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STERN–VOLMER QUENCHING KINETICS IN PHOTOREACTION SYSTEMS WITH STRONG INTERNAL FILTERING: TYPE II PHOTOREACTION OF 2-BENZOYLCYCLOHEXANONE

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The Stern–Volmer quenching equation for a photochemical reaction in the presence of internal filtering was obtained by applying the steady-state approximation to the system. The equation was used for the kinetic analysis of the Type II photoreaction of 2-benzoylcyclohexanone yielding 1-phenylhept-6-ene-1,3-dione, the enol form of which acts as an effective internal filter. The $k_q\tau$ value for quenching of the photoreaction by 2,5-dimethylhexa-2,4-diene was determined to be 9·1 ± 0·5 l mol^{-1}.

INTRODUCTION

Laser-flash techniques make it possible to make direct observations of excited states of photochemically active compounds and of their decay kinetics.[1] However, techniques exploiting energy transfer still continue to play an important role in mechanistic studies of organic photochemical reactions. Stern–Volmer quenching kinetics are very useful and convenient; they provide excited-state lifetimes and allow the calculation of excited-state rate constants.[2] Under steady-state conditions, the only kinetic parameter that can be measured directly for a photochemical reaction is the overall quantum yield, which must be constant in order to apply the normal Stern–Volmer quenching kinetics to the photoreaction. There are at least two phenomena which might change the quantum yield in conversions: internal filtering by a product and quenching of an excited reactant by a product.[3] In these cases, the normal Stern–Volmer kinetics cannot be applied to photoreactions in order to obtain excited-state lifetimes and rate constants because the slopes of the Stern–Volmer plots do not give the $k_q\tau$ values directly.

The Type II photoelimination and cyclization reactions of aryl alkyl ketones having a γ-hydrogen atom have been the subject of extensive investigations in organic photochemistry.[4] These reactions are now well established to involve a 1,4-biradical intermediate, which is formed through γ-hydrogen abstraction by the n, π^* excited carbonyl group.[5,6] Aryl cycloalkyl ketones also undergo the Type II reactions.[7,8] The Type II reaction of 2-benzoylcyclohexanone (**1**) gives 1-phenylhept-6-ene-1,3-dione (**2**),[9,10] which is a β-diketone with keto–enol tautomerism. It can be readily expected that the enol form of the heptene-1,3-dione **2** acts as a strong internal filter. We report here the application of Stern–Volmer quenching kinetics to the Type II photoreaction of 2-benzoylcyclohexanone (**1**) yielding the product **2**, which acts as a strong internal filter.

EXPERIMENTAL

Chemicals. 2-Benzoylcyclohexanone (**1**) was prepared from 1-morpholinocyclohexene[11] and benzoyl chloride; m.p. 91·5–92 °C (lit.[10] m.p., 91–91·5 °C). Valerophenone was purified by fractional distillation with a Taika SM-NB spinning-band distillation apparatus and 2,5-dimethylhexa-2,4-diene (Tokyo Kasei) was purified by distillation. Benzene was washed with sulphuric acid, neutralized, dried and distilled over phosphorus pentoxide.

Irradiation procedures. Benzene solutions of **1** (ca 0·05 mol l^{-1}) containing a known concentration of pentadecane (ca 0·001 mol l^{-1}) as a caliburant, were

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placed in 150 × 15 mm Pyrex culture tubes. In quenching experiments, the solutions also contained appropriate concentrations of 2,5-dimethylhexa-2,4-diene. 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.[12] Analyses were performed on a Shimazu GC-4B or GC-8A gas chromatograph equipped with flame ionization detectors using a 2-m column containing 3% SE-30. Quantum yields were determined by the use of a valerophenone actinometer.[5b]

RESULTS AND DISCUSSION

Irradiation of a cyclohexane solution of **1** has been reported to give the Type II elimination product 1-phenyl-hept-6-ene-1,3-dione (**2**) in 72% yield.[10] No Type II cyclization products have been reported to be obtained in the photoreaction.[9,10] Irradiation of **1** in benzene also gave a similar result (82% yield) with no indication of the formation of the Type II cyclization product.

