

KINETIC RESOLUTION OF OPTICALLY ACTIVE MOLECULES AND ASYMMETRIC CHEMISTRY: ASYMMETRICALLY SENSITIZED PHOTOLYSIS OF *trans*-3,5-DIPHENYLPYRAZOLINE

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(Received November 28, 1980; in revised form March 30, 1981)

Summary

A racemic mixture of optically active *trans*-3,5-diphenylpyrazoline was photolysed with (–)-rotenone and (+)-testosterone as sensitizers. The unusual Stern–Volmer plot of the dynamic quenching of rotenone phosphorescence by the pyrazoline may be interpreted by an energy transfer mechanism via a triplet rotenone–pyrazoline exciplex. A transformation of the time axis affords first-order kinetics of the sensitized photoreaction. The photochemical yield of the triplet pyrazoline molecules formed is unity. Sensitization by rotenone increases the asymmetry of the reaction up to about 150% compared with direct photolysis of diphenylpyrazoline by circularly polarized light, the asymmetry being dependent on the concentration of the sensitizer.

1. Introduction

In our understanding asymmetric chemistry means the reaction of a 1:1 racemic mixture of enantiomers of an optically active molecule with a chiral agent. The chiral agent may be a chemical reagent, circularly polarized light (CPL) or one enantiomer of an optically active sensitizer excited by unpolarized light. In fact, asymmetric reactions are composed of two independent parallel reactions of the enantiomers of the racemic mixture.

Whereas in the literature we find many reports about asymmetric reactions induced by asymmetric chemical agents or by CPL, only a few papers [1 - 7] on asymmetrically sensitized photoreactions have succeeded the publication of Hammond and Cole [8] that opened the field in 1965. These papers report photoenantiomerization [2, 3], asymmetric quenching of the emission of an optically active molecule [4, 5], asymmetric singlet energy transfer [6] and the phenomenon of asymmetric electron transfer [7].

Recently the direct asymmetric photolysis of racemic mixtures of optically active pyrazolines by CPL has been investigated [9, 10]. This paper is a report on the asymmetrically sensitized photolysis of *trans*-3,5-diphenylpyrazoline (4,5-dihydro-3,5-diphenyl-3H-pyrazoline) (DPY) with rotenone (ROT) and testosterone (TEST) as triplet sensitizers. We emphasize the kinetic aspects of the disappearance of DPY in a generalized first-order reaction, which we understand to be an exponential dependence of the concentration of DPY on a suitable variable, not necessarily time. Product formation is discussed in a different publication.

We undertook this work to obtain data for comparison of direct and sensitized asymmetric photoreactions and perhaps to gain some closer insight into the molecular mechanism of energy transfer. We are interested in finding out whether the asymmetry of the reaction can be influenced by using different optically active sensitizers and perhaps increased to higher values than those observed in direct photochemistry. In triplet-triplet (T-T) sensitization, according to Dexter [11], the overlap of wavefunctions determines the exchange integral and energy transfer rate. In this mechanism chiral recognition should be dependent on the partners and should be improved compared with singlet energy transfer [12]. A further question is whether there is a relation between the sign of the long-wavelength circular dichroism (CD) of the sensitizer and the *R* or *S* enantiomer accumulated.

Although we are primarily interested in asymmetric photochemistry, we must know the non-chiral photoreaction, so we first give a description of our photochemical system; then we report the quenching experiments and their possible interpretations. In the third part the results of the non-chiral photoreaction are presented and discussed and in the last part the results of the asymmetric photoreaction are presented and evaluated. The general kinetic scheme for asymmetric reactions is given in Appendix A.

2. Experimental section

2.1. Chemicals

trans-DPY was provided by Dr. M. Schneider, Hohenheim, and used after thin layer chromatography (THLC). TEST (androstene, 17 β -ol-one) (Fluka) was recrystallized three times from ethylacetate; melting point, 156 °C (literature value, 156 °C). ROT (EGA-Chemie) also was recrystallized from ethylacetate; melting point, 220 °C (literature value, 219 °C). The solvent used was benzene (Merck, Uvasol).

2.2. Spectroscopy

UV spectra were taken with a Zeiss DMR 10 spectrophotometer, room temperature emission spectra were taken with a Farrand MK I and low temperature emission spectra were taken with an Aminco-Bowman spectrofluorimeter with a mechanical chopper. For CD spectra a Cary 60 spectropolarimeter with CD attachment 6002 and later a Jasco J500A with micro-

processor were used. Optical rotatory dispersion (ORD) measurements were made by means of a Perkin-Elmer 241 polarimeter.

2.3. Irradiation experiment

A Schoeffel 1600 W source (lamp, Osram XBO 1600) with a predisposition prism was focused on the entrance of a high intensity monochromator (Bausch and Lomb 33/86-79) to give a band 20 nm wide centred at 368 nm (Fig. 1). This wavelength was selected as even prolonged irradiation did not lead to direct photolysis of DPY. Thus the absorbance, solely due to the sensitizer, was constant during the irradiation experiment. A cylindrical cuvette designed for CD and ORD experiments, with a Teflon stopcock, was reproducibly positioned in the exit beam. Solutions were made oxygen free by bubbling nitrogen through them for 1 h and they were stirred during irradiation. Parker's actinometer [13] was used. The incident intensity was kept constant by monitoring with a photodiode and readjusting the power supply of the lamp.

After a period of irradiation the absorption spectrum of the solution was taken using a matching sensitizer solution as a reference. Then the irradiated solution was transferred to the baseline of a TLC sheet (Merck) by means of an automatic applier (Desaga). An ethyl ether-*n*-hexane mixture (1:1) was used as an eluent. 1,2-Diphenylcyclopropane (DCP), DPY and ROT or TEST were completely separated. After elution with hexane, UV and CD spectra of DCP and DPY were taken. From the absorbance of DPY before and after separation, corrections for losses could be applied. This procedure was necessary for each experimental point used in the kinetic analysis.

