

THE ENERGY TRANSFER FROM TRIPLET STATE ACETONE TO 9-BROMOANTHRACENE AND 9,10-DICHLOROANTHRACENE: AN INVESTIGATION UNDER HIGH PRESSURE

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Summary

The intensity of the indirect chemiluminescence of ternary solutions containing tetramethyl-1,2-dioxetane (TMD) and 9-bromoanthracene (BA) or 9,10-dichloroanthracene (DCA) in toluene was investigated as a function of acceptor concentration and pressure at 40 °C. The results are discussed in connection with the pressure dependence of the fluorescence of both acceptors, which was determined in this study, and the pressure dependence of the rate of decomposition of TMD reported earlier. It is shown that the energy transfer from triplet acetone to BA and DCA is a spin-allowed triplet-triplet process, as was found for the energy transfer to 9,10-dibromoanthracene (DBA).

A comparison of the intensities of chemiluminescence, extrapolated to infinitely high concentrations, leads to the determination of the yields of intersystem crossing from the second excited triplet state T_2 to the singlet state S_1 for DBA, BA and DCA, respectively.

Introduction

In a recent publication [1] we showed that in solution the energy transfer from acetone in its triplet state to 9,10-dibromoanthracene (DBA), which is responsible for the indirect chemiluminescence of tetramethyl-1,2-dioxetane (TMD) and DBA, occurs according to a triplet-triplet (TT) mechanism. During this process the energy of triplet acetone is transferred to DBA in a diffusion-controlled step thereby exciting the DBA to its second excited triplet state T_2 . Subsequent intersystem crossing (ISC) leads to the singlet state S_1 , from which emission occurs. In an alternative process, which is also diffusion controlled, the lowest triplet state T_1 of DBA can be reached. However, this state decays without radiation. Thus the second energy transfer process to DBA does not contribute to the indirect chemiluminescence. The

fact that in solution the energy transfer from acetone to DBA, according to a TT mechanism, is substantially more efficient than the direct spin-forbidden triplet-singlet (TS) energy transfer, found by Turro and Steinmetzer [2] in a solid matrix, can be explained as follows.

(1) The T_2 state of DBA is about 1000 cm^{-1} lower than the T_1 state of acetone. Thus the rate constant for the spin-allowed TT energy transfer is diffusion controlled. According to the Debye equation [3]

$$k_{\text{diff}} = \frac{8RT}{3000\eta} \quad (1)$$

k_{diff} can be estimated to have a value of $1.4_5 \times 10^{10}\text{ M}^{-1}\text{ s}^{-1}$ in toluene at 40°C where the solvent has a viscosity η of 0.47 cP. This rate constant exceeds that found by Turro and Steinmetzer [2] for the direct TS energy transfer, which is about $10^9\text{ M}^{-1}\text{ s}^{-1}$, by one order of magnitude.

(2) Obviously the efficiency of ISC from T_2 to S_1 is very high. One reason for this is the inner heavy atom effect caused by two bromine atoms, which weakens the spin restrictions. Another reason is that the S_1 state of DBA is only about 1500 cm^{-1} lower than the T_2 state [4]. As can be seen from Table 1, the energy levels of the S_1 , T_1 and T_2 states for 9-bromoanthracene (BA) and 9,10-dichloroanthracene (DCA) show only small differences compared with those of DBA. For all three compounds the T_2 state lies somewhat lower than the T_1 state of acetone. Thus energy transfer from T_1 acetone to the T_2 level of BA and DCA should be diffusion controlled. Despite these small energy differences between T_1 acetone and the T_2 states of the different acceptors, retransfer of energy to acetone can be excluded on the basis of the short lifetimes of the T_2 states of these compounds. The lifetimes are of the order of $2 \times 10^{-10}\text{ s}$ according to Liu [5].

TABLE 1

Energy levels of the lowest singlet and triplet states of donor acetone and different acceptors and rate constants $k_{\text{ISC}}(a)^a$ of the isoenergetic ISC between the S_1 and T_2 states of anthracene derivatives

Compound	$\Delta E(\text{cm}^{-1})$			$10^9 \times k_{\text{ISC}}(0) (\text{s}^{-1})$	
	S_1	T_1	T_2		
Acetone	29700 [8]	27300 [8]	—		
DBA	24800 [4]	14060 [7]	26300 [4]	910 ± 350 [6] ^c	1100 [4] ^d
BA	25600 [4]	14000 ^b	26600 [4]	580 ± 70 [6] ^c	610 [4] ^d
DCA	24900 [4]	14150 [7]	26400 [4]	72 ± 20 [6] ^c	170 [4] ^d

^a $k_{\text{ISC}} = k_{\text{ISC}}(0) \exp(-\Delta E/RT)$.

