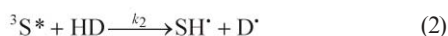


**Fig. 1** Saturation behavior of the observed rate constant ( $k_{obs}$ ) for the quenching of (*S*)-1 (○) and (*R*)-1 (■) triplet excited state by (*R*)-2 in dichloromethane.

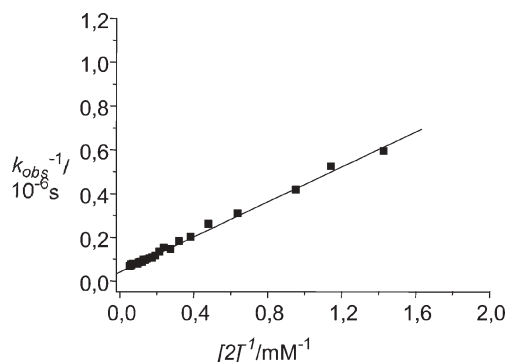
dichloromethane),<sup>9</sup> the bimolecular hydrogen abstraction from phenol by BT triplet is retarded, due to a decreased concentration of free phenol;<sup>6</sup> this explains the comparatively lower  $k_2$  values found in this solvent when using (*R*)-2 as quencher. As expected,<sup>6</sup> such effect was not observed for the BT/indole pair.



$$k_{obs} = k_2[HD] = K_{EC}k_d[HD] \quad (4)$$

At higher donor concentrations the  $k_2$  values did not increase linearly, but they rather approached a plateau, indicating the existence of a pre-equilibrium intermediate, *i.e.* the encounter complex between the triplet excited ketone and the aromatic donor (Fig. 1 and eqn. 3).<sup>10</sup>

The plots of  $k_{obs}$  vs. quencher concentration nicely show the saturation behaviour of the kinetics; unfortunately, it is not possible to obtain accurate values for  $K_{EC}$  and  $k_d$  from these plots. Rearranged equations are thus needed that allow the experimental data to be plotted in linear form. Therefore following Kochi's methodology for related cases,<sup>3</sup> the curved kinetic plots were evaluated in a double-reciprocal representation following eqn. 5<sup>11</sup> (see Fig. 2 for the (*R*)-1/(*R*)-2 pair in dichloromethane).



**Fig. 2** Double reciprocal evaluation according to eqn. 5 for the quenching of (*R*)-1 triplet excited state by (*R*)-2 in dichloromethane.

The pre-equilibrium constants ( $K_{EC}$ ) and the intrinsic decay rate constants ( $k_d$ ) of the encounter complex were thus obtained for all pairs (see Table 1).<sup>10</sup>

$$1/k_{obs} = 1/k_d + 1/(K_{EC}k_d[HD]) \quad (5)$$

The  $K_{EC}$  values deviated considerably from the unity expected for the purely diffusional encounters.<sup>12</sup> Taking into account that this constant depended on the effective approach distance between the donor and acceptor, the results indicated the formation of strong encounter complexes, except for the phenolic derivative in acetonitrile. The most striking result was the remarkable stereodifferentiation observed in some cases for both the formation and decay of the encounter complex (see curved kinetic plots for (*S*)-1/(*R*)-2 and (*R*)-1/(*R*)-2 diastereomeric pairs in Fig. 1). For the ketone/tryptophan pairs a considerably higher chiral recognition was observed in acetonitrile than in dichloromethane. A much less important solvent effect was observed for the ketone/tyrosine pairs (see Table 1).

In summary, the involvement of encounter complexes between both enantiomers of a  $\pi,\pi^*$  triplet excited ketone and a chiral phenol or indole has been experimentally established. Determination of the pre-equilibrium constants ( $K_{EC}$ ) and the intrinsic decay rate constants ( $k_d$ ) for each diastereomeric pair has evidenced a significant stereodifferentiation in both steps of the quenching process, which depends on the solvent properties. Due to the potential interest of these findings in connection with asymmetric photochemistry from the triplet excited state, current efforts are addressed to study the influence of substitution on the

**Table 1** Kinetic parameters for the quenching of photoexcited (*R*)-1 and (*S*)-1 by (*R*)-2 or (*R*)-3 in acetonitrile and dichloromethane<sup>a</sup>

Constants	( <i>R</i> )-1/( <i>R</i> )-2	( <i>S</i> )-1/( <i>R</i> )-2	( <i>R</i> )-1/( <i>R</i> )-3	( <i>S</i> )-1/( <i>R</i> )-3
$k_2 \times 10^{-9} \text{ (M}^{-1}\text{s}^{-1})^b$	0.209 ± 0.008 (2.30 ± 0.09)	0.232 ± 0.008 (2.13 ± 0.08)	1.75 ± 0.08 (2.86 ± 0.09)	1.64 ± 0.06 (2.9 ± 0.1)
$K_{EC} \text{ (M}^{-1})^c$	6.7 ± 0.7 (119 ± 8)	9.2 ± 0.8 (177 ± 14)	61 ± 7 (64 ± 7)	90 ± 9 (77 ± 6)
$k_d \times 10^{-7} \text{ (s}^{-1})^d$	2.9 ± 0.2 (2.1 ± 0.1)	2.2 ± 0.2 (1.45 ± 0.08)	3.7 ± 0.4 (4.81 ± 0.09)	2.4 ± 0.2 (4.1 ± 0.3)
$K_{EC}k_d \times 10^{-9} \text{ (M}^{-1}\text{s}^{-1})^e$	0.19 ± 0.03 (2.5 ± 0.3)	0.20 ± 0.04 (2.6 ± 0.3)	2.2 ± 0.5 (3.1 ± 0.4)	2.4 ± 0.4 z(3.2 ± 0.5)

<sup>a</sup> Values in CH<sub>2</sub>Cl<sub>2</sub> in parentheses. <sup>b</sup> Rate constants for bimolecular quenching determined from the slopes of the initial linear portion of the kinetic plots (see Fig. 1). <sup>c</sup> Equilibrium constants for encounter complex formation as determined using eqn. 5. <sup>d</sup> Intrinsic rate constants for the encounter complex decay as determined using eqn. 5. <sup>e</sup> Values determined from the slopes of the double-reciprocal plots (see Fig. 1) using eqn. 5.

donor and the acceptor, as well as the polarity of the solvent, on stereodifferentiation.

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