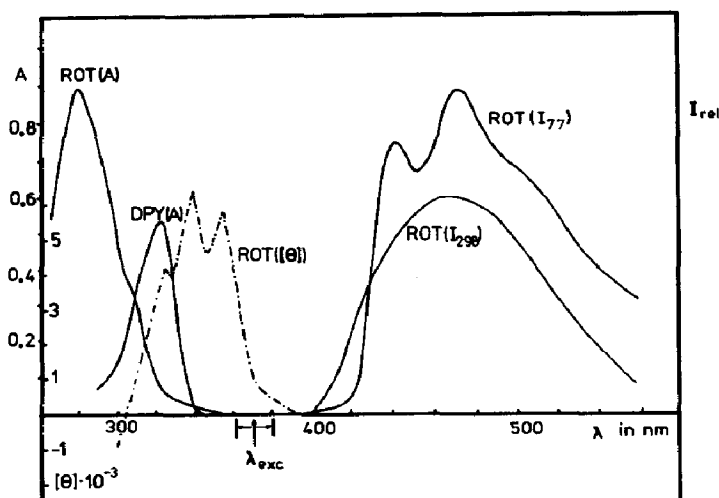


Fig. 1. Absorption and emission spectra of ROT (concentration, 4.5×10^{-5} M), the absorption spectrum of DPY (concentration, 1.5×10^{-3} M) in benzene and the CD spectrum of ROT in benzene.

2.4. Lifetime and quenching experiments

The lifetime of ROT phosphorescence in the quenching experiments at room temperature was measured by laser flash excitation ($\tau = 15$ ns) (excimer laser, Lambda-Physik) with the 308 nm line of XeCl. Only a small part of the laser intensity was reflected by a quartz plate into the rectangular four-sided cuvette containing oxygen-free (nitrogen-saturated) solutions. Right-angle geometry was used for emission and a double monochromator (Oriel) suppressed scattered light. An RCA C 31034 A photomultiplier with a Knott SKD emitter-follower base provided the signal for a 7834 Tektronix storage oscilloscope. The traces were monoexponential provided that the laser intensity was attenuated properly. Room temperature steady state quenching experiments were made with a Farrand MK I spectrofluorimeter. Excitation of ROT solutions at 315 nm gave the highest phosphorescence signals. As DPY also absorbs at 315 nm, a correction was made using the ratio of $(1 - 10^{-E})/E$ (where E is the absorbance) with quencher added and without quencher. Uncorrected steady state quenching curves branch off the Stern-Volmer straight line at concentrations of about 10^{-3} M DPY.

This correction factor has been obtained by integration over the window seen by the analysing monochromator-photomultiplier system, and we have verified the linearity of the corrected signal for a series of concentrations up to optical densities (ODs) of 1.5. Triplet-triplet absorption measurements with ROT and TEST were performed for comparison with a laser and conventional flash apparatus.

3. Results and discussion

3.1. The reaction system

DPY, a cycloaliphatic azo compound, is photochemically unstable. From direct photolysis experiments [14] we know that DPY is photolysed according to Fig. 2. The percentages given are for benzene solution; they are solvent dependent. The only optically active product is DCP.

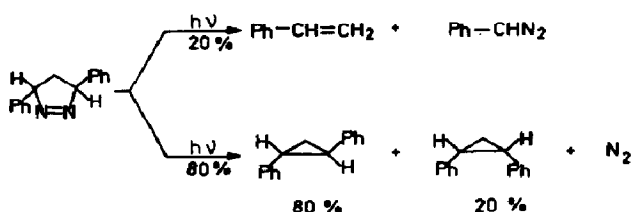


Fig. 2. The photolysis of DPY.

The sensitized photolyses of cycloaliphatic azo compounds have been studied by Engel and Steel [15] who reported the triplet energy $E_{T,DPY}$ of DPY to be 55 kcal mol^{-1} . For optimum performance we looked for an

optically active sensitizer which met the following demands: (a) absorption in a spectral region where the acceptor does not absorb; (b) photochemical stability; (c) a value of the triplet energy E_T that is higher than that of the acceptor; (d) phosphorescence at room temperature; (e) no sensitization of the reaction products; (f) facile separation from the acceptor molecule. We found this sensitizer from a selection of ketones in ROT (a natural product) in benzene solution. TEST did not fulfil requirement (d) and we obtained less information from it. However, requirement (d) can be replaced by another requirement, a measurable triplet-triplet absorption. The structures of ROT and TEST are shown in Fig. 3.

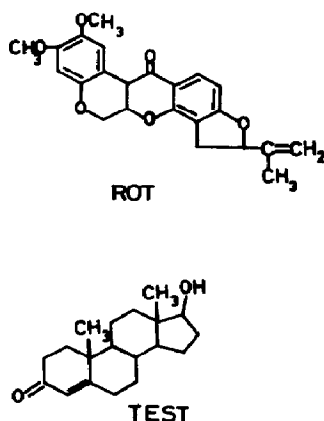


Fig. 3. The structures of ROT and TEST.

In benzene, ROT (Fig. 1) has a weak $n \rightarrow \pi^*$ band near $29\,500\text{ cm}^{-1}$ (340 nm) which is not totally separated from the intense $\pi \rightarrow \pi^*$ band with a maximum at $34\,500\text{ cm}^{-1}$ (290 nm; extinction coefficient $\epsilon = 19\,500$). The CD spectrum resolves the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands, the $n \rightarrow \pi^*$ band being positive with molar ellipticity $[\theta]_{338} = 6500\text{ deg cm}^2\text{ dmol}^{-1}$ (Fig. 1). The ORD value $[\alpha]_D^{25}$ of -226° is determined by the negative $\pi \rightarrow \pi^*$ band. ROT shows phosphorescence at low temperature and at room temperature, if oxygen is carefully excluded. At 77 K the triplet lifetime $\tau_0(77)$ is $22 \times 10^{-3}\text{ s}$; at 298 K, $\tau_0(298) = 1.15 \times 10^{-6}\text{ s}$ by either emission or T-T absorption measurements.