^bEstimated value.

^cIn ethanol.

^dIn n-heptane.

For all three compounds the S_1 state is placed only slightly below the T_2 level, thereby establishing the energy requirement for a high yield of ISC.

However, an important role in this process is played by the inner heavy atom effect which decreases substantially in the series DBA, BA and DCA. A measure of the inner heavy atom effect is given by the rate constant $k_{ISC}(0)$ for the isoenergetic ISC [4, 6], values for which are included in Table 1. $k_{ISC}(0)$ for DBA is about twice as large as for BA and ten times that of DCA. This leads to the expectation that the yield ϕ_{ISC}^{TS} of ISC from T_2 to S_1 should be only slightly smaller for BA, but essentially reduced for DCA compared with DBA.

Furthermore, one can expect that energy transfer from T_1 acetone to BA proceeds through a TT mechanism as in the case of DBA. However, should the rate constant for the direct spin-forbidden TS energy transfer not be as strongly influenced by the inner heavy atom effect as ϕ_{ISC}^{TS} , then the direct TS energy transfer in solution could be of importance when DCA is the acceptor.

In order to prove this hypothesis the fluorescence of BA and DCA was investigated as a function of pressure while the indirect chemiluminescence of TMD/BA and TMD/DCA was determined as a function of pressure and acceptor concentration.

Experimental

The preparation and purification of TMD was conducted according to procedures described in the literature [9]. BA and an isomeric mixture of 2,4-hexadiene were obtained from Aldrich Europe and DCA from Ferak. Both BA and DCA were recrystallized several times from ethanol, whereas 2,4-hexadiene was used without further purification. Toluene, Uvasol grade from Merck, was used as the solvent. Air-saturated solutions were employed for the investigations.

For the determination of the pressure dependence of the fluorescence of BA and DCA, as well as the concentration and pressure dependences of the indirect chemiluminescence, the same procedures were followed as reported for the system using DBA as an acceptor [1]. Fluorescence yields were obtained using an apparatus described earlier [10]. 9,10-Diphenylanthracene (DPA), having a fluorescence yield of 0.82 in degassed benzene solutions [11], was used as a standard. Since the refraction indices of benzene and toluene are nearly identical, no corrections with respect to this solvent property were necessary.

Results

It is known that during the thermolysis of TMD about 50% acetone in its ground state, 0.1% in its excited singlet state and about 50% in its triplet state is formed [12, 13]. If one adds an anthracene derivative as acceptor to a solution of TMD the energy can be transferred to the acceptor from the S_1

state of acetone, as well as from its T_1 state [8]. DBA and BA are typical triplet acceptors obtaining the energy nearly exclusively from the T_1 acetone [9]. DPA is considered to be a typical singlet acceptor being excited mainly by S_1 acetone and to a lesser degree also by T_1 acetone [9, 14, 15]. An analysis of the energy transfer from excited acetone (S_1 and T_1 states) to DPA during the indirect chemiluminescence using TMD as an energy source is therefore more complicated.

At this point it appears to be necessary to determine to which type of acceptor DCA belongs. This can be done by using the triplet quencher 2,4-hexadiene. This compound does not significantly quench the S_1 state of acetone, whereas the T_1 state is efficiently quenched.

Stern-Volmer plots of the intensity of indirect chemiluminescence with DBA as acceptor and 2,4-hexadiene as quencher are linear up to a diene concentration of 1 M showing a slope of about 200 M^{-1} . With BA one can observe a slight curvature at high concentrations (1 M). DCA as acceptor shows a distinct curvature shifted to lower concentrations (0.1 M), whereas with DPA a strong curvature appears below 10^{-2} M diene leading to a slope of approximately 0.5 M^{-1} . An analysis of these quenching curves shows that for DCA as acceptor at concentrations of $1.3 \times 10^{-3} \text{ M}$ only about 6% of the indirect chemiluminescence is caused by an energy transfer from S_1 acetone to the acceptor; about 94% originates in an energy transfer process from T_1 acetone to the acceptor [14]. As a consequence of these results DCA must be considered to be a triplet acceptor. The small portion of energy transfer from S_1 acetone to DCA is neglected in the following discussion. The Stern-Volmer constants for the quenching of the indirect chemiluminescence of solutions containing TMD and DBA, BA or DCA as acceptors and 2,4-hexadiene as quencher, calculated from the linear portions of the plots, result in