Quantum yields for the disappearance of **1** were determined. Degassed benzene solutions of **1** were irradiated with 313-nm light for reactions periods. The observed quantum yields were not constant and decreased with increasing conversion (Figure 1). This is attributable to the internal filter effect by the enol form of the photoproduct **2**. The following kinetic treatment provides evidence for very effective internal filtering by the enol form of **2**.

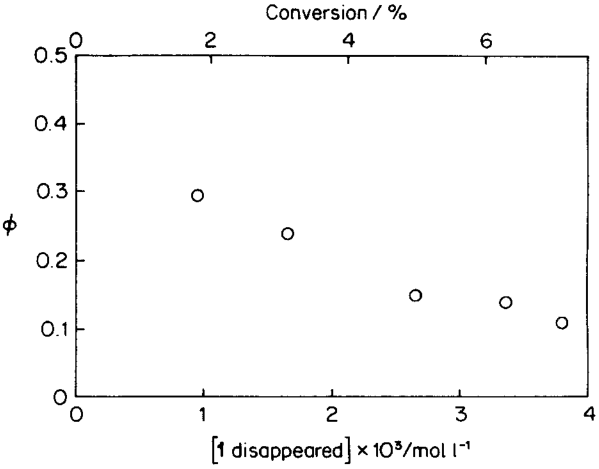
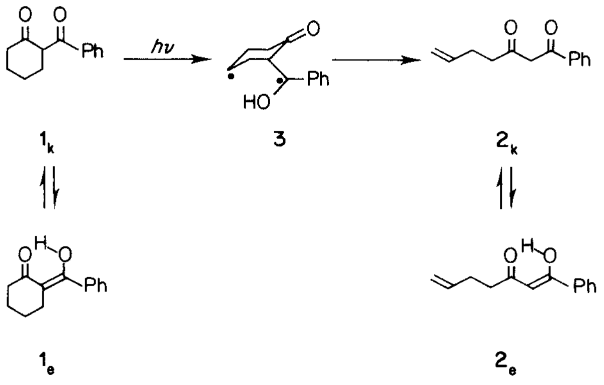


Figure 1. Dependence of quantum yield for disappearance of 2-benzoylcyclohexanone (**1**) on conversion



Scheme 1

The cyclohexanone **1** exists as a mixture of the keto and enol tautomers. The Type II photoreaction should occur only from the keto form. The photoproduct **2** also exists as a keto–enol mixture. Both of the enol forms of **1** and **2** absorb 313-nm light strongly and, therefore, can act as effective internal filters. The keto form of **2** might act as a sensitizer because acetophenone produced from the Type II photoreaction of butyrophenone or valerophenone acts as a sensitizer.[13] A simple scheme for the photoreaction of **1** containing the internal filtering by the enol form of **1** and the photoproduct **2** is shown in Scheme 1, where BR is the 1,4-biradical intermediate

$$1_k \underset{k_1}{\overset{h\nu}{\rightleftharpoons}} 1_k^{*1} \tag{1}$$

(effective light intensity = I_x)

$$1_k^{*1} \xrightarrow{k_2} 1_k^{*3} \tag{2}$$

$$1_k^{*3} \xrightarrow{k_3} \mathrm{BR} \tag{3}$$

$$1_k^{*3} \xrightarrow{k_4} 1_k \tag{4}$$

$$\mathrm{BR} \xrightarrow{k_5} 2 \tag{5}$$

$$\mathrm{BR} \xrightarrow{k_6} 1_k \tag{6}$$

Sensitization:

$$2_k \underset{k_7}{\overset{h\nu}{\rightleftharpoons}} 2_k^{*1} \tag{7}$$

(effective light intensity = I_x')

$$2_k^{*1} \xrightarrow{k_8} 2_k^{*3} \tag{8}$$

$$2_k^{*3} \xrightarrow{k_9} 2_k \tag{9}$$

$$2_k^{*3} \xrightarrow[{[1_k]}]{k_{10}} 1_k^{*3} + 2_k \tag{10}$$

Internal filtering:

$$1_e \overset{h\nu}{\rightleftharpoons} 1_e^{*} \longrightarrow 1_k \tag{11}$$

$$2_e \overset{h\nu}{\rightleftharpoons} 2_e^{*} \longrightarrow 2_k \tag{12}$$

and subscripts k and e represent the keto and the enol form, respectively. The steady-state approximation gives the rate of product formation, equation (13), where x is the molar

$$\frac{\mathrm{d}x}{\mathrm{d}t}=\frac{k_2}{k_1+k_2}\cdot\frac{k_3}{k_3+k_4}\cdot\frac{k_5}{k_5+k_6}\times\left[I_x+\frac{k_8/(k_7+k_8)k_{10}[\mathbf{1}_\mathrm{k}]/(k_9+k_{10}[\mathbf{1}_\mathrm{k}]}{k_2/(k_1+k_2)}\cdot I_x'\right] \tag{13}$$

$$=\phi^0(I_x+\rho I_x') \tag{14}$$

$$=\phi^\circ F_\rho(x)I \tag{15}$$

concentration of **2**, I is the whole absorbed light intensity, I_x and $I_x{}'$ are the light intensities absorbed by the keto form of **1** and **2**, respectively, and ρ is a parameter representing the efficiency of sensitization by the keto form of **2** ($0 \leqslant \rho \leqslant 1$). The term $F_\rho(x)I$ is the effective light intensity for the photoreaction of $\mathbf{1}_\mathrm{k}$. The function $F_\rho(x)$ expresses the probability that the excited state of the reactive keto form of the reactant will be produced. If the keto form of the Type II photoproduct **2** acts as a 100% effective sensitizer, ρ should be unity. The function $F_\rho(x)$ can be

$$F_\rho(x)=\frac{[\varepsilon_{1_e}(1-\mathrm{en}_1)[C_0-x/\mathrm{cy}]+\rho\varepsilon_{2_k}(1-\mathrm{en}_2)x]}{[\{\varepsilon_{1_k}(1-\mathrm{en}_1)+\varepsilon_{1_e}\mathrm{en}_1\}[C_0-x/\mathrm{cy}]+\{\varepsilon_{2_k}(1-\mathrm{en}_2)+\varepsilon_{2_e}\mathrm{en}_2\}x]} \tag{16}$$

defined as equation (16) where $[C_0]$ is the initial concentration of 1, cy is the chemical yield of **2**, ε_{1_k}, ε_{1_e}, ε_{2_k}, and ε_{2_e} are the

$$\int_0^x \frac{1}{F_\rho(x)}\,\mathrm{d}x = Ax + AB\ln(1+Cx) \qquad (17$$

$$=\Phi^0 It \tag{18}$$

where

$$A=\frac{\varepsilon_{2_k}(1-\mathrm{en}_2)\mathrm{cy}-\varepsilon_{1_k}(1-\mathrm{en}_1)-\varepsilon_{1_e}\mathrm{en}_1+\varepsilon_{2_e}\mathrm{en}_2\mathrm{cy}}{\rho\varepsilon_2(1-\mathrm{en}_2)\mathrm{cy}-\varepsilon_{1_k}(1-\mathrm{en}_1)} \tag{19}$$

$$\mathrm{B}=\frac{\varepsilon_{1_k}(1-\mathrm{en}_1)C_0\mathrm{cy}+\varepsilon_{1_e}\mathrm{en}_1C_0\mathrm{cy}}{\varepsilon_{2_k}(1-\mathrm{en}_2)\mathrm{cy}-\varepsilon_{1_k}(1-\mathrm{en}_1)-\varepsilon_{1_e}\mathrm{en}_1+\varepsilon_{2_e}\mathrm{en}_2\mathrm{cy}}-\frac{\varepsilon_{1_k}(1-\mathrm{en}_1)C_0\mathrm{cy}}{\rho\varepsilon_{2_k}(1-\mathrm{en}_2)\mathrm{cy}-\varepsilon_{1_k}(1-\mathrm{en}_1)} \tag{20}$$

$$C=\frac{\rho\varepsilon_{2_k}(1-\mathrm{en}_2)\mathrm{cy}-\varepsilon_{1_k}(1-\mathrm{en}_1)}{\varepsilon_{1_k}(1-\mathrm{en}_1)C_0\mathrm{cy}} \tag{21}$$