From the low temperature phosphorescence spectrum we find the triplet energy $E_{T,ROT}$ for ROT to be 65 kcal mol^{-1} from the room temperature spectrum $E_{T,ROT} = 70\text{ kcal mol}^{-1}$ (10% intensity), so ROT is a high energy sensitizer towards DPY. ROT is very unstable in ethanol [16], so all experiments were performed in benzene solution.

TEST has a well-separated weak $n \rightarrow \pi^*$ absorption band at $30\,000\text{ cm}^{-1}$ (330 nm; $\epsilon = 44$) in benzene solution. The CD spectrum shows a negative $n \rightarrow \pi^*$ band which is more sharply structured than the absorption band.

This indicates the importance of the vibrational contributions [17]. $[\alpha]_D^{25^\circ} = +130^\circ$ and the sign is determined by the $\pi \rightarrow \pi^*$ band contribution as well. TEST shows a broad emission band in benzene at 77 K with a maximum at $21\,450\text{ cm}^{-1}$ from which we find the triplet energy $E_{T,\text{TEST}}$ for TEST to be 70 kcal mol^{-1} , in agreement with the result of Marsh *et al.* [18] ($E_{T,\text{TEST}}$ for methyl tetrahydrofuran at 77 K is 74 kcal mol^{-1}).

The character of the lowest triplet state is predominantly π, π^* . The intersystem crossing yield is 1.12 ± 0.2 [18]. Triplet lifetimes are $\tau_0(77) = 0.196\text{ s}$ (emission) and $\tau_0(298) \approx 7 \times 10^{-5}\text{ s}$ (T-T absorption, not strictly exponential, as $C_{\text{TEST}} = 2 \times 10^{-2}\text{ M}$). TEST is less suitable for our investigation as there is no phosphorescence at 298 K and because of its low value of ϵ . High sensitizer concentrations are necessary so that concentration quenching is important.

3.2. The quenching experiments

Steady state (I_0/I versus C_A) and dynamic (τ_0/τ versus C_A) quenching experiments have been performed with ROT as a sensitizer. ROT is self quenching: the limiting value of the phosphorescence lifetime at 298 K in benzene ($\tau_0 = 1150 \pm 70\text{ ns}$) is observed at concentrations below $8.5 \times 10^{-5}\text{ M}$; at $4.5 \times 10^{-4}\text{ M}$ we find $\tau_0 = 510\text{ ns}$.

Figure 4 displays the results of four quenching experiments presented as Stern-Volmer plots with (a) shortening of ROT phosphorescence lifetime and (b) a decrease of ROT phosphorescence intensity by increased DPY concentration. In these experiments the concentration C_{DPY} of DPY was adjusted by addition of increasing amounts of DPY.

The plot of τ versus C_{DPY} during irradiation represents dynamic quenching in the course of a photolysis experiment. Here the concentration of DPY

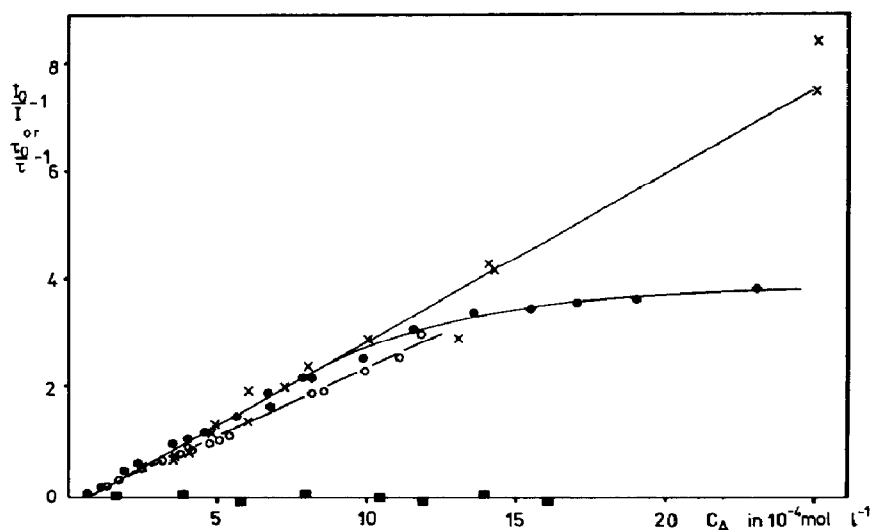


Fig. 4. Stern-Volmer plots of ROT in benzene ($C_{\text{ROT}} = 8.2 \times 10^{-5}\text{ M}$): ●, τ vs. C_{DPY} ; ×, I vs. C_{DPY} ; ○, τ vs. C_{DPY} during irradiation; ■, τ vs. C_{DCP} .

is determined by the extent of the photoreaction. All three experiments were performed for the same sensitizer concentration $C_{\text{ROT}} = 8.2 \times 10^{-5} \text{ M}$. The plots of τ versus C_{DPY} , I versus C_{DPY} and τ versus C_{DPY} during irradiation are nearly coincident, indicating that DPY is the only quencher in this system. This is confirmed by the plot of τ versus C_{DCP} ; the quenching curve of DCP that proves that ROT is not quenched by DCP although the triplet energies are not unfavourable. Further support for the indifference of DCP towards the triplet state of ROT is drawn from futile attempts to isomerize *cis*-DCP to *trans*-DCP by ROT sensitization (gas chromatography analysis). This behaviour of DCP is in accordance with the singlet exciplex energy transfer mechanism of sensitized isomerization [2, 8].