$$\begin{aligned} K(\text{DBA}) &= 200 \text{ M}^{-1} \quad \text{at} \quad [\text{DBA}] = 1 \times 10^{-3} \text{ M} \\ K(\text{BA}) &= 190 \text{ M}^{-1} \quad \text{at} \quad [\text{BA}] = 1.07 \times 10^{-3} \text{ M} \\ K(\text{DCA}) &= 176 \text{ M}^{-1} \quad \text{at} \quad [\text{DCA}] = 1.3 \times 10^{-3} \text{ M} \end{aligned}$$

The intensity I_{ch} of chemiluminescence of a solution containing TMD and triplet acceptor can be expressed by the relationship

$$I_{\text{ch}} = ak_{\text{th}}[\text{TMD}] \phi_{\text{T}}^{\text{T}} \phi_{\text{ET}} \phi_{\text{FL}}^{\text{acc}} \quad (2)$$

in which a is the apparatus constant, k_{th} the rate constant of the thermal decomposition of TMD, $\phi_{\text{T}}^{\text{T}}$ the yield of T_1 acetone, ϕ_{ET} the yield of the direct and indirect energy transfer from T_1 acetone to the S_1 state of the acceptor and $\phi_{\text{FL}}^{\text{acc}}$ the quantum yield for the fluorescence of the acceptor. Of all quantities in eqn. (2) ϕ_{ET} is particularly dependent on the acceptor concentration. Only at very high acceptor concentrations does $\phi_{\text{FL}}^{\text{acc}}$ also become concentration dependent owing to concentration quenching. For this reason the plots of the reciprocal of the intensity of chemiluminescence *versus* the reciprocal of the acceptor concentration deviate from linearity for BA and DCA above 10^{-2} M , while the plot remains linear for DBA over the whole

range investigated. The reciprocal of the chemiluminescence intensities as a function of acceptor concentrations are listed in Table 2 for BA and DCA together with the values for the slopes SL and intercepts INT and the ratios SL/INT.

TABLE 2

Dependence of the intensity of the chemiluminescence on the concentration of the acceptor (intensities in relative units)

$1/c_{\text{acc}}(\text{M}^{-1})$	50	200	500	1000	2000	5000
$1/I_{\text{ch}}^{\text{BA}} \times 10^3$	69.7 ^a	68.8	109	171	296	623
$1/I_{\text{ch}}^{\text{DCA}} \times 10^3$	47.0 ^a	37.0	56.9	85.5	—	299
BA: SL = 11.5×10^{-5} M, INT = 53.7×10^{-3} , SL/INT = 2.14×10^{-3} M						
DCA: SL = 5.40×10^{-5} M, INT = 28.9×10^{-3} , SL/INT = 1.87×10^{-3} M						

[TMD] = 3.3×10^{-3} M, error about $\pm 5\%$.

^aThis value was not used for the least squares treatment because of the influence of concentration quenching.

Table 3 contains the relative changes $I_{\text{ch}}(p)/I_{\text{ch}}(1) = A$ of I_{ch} with pressure for different concentrations of BA. In addition, the reciprocal intensities $1/I_{\text{ch}}(1)$ of chemiluminescence at normal pressure which were calculated from a least squares analysis are listed. Using these values $1/I_{\text{ch}}(p)$ could be calculated and plotted against $1/c_{\text{BA}}$ at different pressures. These plots were all linear. In this procedure the pressure coefficient of the intercept was taken to be equal to the pressure coefficient of $1/I_{\text{ch}}$ of a solution containing 0.02 M BA. The concentration quenching in a 0.02 M solution of BA has no influence on the ratio $I_{\text{ch}}(p)/I_{\text{ch}}(1)$, since the pressure coefficient of the fluorescence is independent of concentration over the range covered. Slope, intercept and the ratio of slope to intercept as functions of pressure are also included in Table 3.