absorption coefficients for the keto and the enol forms of **1** and **2**, respectively, and en_1 and en_2 are the enol contents of **1** and **2**, respectively. Integration of equation (15) gives equation (18). This equation describes the dependence on the amount of the product x on time t. The enol contents en_1 and en_2 were determined to be 0·07 and 0·89, respectively, from the NMR analyses of **1** and **2** in benzene-d_6. The observed absorption coefficients of **1** and **2** at 313 nm are 230 and 16 600 $\mathrm{l\,mol^{-1}\,cm^{-1}}$, respectively. Both of the absorption coefficients of 2-methyl-2-benzoylcyclohexanone and 3-benzoyl-3-methylbutan-2-one, non-enolizable analogues, are commonly 100 $\mathrm{l\,mol^{-1}\,cm^{-1}}$ at 313 nm in benzene. We used this value for ε_{1_k} and ε_{2_k} in benzene at 313 nm. The absorption coefficients of the enol forms of **1** and **2** at 313 nm can be calculated to be 2000 and 18 600 $\mathrm{l\,mol^{-1}\,cm^{-1}}$, respectively.

Figure 2 shows the rate of product formation as a function of time. Least-squares analysis of the experimental data according to equation (18) gives a best-fit plot in Figure 2, which gives the quantum yield (ϕ^0) to be 0·82. The straight line shows the rate expected for the reaction without internal filtering. Figure 2 indicates that the enol forms of **1** and **2** act as very effective internal filters and that the true quantum yield (the quantum yield at zero conversion) for formation of the photoproduct **2** is 0·82. Therefore, the true quantum yield for disappearance of the reactant **1** should be unity because the chemical yield of **2** from **1** is 82%. These high values of quantum yields indicate the complete absence of the reverse hydrogen transfer process,[14] equation (6), which yields the starting compound from the 1,4-biradical intermediate **3**. The intramolecular hydrogen bonding between the hydroxyl and the ketone-carbonyl group in the biradical intermediate might prevent the reverse hydrogen migration.[15] The quantum yield for the Type II photoreaction of benzoylcyclohexane has been reported to be remarkably low, being explained in terms of the ready regression of the 1,4-biradical intermediate to the ground-state ketone.[7d]

Usual Stern–Volmer quenching kinetics cannot be applied straightforwardly to such a photochemical

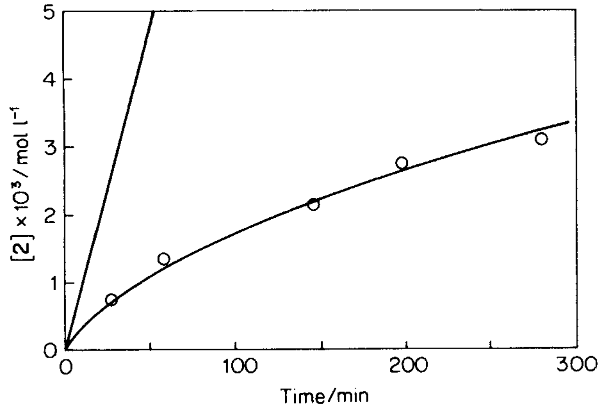


Figure 2. Rate of product formation from the Type II photoreaction of 2-benzoylcyclohexanone (**1**) as a function of irradiation time. Irradiation times were corrected by using a valerophenone actinometer. Straight line: the rate expected for the reaction without filtering. Curved line: the rate calculated by using equation (18).

system in which a product acts as a strong internal filter. The number of photons absorbed by the reactant is not constant and changes with conversion. We derived a Stern–Volmer quenching equation applicable to photoreactions accompanied by strong internal filtering.