From the plots of τ versus C_{DPY} and I versus C_{DPY} we find a Stern-Volmer quenching constant of 2950 M^{-1} which would lead to a bimolecular quenching constant $k_q = 2.56 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ if a collisional mechanism of energy transfer were active. As in benzene the experimental value for the diffusion-controlled energy transfer rate [18 - 20] is $5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ and the observed transfer is 50% effective.

The results of steady state and dynamic quenching experiments are in good agreement at lower concentrations. At higher concentrations, however, they diverge. The steady state quenching curve, after correction for the increasing absorption of the quencher, stays linear; the τ/τ_0 plot levels off and the phosphorescence lifetime becomes nearly independent of quencher concentration. All decay curves are monoexponential within the limits of evaluation of photographs of oscilloscope traces.

The results of our quenching experiments are in some respects not compatible with the simple collisional mechanism that is the basis of Stern-Volmer-type kinetics. Hence we discuss an exciplex mechanism [21] represented by the following scheme.



$k_T = 1000I_0\epsilon_{\alpha, \text{D}}\phi_{\text{isc}, \text{D}}(1 - 10^{-E_\alpha})/E_\alpha$ is the rate constant of sensitizer triplet production for the absorbance E_α at the irradiation wavelength α , $k_D = k_{\text{phos}} + k_{\text{nr}}$ (the sum of the rate constants for phosphorescence and the non-radiative process) is the rate constant for photophysical deactivation of ${}^3\text{D}$ and the other rate constants are defined in the scheme. It is assumed that the exciplex does not decay to P (products) and D directly [22].

The kinetic treatment of this reaction scheme is formally similar to that of singlet excimers [23]. For steady state quenching we obtain a Stern-Volmer-type linear quenching curve (compare ref. 23, p. 443, eqn. (9.92) with $\alpha = 0$)

$$\frac{\phi_0}{\phi} = 1 + \tau_0 k_a (1 - \phi_{\text{diss}}) C_A \quad (1)$$

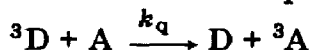
where $\phi_{\text{diss}} = k_d / (k_d + k_y + k_z)$ is the fraction of back dissociation of the exciplex; in the ROT-DPY system $\phi_{\text{diss}} = 0.5$. The non-linear dynamic quenching curve (Fig. 4) may indicate a diffusion-controlled association at low quencher concentrations ($\tau = 1 / (k_D + k_a C_A)$) and an irreversible decay of the exciplex in equilibrium with ^3D and A at high quencher concentrations ($\tau_\infty = 1 / (k_y + k_z)$); in the ROT-DPY system τ_∞ is approximately 200 ns). However, the dynamic quenching experiments should show biexponential decay curves [24, 25], whereas all our experimental decay curves are mono-exponential. A detailed estimate shows that the second component of the biexponential decay curve is beyond our experimental capacity.

With formulae of refs. 25 and 26, $\phi_{\text{diss}} = 0.5$ and $\tau_\infty = 200$ ns, calculation of the dynamic quenching curve, *i.e.* $\tau = f(C_A)$, indeed gives a good straight line up to concentrations of about 10^{-3} M. The slope is too small by a factor of 1.4, which is comparable with data in ref. 21. The concept of a long-lived exciplex, as discussed by Singer *et al.* [21], is consistent with the steady state and dynamic quenching curves. Unfortunately no property of the exciplex has been observed directly in our system, but there might be a temperature and viscosity region that is more favourable.

Similar experiments with TEST have not been possible because of the lack of room temperature phosphorescence of TEST.

3.3. The non-chiral photoreaction

Sensitized as well as direct photoreactions are usually not first order in irradiation time. The number of quanta transferred or absorbed per unit time changes with the extent of reaction. This is the reason that initial slope techniques are common in photochemistry. We have transformed the irradiation time into a quantity which is proportional to the total number of photons absorbed in direct photochemistry [9, 10] and we will now transform irradiation time into a quantity which is proportional to the number of quanta transferred in sensitized photochemistry. The normal bimolecular collisional quenching mechanism is characterized by the reaction



This leads to the Stern-Volmer quenching equation $\phi_0/\phi = \tau_0/\tau = 1 + \tau_0 k_q C_A$. Under photochemical irradiation conditions when the absorbance E_α is solely due to the sensitizer, the rate equation for disappearance of A is

$$\frac{dC_A}{dt} = - \frac{\phi_{\text{phot,A}} k_T C_D k_q C_A}{k_D + k_q C_A} \quad (2)$$

$\phi_{\text{phot,A}} = k_1 / (k_1 + k_x)$ is the fraction of ^3A molecules that form products. Introducing the quenching equation we find

$$\frac{dC_A}{dt} = -k_T C_D \phi_{\text{phot,A}} k_q \tau(t) C_A(t) \quad (2a)$$

and by integration

$$\ln\left(\frac{C_A}{C_{A_0}}\right) = K \int_0^t \tau(t) dt = Kz \quad (3)$$

By this transformation we can use first-order equations. It is necessary, however, that the quantum yield or the triplet lifetime of the sensitizer is known. The lifetime may be observed in phosphorescence or in triplet-triplet absorption experiments.

The rate equation for disappearance of A via the exciplex mechanism is different from eqn. (2):

$$\frac{dC_A}{dt} = - \frac{k_T \phi_{\text{phot},A} \phi_{\text{phot},^3(\text{AD})} C_D k_a C_A}{k_D + k_a(1 - \phi_{\text{dis}}) C_A} \quad (4)$$

$\phi_{\text{phot},^3(\text{AD})} = 1 - (k_d + k_z)/(k_d + k_y + k_z)$ is the fraction of exciplexes that decay into the photochemical channel.

