag{1}$$

$$1^{*1} \xrightarrow{k_{isc}} 1^{*3} \tag{2}$$

$$1^{*3} \xrightarrow{k_r} \mathrm{BR} \tag{3}$$

$$1^{*3} \xrightarrow{k'_d} 1 \tag{4}$$

$$1^{*3} \xrightarrow{k_q[\mathrm{Q}]} 1 \tag{5}$$

$$\mathrm{BR} \xrightarrow{k_p} \text{products} \tag{6}$$

$$\mathrm{BR} \xrightarrow{k''_d} 1 \tag{7}$$

$$\mathrm{BR} \xrightarrow{k_x[\mathrm{Q}]} (\mathrm{BR}\cdots\mathrm{Q}) \rightarrow \text{products} \tag{8}$$

Equation (5) indicates the quenching process and equation (8) shows the reaction-promoting process. The later process is absent in the case of quenching with dienes. The steady-state approximation gives the equation

$$\frac{\phi^0}{\phi} = \left(1 + \frac{k_q}{k_r + k'_d}[\mathrm{Q}]\right)\left\{1 + \frac{\left(\frac{k_x}{k_p + k''_d} - \frac{k_x}{k_p}\right)[\mathrm{Q}]}{1 + \frac{k_x}{k_p}[\mathrm{Q}]}\right\} \tag{9}$$

$$= (1 + a[\mathrm{Q}])\left(1 + \frac{b[\mathrm{Q}]}{1 + c[\mathrm{Q}]}\right) \tag{10}$$

The second term of equation (9) is related to the promotion of product formation by the quencher. When the promotion process or the reverse hydrogen-transfer process is absent ($k_x = 0$ or $k_d'' = 0$), equation (9) reduces to the normal Stern–Volmer equation and a linear relationship between ϕ^0/ϕ and the quencher concentration must be observed. However, when triethylamine was used as the quencher for the type II photoreaction of valerophenone, a plot of ϕ^0/ϕ vs the quencher concentration showed a non-linear relationship with a minimum below unity, indicating that both k_x and k_d'' are not negligible.

The values for a, b and c that give the closest agreement between experimental data and equation (10) were determined by curve fitting based on the non-linear least-squares method. The curved line in Figure 1 was obtained using equation (10) and the variable set of $a = 18$, $b = -453$ and $c = 2966$. The value of a indicates the value of $kq\tau$. The rate constant of the electron-transfer quenching by triethylamine for the type II reaction of valerophenone can be calculated to be $2{\cdot}3 \times 10^9$ s^{-1} using the a value and reported τ value of 8×10^{-9} s obtained from the Stern–Volmer quenching analysis by 2,5-dimethylhexa-2,4-diene.[13]

If k_d'' is negligible compared with k_p, a linear relationship between ϕ^0/ϕ and the quencher concentration must be observed. Pyridine is known to increase the quantum yield of the type II reaction of valerophenone, that is, increase the rate of product formation, because of intermolecular hydrogen bonding with the 1,4-biradical intermediate.[9] The value of k_d'' may be negligible in the reaction system containing pyridine. When the type II reaction of valerophenone in benzene was conducted in the presence of various amounts of triethylamine and 0·5 M pyridine, linear Stern–Volmer plots was obtained (Figure 1). The slope of the line gives a $kq\tau$ value of 19 l mol^{-1}. The $kq\tau$ value of the type II reaction in benzene is independent of whether pyridine is present or absent.[9,12,13] The $kq\tau$ value obtained from quenching by triethylamine in benzene using equation (10) was in good agreement with that obtained in the same system but containing pyridine. This indicates that the curve fitting using equation (10) can be generally used for the determination of the rate constant of quenching by amines or other dualistic quenchers.

A linear relationship may not be observed even in the presence of a large amount of pyridine in other cases. The appearance of the linear relationship depends on the relative magnitude of the values of k_d'' and the rate of product formation in the presence of pyridine.

CONCLUSION

The normal Stern–Volmer equation cannot be used straightforwardly in kinetic analysis of a system involving an excited-state quencher which also acts as a promoting agent for the reaction, such as an amine in the type II photoreaction of alkyl aryl ketones. The steady-state approximation to a photoreaction system involving quenching and reaction-promoting processes by the dualistic quencher gave the generalized Stern–Volmer quenching equation (9). This equation shows that even when a dualistic quencher is used the normal Stern–Volmer equation can be applied for the analysis of the photoreaction system if k_d'' is negligible compared with k_p. The $kq\tau$ value in the type II reaction of valerophenone involving electron-transfer quenching was determined to be 18 in benzene by curve fitting based on the non-linear least-squares method.

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