For the quenching system, we can add equation (22) to the equations in Scheme 1, where Q is the quencher. The triplet

$$1_K^{*3} + Q \xrightarrow{kq} 1 + Q^{*3} \qquad (22)$$

state of the product 2_K might also be quenched. However, this process can be neglected when the conversion is not so high. Application of the steady-state approximation to the quenching systems gives equation (23) and integration of this equation gives equation (26).

$$\frac{dx}{dt} = \frac{k_2}{k_1 + k_2} \cdot \frac{k_3}{k_3 + k_4 + kq[Q]} \cdot \frac{k_5}{k_5 + k_6} \cdot F_\rho(x) I \qquad (23)$$

$$= \phi F_\rho(x) I \qquad (24)$$

$$\int_0^x \frac{1}{F_\rho(x)} \, dx = Ax + AB \ln(1 + Cx) \qquad (25)$$

$$= \Phi It \qquad (26)$$

Dividing equation (18) by equation (26) gives equation (29), a generalized Stern–Volmer quenching equation applicable to a photochemical system changing the light intensity absorbed by a reactant with conversion, that is, the equation for the photoreaction in the presence of internal filtering. The Stern–Volmer quenching plots corrected by equation (27) show the linear relationship (Figure 3). The straight line in Figure 3 was obtained by the least-squares method for the corrected plots. The slope of the line gives the $kq\tau$ value. The $kq\tau$ value was determined to be $9{\cdot}1 \pm 0{\cdot}5 \, \mathrm{l\,mol^{-1}}$, from which the lifetime and the $1/\tau$ value were calculated to be $1{\cdot}8 \times 10^{-9}$ s and $5{\cdot}5 \times 10^{8} \, \mathrm{s^{-1}}$, respectively, assuming a diffusion-controlled rate for kq ($5 \times 10^{9} \, \mathrm{l\,mol^{-1}\,s^{-1}}$). The lifetime is about four times shorter than those of butyrophenone and valerophenone.[5] This might be due to an increase in the population of geometries favourable for γ-hydrogen abstraction because of the decrease in conformational flexibility.

$$\frac{\phi^0}{\phi} = \frac{Ax_0 + AB \ln(1 + Cx_0)}{Ax + AB \ln(1 + Cx)} \qquad (27)$$

$$= 1 + \frac{kq}{k_3 + k_4}[Q] \qquad (28)$$

$$= 1 + kq\tau[Q] \qquad (29)$$

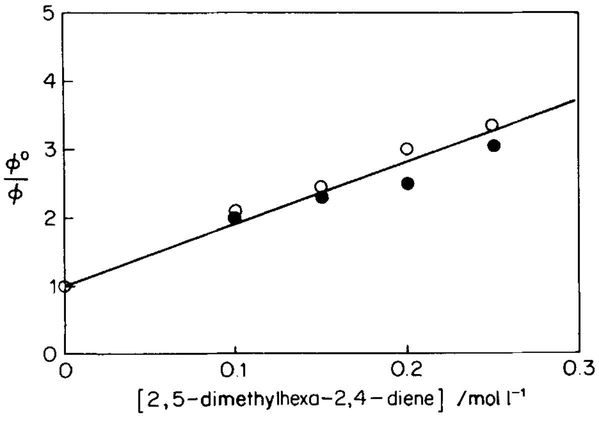


Figure 3. Corrected Stern–Volmer plots for quenching of 1-phenylhept-6-ene-1,3-dione (**2**) formation from 2-benzoylcyclohexanone (**1**). ○, $0{\cdot}050 \, \mathrm{mol\,l^{-1}}$ of **1** was used and the conversion at zero quencher concentration was 2·6%; ●, $0{\cdot}050 \, \mathrm{mol\,l^{-1}}$, 10·1%

CONCLUSIONS

The Type II photoreaction of 2-benzoylcyclohexanone (**1**) afforded 1-phenylhept-6-ene-1,3-dione (**2**), which acts as a very effective internal filter. The steady-state approximation was applied to a photoreaction in the presence of internal filtering and the generalized Stern–Volmer quenching equation (29) was obtained. The $kq\tau$ value in the Type II photoreaction of **1** was determined to be $9{\cdot}1 \pm 0{\cdot}5 \, \mathrm{l\,mol^{-1}}$ by applying the equation, and the lifetime of the triplet excited state of **1** was calculated to be $1{\cdot}8 \times 10^{-9}$ s.

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