By introducing the quenching equation (eqn. (1)) we find

$$\frac{dC_A}{dt} = -k_T \phi_{\text{phot},A} \phi_{\text{phot},^3(\text{AD})} C_D \tau_0 k_a \frac{\phi(t)}{\phi_0} C_A(t) \quad (4a)$$

and by integration we find

$$\ln\left(\frac{C_A}{C_{A_0}}\right) = K' \int_0^t \phi(t) dt = K'y \quad (5)$$

This transformation also leads to first-order equations, but for the exciplex mechanism the quantum yield dependence of the sensitizer on irradiation time must be known. This reduces the number of suitable sensitizers whose photoreactions via the exciplex mechanism can be evaluated by this method to the few that phosphoresce at room temperature.

This time-axis transformation has its advantages for non-chiral photo-reactions but it is necessary for the evaluation of asymmetric photochemistry (*vide infra*). For non-chiral photochemistry there is another way that leads to the constant K . Using the initial slope of the disappearance of the acceptor molecule as a function of its concentration [26], we find

$$\frac{1}{\dot{E}_0} = \frac{1}{K\epsilon_A} \left(1 + \frac{1}{\tau_0 k_q C_{A_0}} \right) \quad (6)$$

In our experiments we took the reaction spectra in differential absorption: a simple decrease of the $n \rightarrow \pi^*$ band of DPY was observed. The initial concentrations of DPY were about 10^{-3} M; the concentrations were within the linear part of the quenching curves where ϕ_0/ϕ and τ_0/τ are equal. For reasons of experimental convenience we used the decay times for the time-axis transformation, which was performed by graphical evaluation of the integral.

A plot of the maximum of the reaction spectra *versus* the transformed time axis z is shown in Fig. 5. Good linearity is obtained up to 90% of the reaction. This is clearly an advantage compared with plotting $\ln C$ against irradiation time, where deviations from linearity occur early and initial slope techniques are necessary.

Evaluation of a plot of $\ln(E - E_\infty)$ *versus* $\int \tau_D(t) dt$ according to eqn. (3) leads to a slope $K = -180 \text{ s}^{-2}$. From quenching experiments we know that k_q (collisional mechanism) or $k_a \phi_{\text{phot},^3(\text{AD})}$ (exciplex mechanism) is $2.5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. With these numbers, the incident light intensity $I_0 = 3.13 \times 10^{-9} \text{ einsteins cm}^{-2} \text{ s}^{-1}$, $\epsilon_{\text{ROT},368} = 135 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $C_{\text{ROT}} = 8.2 \times 10^{-5} \text{ M}$ we calculate

$$\phi_{\text{isc},\text{D}} \phi_{\text{phot},\text{A}} = 0.92$$

The evaluation of initial slopes according to eqn. (6) gives a linear plot for $1/\dot{E}_0$ against $1/C_{0,\text{DPY}}$. From the intersection of the ordinate of the straight line we calculate

$$\phi_{\text{isc},\text{D}} \phi_{\text{phot},\text{A}} = 0.98$$

The excellent agreement with an estimated error of ± 0.1 justifies the conclusion that $\phi_{\text{isc},\text{D}} = 1$ and $\phi_{\text{phot},\text{A}} = 1$, *i.e.* all the triplet DPY molecules decay.

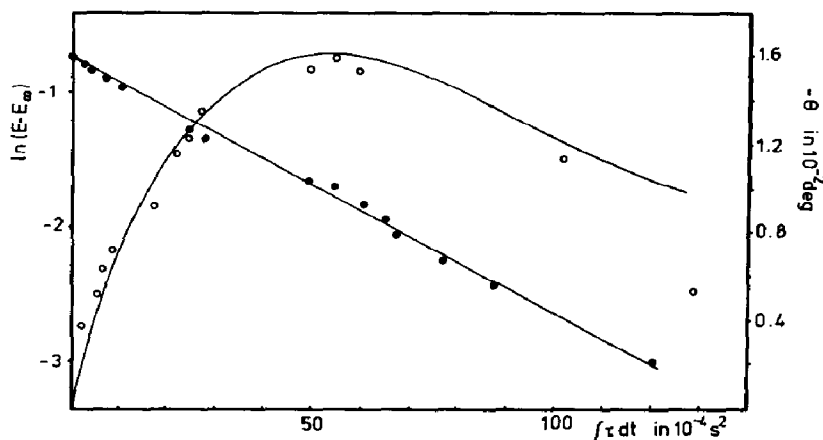
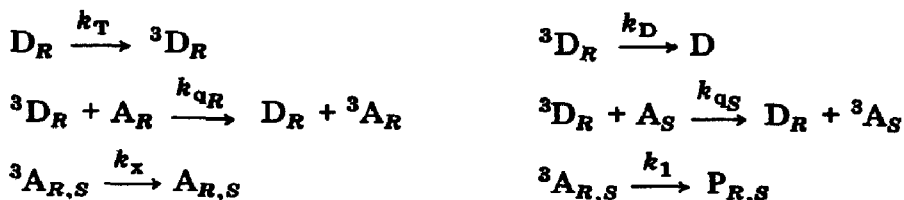


Fig. 5. ROT-sensitized DPY decay (●) as a first-order reaction in the transformed time axis $z = \int \tau dt$: $C_{\text{DPY}}(t = 0) = 1.25 \times 10^{-3} \text{ M}$; $C_{\text{ROT}} = 8.2 \times 10^{-5} \text{ M}$ (left-hand scale). Development of CD *versus* transformed time axis: —, calculated curve; ○, experimental points (right-hand scale).

3.4. Asymmetric photochemistry

According to the definition of an asymmetric photoreaction given in the introduction to this paper, a photoreaction sensitized by, say, the *R* form of the sensitizer in a bimolecular Stern–Volmer–quenching mechanism is represented by the following scheme:



The only phase of the reaction where asymmetry can be introduced is during the interaction of sensitizer and acceptor leading to a different number of 3A_R and 3A_S molecules. These react with identical rate constants k_x and k_1 (for triplet DPY $k_x \ll k_1$). In fact this reaction sequence is composed of two independent parallel reactions of A_R and A_S , the concentrations of which are equal at the beginning of the reaction. Thus eqn. (3) holds for both A_R and A_S with different rate constants K_R and K_S . The asymmetry of the reaction is defined by $\kappa = K_S/K_R$.

