Letter to the Editor

Reply to comments on "The energy transfer from triplet state acetone to 9-bromoanthracene and 9,10-dichloroanthracene: an investigation under high pressure"

In the comments by Wu [1] concerning two of our papers [2, 3] dealing with the energy transfer from triplet state acetone to 9,10-dibromoanthracene (DBA), 9,10-dichloroanthracene (DCA) and 9-bromoanthracene (BA), he criticizes the fact that we did not consider the direct spin-forbidden triplet–singlet (TS) energy transfer according to the exchange mechanism in our interpretation. In Wu's opinion our results can be explained just as well on the basis of this mechanism. This would mean that the two-stage triplet–triplet (TT) energy transfer (during which first the T_2 state of the acceptor is excited and then by subsequent intersystem crossing (ISC) the S_1 state is excited) which we suggested is unnecessary for the interpretation of the data. In the following we will show that Wu's interpretation of the results on the energy transfer from triplet state acetone to heavy-atom-substituted anthracene derivatives, especially to DBA, is incorrect.

It was our aim with the criticized papers to clarify the question of whether the energy transfer from triplet state acetone to DBA (or to BA or DCA) in solution follows the aforementioned TT energy transfer or a long-range TS energy transfer, which has already been observed by Steinmetzer and coworkers for a rigid matrix [4, 5]. By means of studies of the pressure dependence we were able to show that the formation of the S_1 state of the acceptor is diffusion controlled, so that a long-range TS energy transfer can be excluded.

Alternatively, as Wu correctly remarks, a TS energy transfer following the short-range exchange mechanism is in principle also possible in this case. However, the restrictions from spin selection rules for this process are not decreased to such an extent as Wu suggests. The rate constant for the ISC $S_1 \rightarrow T_2$ of the acceptor DBA does not amount to 10^{13} s^{-1} without the energy factor but only to a tenth of this value [6 - 8].

We do not know of any rate constants for an incontestable TS energy transfer following the exchange mechanism. A comparison of rate constants of the reverse process given in Table 1 shows that a distinct restriction of the collisional ST energy transfer by spin prohibition remains in spite of heavy atom substitution. With the participation of bromo-substituted compounds either as donor or as acceptor, the k_{ET}^{ST} values lie with one exception distinctly below 10^9 M^{-1} s^{-1}. The rate constant for the TS energy transfer from triplet state acetone to DBA according to the exchange mechanism is therefore

TABLE 1

Rate constants k_{ET}^{ST} of ST energy transfer

Donor	Acceptor	Rate constant $(M^{-1} s^{-1})$
DBA [9]	Fluorene	1.5×10^9
	Naphthalene	5×10^8
	Biphenyl	2×10^7
	Stilbene	$< 10^7$
Perylene [10]	1-Iodonaphthalene	1.1×10^9
	1-Bromonaphthalene	1.3×10^8
	1-Chloronaphthalene	9×10^6

expected to be considerably smaller than that for the long-range mechanism, for which a value of 10^9 M^{-1} s^{-1} has been determined [5]. Consequently, only the long-range TS energy transfer was discussed in our papers as the most important alternative to the two-stage TT energy transfer.

Furthermore, the TS energy transfer according to the exchange mechanism can also be excluded for the donor—acceptor systems that we investigated. As pointed out by Wu, it is true that a distinction between short-range TS energy transfer and TT energy transfer is not possible by means of a study of the pressure dependence. However, a consideration of the magnitude of the competing processes shows that the high efficiency of the observed energy transfer cannot be explained by the TS energy transfer alone.

In the kinetic scheme proposed by Wu $\alpha = k_2/(k_2 + k_3 + k_4)$ is the probability for TS energy transfer in the "encounter complex" of triplet state acetone and the acceptor, the formation of which is diffusion controlled. In this derivation it is supposed that this complex only reacts to produce ground state acetone and the acceptor in the S_1 state (k_2), in the T_2 state (k_3) or in the T_1 state (k_4) [1]. The rate at which DBA quenches triplet state acetone is diffusion controlled with a rate constant of 2.6×10^{10} M^{-1} s^{-1} [2, 3]. Therefore, the sum of the energy transfer rate constants must amount to $k_2 + k_3 + k_4 \gg 2.6 \times 10^{10}$ M^{-1} s^{-1}. However, it must be assumed (see Table 1) that k_2 is less than 10^9 M^{-1} s^{-1}. It follows that $\alpha \ll 0.04$ for the probability of TS energy transfer. Therefore, the efficiency of TS energy transfer for infinitely high acceptor concentrations should also be much less than 0.04. In fact a much larger value of 0.2 has been found [11].

This extraordinarily high efficiency can on the contrary be easily explained within the concept of the two-stage TT transfer by a high yield ϕ_{ISC}^{TS} of ISC from T_2 to S_1 in the acceptor.

The unusual ISC from a higher excited triplet state to S_1, which is essential for the two-stage TT transfer, could be proved almost simultaneously and independently of us by Kobayashi et al. [12,13] for some anthracene derivatives. The ϕ_{ISC}^{TS} values determined by these authors by means of a double excitation method are compared in Table 2 with our values found in the analysis

TABLE 2

Yields ϕ_{ISC}^{TS} of ISC $T_2 \rightarrow S_1$

Acceptor	ϕ_{ISC}^{TS} [13]	ϕ_{ISC}^{TS} [2, 3, 14]
DBA	0.27	0.4
BA	—	0.21
DCA	0.015	0.025
9-Methylanthracene	0.00036	0.00069

of the indirect chemiluminescence [2, 3, 14]. In view of the various errors involved the agreement is very good.

The ϕ_{ISC}^{TS} values confirm the high yield of ISC $T_2 \rightarrow S_1$ in the acceptors, such that the validity of the two-stage TT energy transfer mechanism in the investigated donor–acceptor systems is further underlined.

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