In Appendix A we present the development of a general kinetic scheme for the evaluation of asymmetric photoreactions. The importance of the time-axis transformation is now evident as we need first-order equations for that evaluation.

The asymmetric photoreaction is monitored by the UV and the CD spectra of DPY (after separation from optically active sensitizer, see Section 2). We use the $[\theta]_{330} - R_{330}$ plot (see eqns. (A2) and (A6)) of a starting mixture with $C_{ROT} = 8.2 \times 10^{-5}$ M and $C_{DPY} = 1.4 \times 10^{-3}$ M with the molar ellipticity of DPY $[\theta]_{330} = 79\,000$ deg $\text{cm}^2 \text{dmol}^{-1}$ [27] to evaluate the initial slope and the height of the maximum CD of DPY (Fig. 6). This maximum is at $R = 0.37$, indicating that κ is almost unity. This is the justification for treating this asymmetric reaction as a non-chiral reaction as we did in the previous section. The slope m_0 for $z = t = 0$ is -0.0421° , leading to $\kappa = 1.080$. Introducing this value into the proper formula (eqn. (A5)) we calculate $[\theta]_{330}(z_{\max}) = 0.0157^\circ$, which is in good agreement with the experimental value 0.0160° .

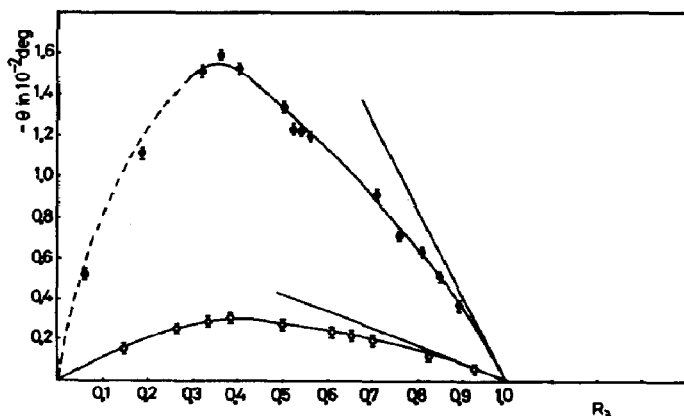


Fig. 6. $[\theta]_{330}$ vs. R_{330} plots for ROT-sensitized (\bullet) and TEST-sensitized (\circ) DPY decay: $C_{DPY}(t=0) = 1.4 \times 10^{-3}$ M; $C_{ROT} = 8.2 \times 10^{-5}$ M; $C_{TEST} = 6.9 \times 10^{-3}$ M.

From the average first-order rate constant $K = -180 \text{ s}^{-2}$ and κ we find the rate constants $K_S = -187 \text{ s}^{-2}$ and $K_R = -173 \text{ s}^{-2}$. With these constants we have calculated the $[\theta]_{330-z}$ curve (Fig. 5). The agreement with the experimental data is satisfactory up to 80% completion of the reaction.

In the $\theta_\lambda - R_\lambda$ plots the reaction coordinate appears as a parameter only so it is possible to plot θ_λ against R_λ at the same irradiation time and therefore we can evaluate the data of the TEST-sensitized DPY decay (Fig. 6). From the initial slope (of a larger scale plot) we obtain $\kappa = 1.016$ which is corroborated by the experimental value of the maximum CD.

The relevant data of the asymmetry of direct and sensitized photochemistry of *trans*-DPY are collected in Table 1. In direct photochemistry the asymmetry of the reaction is tied to the maximum g factor at the irradiation wavelength [10] $g_\alpha = 2(\kappa - 1)/(\kappa + 1)$. This g factor is normally about 0.01 or less corresponding to $\kappa = 1.01$ or less and only in a few cases is it greater than 0.1 (κ about 1.10). Nicoud *et al.* [28] discuss a maximum value of $g = 0.37$ for ketones and this value would limit the asymmetry obtainable by direct ketone photochemistry to $\kappa = 1.5$.

For *trans*-DPY $g_{332} = 0.058$ and $\kappa = 1.059$ for 332 nm irradiation by CPL [9]. The results in Table 1 indicate that this value can be surpassed by sensitized photochemistry: ROT shows a value of $\kappa = 1.080$ corresponding to a 50% increase in optical yield. Hope for finding sensitizing systems that may induce much higher asymmetry than found hitherto is therefore justified. TEST is less effective than is ROT or CPL in inducing asymmetry in the photodecomposition of DPY. However, considering the concentration dependence of κ (*vide infra*), the low value of κ for our TEST experiments may give a wrong impression. We had to use high TEST concentrations ($\approx 10^{-2}$ M) as TEST absorbs only weakly in the $n \rightarrow \pi^*$ band.

We know that there are other important factors besides the nature of the sensitizer. There is the influence of the solvent to be considered and we also assume that there is some influence of temperature [29]. In addition, we observe a distinct dependence of the asymmetry of the reaction on the concentration of the sensitizer. Figure 7 shows this for a fixed concentration of DPY of 1.4×10^{-3} M. κ has been taken from the maximum CD value during

TABLE 1

Asymmetric photolysis of *trans*-3,5-diphenylpyrazoline

Sensitizer	κ	$P_{\text{rel,max}}^a$ (%)	P_{en}^b (63%) (%)
Rotenone	1.080	1.5	4.05
Testosterone	1.016	0.3	0.75 (60%)
Direct (CPL)	1.058	0.98	2.65

^a $P_{\text{rel}} = (C_R(z) - C_S(z))/(C_R(0) + C_S(0))$ has its maximum value at an extent of reaction $\xi = 0.63$ if $\kappa \approx 1$.

^b $P_{\text{en}} = (C_R(z) - C_S(z))/(C_R(z) + C_S(z))$ is zero at $\xi = 0$ and unity at $\xi = 1$.

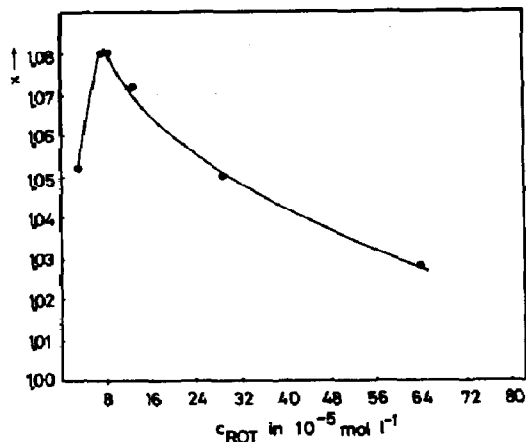


Fig. 7. Dependence of asymmetry κ on sensitizer concentration ($C_{\text{DPY}} = 1.4 \times 10^{-8} \text{ M}$).

photolysis. There is an optimum at $(8 - 9) \times 10^{-5} \text{ M}$ ROT. Increasing the ROT concentration leads to a decrease in κ , combined, however, with a faster total DPY photolysis. At lower concentrations there is a very sharp drop in the asymmetry of the reaction, in this case concomitant with a very slow total reaction.

The concentration dependence of κ could be understood if three molecules took part in the energy transfer process. A termolecular encounter is unlikely but we may recall the self-quenching properties of ROT. If we assume that a triplet ROT excimer lives long enough to be quenched by DPY, this energy transfer might have an effect on the asymmetry of the reaction opposite to the effect of energy transfer to DPY from a triplet ROT molecule. If we assume that ROT excimer formation energies do not greatly exceed those of aromatic hydrocarbons [30], energy transfer to DPY would still be exothermic by a few kilocalories per mole. Because of this and the fact that the photochemical rate constant increases with sensitizer concentration we prefer the idea that DPY quenches a ROT excimer rather than that a second ROT molecule quenches the triplet ROT-DPY exciplex, the possible existence of which has been the subject of our discussion. As the asymmetry effects reported are not too great, we are continuing the search for reaction systems with higher asymmetry, which may be necessary for comparison with theoretical calculations. Investigations at higher concentrations and in micellar solutions are in progress but these require modification of our experimental techniques.

Acknowledgments

This work was supported by the Fonds der Chemie, Frankfurt, and by the Deutsche Forschungsgemeinschaft.

The assistance of Mr. D. Ufermann and Miss B. Rexer is gratefully acknowledged. We thank Professor H. E. A. Kramer and his group for

continuing discussion and for making the equipment available for test measurements. The discussion with and the active interest of Professor L. Salem are highly valuable.

The development of the kinetics of asymmetric chemistry was partly due to Dr. R. Blume, Bielefeld.

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Appendix A

A.1. Kinetics of asymmetric chemistry

Asymmetric chemistry can be analysed in terms of two independent parallel reactions of the *R* and *S* enantiomers. For first-order kinetics and a

general reaction parameter z

$$\begin{aligned} C_R(z) &= C_{OR} \exp(-k_R z) \\ C_S(z) &= C_{OS} \exp(-k_S z) \end{aligned} \quad (\text{A1})$$

with $C_{OR} = C_{OS} = C_0$, the initial concentration of each of the enantiomers of the racemic mixture. We define the asymmetry of the reaction to be $\kappa = k_S/k_R$.

We developed a kinetic scheme to evaluate photoreactions induced by circularly polarized light [A1, A2]. Similar procedures have been used for reactions induced by an asymmetric catalyst [A3], circularly polarized light [A4] or a complexing agent [A5]. Higher than first-order parallel reactions have been systematically discussed as well [A6]. The essential feature of these developments is the combination of non-chiro-specific measurements, such as those of UV spectroscopy, gas chromatography or others, which provide the sum of concentrations of the enantiomers, and of circular dichroism (CD) or optical rotatory dispersion (ORD), which provide the difference of the concentrations of the enantiomers.

We use UV absorption data and define a reduced absorption difference $R_\lambda(z)$ to indicate the extent of reaction ($R_\lambda = 1 - \zeta$):

$$\begin{aligned} R_\lambda(z) &= \frac{A_\lambda(z) - A_{\infty\lambda}}{A_{0\lambda} - A_{\infty\lambda}} \\ &= \frac{C_R(z) + C_S(z)}{2C_0} \\ &= \frac{1}{2} \{ \exp(-k_R z) + \exp(-k_S z) \} \end{aligned} \quad (\text{A2})$$

Here $A_{\infty\lambda}$ is the absorbance at the end of the reaction.

We select an arbitrary wavelength Λ that is independent of λ where only the disappearing educt has a contribution to the CD spectrum. (It would be easy to find an expression in reduced terms as for absorbance, but usually the molar ellipticities of the reaction products are unknown. Therefore there is a restriction on the wavelength.)

Then

$$\begin{aligned} \theta_\Lambda(z) &= [\theta]_\Lambda \{ C_R(z) - C_S(z) \} \times 10^{-2} \\ &= \theta_{0\Lambda} \{ \exp(-k_R z) - \exp(-k_S z) \} \end{aligned} \quad (\text{A3})$$

where $\theta_{0\Lambda} = [\theta]_\Lambda C_0/100$ and the factor 1/100 stems from the dimensions of the molar ellipticity $[\theta]_\Lambda$ which is in $\text{deg cm}^2 \text{ dmol}^{-1}$ (e.g. see text, Fig. 5). We emphasize the importance of two points on this curve, the maximum and the inflection point. The peak is at $z_{\max} = \ln \kappa / (k_S - k_R)$ and the inflection point is at $z_{IP} = 2z_{\max}$.

$$\frac{C_R(z_{\max})}{C_S(z_{\max})} = \kappa \quad (\text{A4a})$$

$$\frac{C_R(2z_{\max})}{C_S(2z_{\max})} = \kappa^2 \quad (\text{A4b})$$

$$\theta_{\Lambda}(z_{\max}) = \theta_{0\Lambda} \left(1 - \frac{1}{\kappa}\right) \exp\left(\frac{\ln \kappa}{1 - \kappa}\right) \quad (\text{A5})$$

$$\theta_{\Lambda}(2z_{\max}) = \theta_{0\Lambda} \left(1 - \frac{1}{\kappa^2}\right) \exp\left(2\frac{\ln \kappa}{1 - \kappa}\right)$$

Simultaneous evaluation of UV and CD data leads to an elimination of the independent reaction coordinate z from the equations, which may be advantageous. By simply dividing suitable forms of eqn. (A2) and eqn. (A3) we arrive at

$$\theta_{\Lambda}(z) = 2\theta_{0\Lambda} \frac{\exp(-k_R z) - \exp(-k_S z)}{\exp(-k_R z) + \exp(-k_S z)} R_{\lambda}(z) \quad (\text{A6})$$

In Fig. A1 calculated $\theta_{\Lambda}-R_{\lambda}$ values are plotted with $\theta_{0\Lambda} = 100^\circ$ and κ as a parameter. The slopes at the start ($R_{\lambda} = 1$) and at the end of the reaction can be evaluated:

$$\left. \frac{d\theta_{\Lambda}}{dR_{\lambda}} \right|_{z=0} = -2\theta_{0\Lambda} \frac{\kappa - 1}{\kappa + 1} \quad (\text{A7a})$$

$$\left. \frac{d\theta_{\Lambda}}{dR_{\lambda}} \right|_{z \rightarrow \infty} = 2\theta_{0\Lambda} \quad (\text{A7b})$$

The peak value contains the same information as eqn. (A7a) does so there is an internal criterion for consistency. $\theta_{0\Lambda}$ and κ can be evaluated graphically.

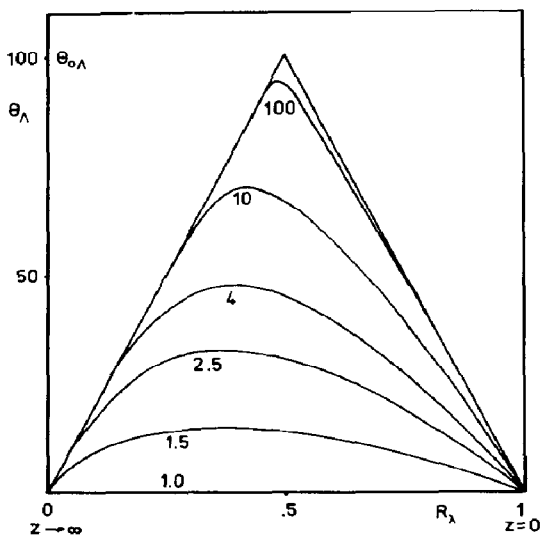


Fig. A1. $\theta_{\Lambda}-R_{\lambda}$ diagrams simulated according to eqn. (A6) with $z = t$, $\theta_{0\Lambda} = 100^\circ$ and $k_R = 0.01 \text{ min}^{-1}$ (arbitrary), for various values of κ .

There is also a method of numerical evaluation: from eqns. (A4a) and (A4b) we find

$$(C_R - C_S)_{\max} = \frac{\kappa - 1}{\kappa + 1} (C_R + C_S)_{\max}$$

or

$$\theta_{\Lambda}(z_{\max}) = 2\theta_{0\Lambda} \frac{\kappa - 1}{\kappa + 1} R_{\lambda}(z_{\max}) \quad (\text{A8})$$

and

$$\theta_{\Lambda}(2z_{\max}) = 2\theta_{0\Lambda} \frac{\kappa^2 - 1}{\kappa^2 + 1} R_{\lambda}(2z_{\max}) \quad (\text{A9})$$

Hence we have two equations for κ and $\theta_{0\Lambda}$. These yield

$$\kappa = (M - N)^{-1} [\{M(2N - M)\}^{1/2} + N] \quad (\text{A10})$$

with $M = \theta_{\Lambda}(2z_{\max})/\theta_{\Lambda}(z_{\max})$ and $N = R_{\lambda}(2z_{\max})/R_{\lambda}(z_{\max})$, and

$$\theta_{0\Lambda} = \frac{\theta_{\Lambda}(z_{\max})}{2\{R_{\lambda}(2z_{\max}) - R_{\lambda}^2(z_{\max})\}^{1/2}} \quad (\text{A11})$$

Some comments should be made.

(1) To find the inflection point, derivation of the θ - z curve is recommended.

(2) The calculation of $\theta_{0\Lambda}$ from κ introduces considerable errors: direct calculation from eqn. (A11) is recommended.

(3) The simultaneous evaluation of $\theta_{0\Lambda}$ and κ is restricted to values of κ greater than 1.5; high precision of CD measurements is assumed.

(4) For direct photochemistry there exists an additional relation between $[\theta]_{0\Lambda} = 3300(\epsilon_R - \epsilon_S)$ and κ which is ϵ_S/ϵ_R at the irradiation wavelength. This can be used to circumvent the difficulties found for small values of κ . Simple equations have been developed [A1, A2]. For ORD data or sensitized photochemistry there is no such relation to κ .

(5) To enter this kinetic scheme it is necessary to have genuine first-order rate equations. Transformation of time axes to the true independent reaction parameter z might be necessary.

References for Appendix A

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