The relative changes of I_{ch} with pressure, *i.e.* $I_{\text{ch}}(p)/I_{\text{ch}}(1) = A$, as a function of DCA concentration are summarized in Table 4. The reciprocal intensities $1/I_{\text{ch}}(1)$ of chemiluminescence at normal pressure, as obtained from a least squares treatment, are also listed in Table 4. In addition, Table 4 contains the pressure dependence $\phi_{\text{FL}}^{\text{DCA}}(p)/\phi_{\text{FL}}^{\text{DCA}}(1) = B$ of the quantum yields of fluorescence. As can be observed from the data, B is independent of concentration in dilute solutions. In 0.02 M solution, however, the value of B is clearly larger. Obviously this is due to the stronger pressure dependence of the concentration quenching. For the same reason plots of $1/I_{\text{ch}}(p)$ versus $1/c_{\text{DCA}}$ at different pressures cannot be linear. Only after correction is made for the concentration dependence of $\phi_{\text{FL}}^{\text{DCA}}(p)/\phi_{\text{FL}}^{\text{DCA}}(1) = B$ are plots of $B/I_{\text{ch}}(p) = C$ versus $1/c_{\text{DCA}}$ again linear. The slopes SL and intercepts INT of these straight lines and the ratios SL/INT are also included in Table 4 together with the values of C . The pressure dependence of the intercept of C was taken to be equal to the experimentally obtained pressure dependence of $\phi_{\text{FL}}^{\text{DCA}}/I_{\text{ch}}$ for a solution containing 0.02 M DCA.

TABLE 3

Concentration and pressure dependences of the indirect chemiluminescence with BA as acceptor^a

<i>p</i> (bar)	$1/c_{BA} (M^{-1})$				$10^3 \times INT$	$10^5 \times SL (M)$	$10^3 \times SL/INT (M)$
	5000	1000	200	50			
1	$1/I_{ch}(1) \times 10^3$	628	169	76.7	53.7	11.5	2.14
200	A^b $1/I_{ch}(p) \times 10^3$	0.957 656	0.970 174	1.025 74.8	1.08 49.6	12.1	2.44
400	A $1/I_{ch}(p) \times 10^3$	0.903 696	0.934 181	1.03 74.4	1.15 51.7	13.0	2.78
600	A $1/I_{ch}(p) \times 10^3$	0.858 732	0.891 190	1.025 74.8	1.215 49.0	13.7	3.10
1000	A $1/I_{ch}(p) \times 10^3$	0.764 822	0.813 208	1.00 76.9	1.31 45.4	15.6	3.81

^a Intensities in relative units; $[TMD] = 3.3 \times 10^{-3} M$; error about $\pm 7\%$ at 1000 bar.^b $A = I_{ch}(p)/I_{ch}(1)$.

TABLE 4

Concentration and pressure dependences of indirect chemiluminescence with DCA as acceptor^a and concentration and pressure dependences of the quantum yield of fluorescence of DCA in air-saturated toluene^b

p (bar)	$1/c_{\text{DCA}} (\text{M}^{-1})$					$10^3 \times \text{INT}$	$10^5 \times \text{SL} (\text{M})$	$10^3 \times \text{SL}/\text{INT} (\text{M})$
	5000	1000	200	50	50			
1	$1/I_{\text{ch}}(1) \times 10^3$	299	83.0	39.7	31.6	28.9	5.40	1.87
200	A ^c	0.907	0.923	0.980	1.044			
	B ^c	1.043	1.043	1.043	1.046			
400	$10^3 \times C^c$	344	93.8	42.3	31.7	29.0	6.29	2.17
	A	0.831	0.849	0.955	1.080			
600	B	1.083	1.083	1.083	1.102			
	$10^3 \times C$	390	106	45.0	32.1	29.5	7.20	2.44
1000	A	0.763	0.786	0.923	1.105			
	B	1.123	1.123	1.123	1.141			
1000	$10^3 \times C$	440	119	48.3	32.6	29.8	8.18	2.75
	A	0.642	0.682	0.860	1.165			
1000	B	1.200	1.200	1.200	1.250			
	$10^3 \times C$	559	146	55.4	33.9	31.0	10.5	3.39

^a Intensities are given in relative units; $[\text{TMD}] = 3.3 \times 10^{-3} \text{ M}$; error about $\pm 7\%$ at 1000 bar.

^b $T = 40^\circ \text{C}$; $\lambda_{\text{exc}} = 365 \text{ nm}$; error about $\pm 3\%$ at 1000 bar.

^c $A = I_{\text{ch}}(p)/I_{\text{ch}}(1)$; $B = \phi_{\text{FL}}^{\text{DCA}}(p)/\phi_{\text{FL}}^{\text{DCA}}(1)$; $C = \phi_{\text{FL}}^{\text{DCA}}(p)/\{I_{\text{ch}}(p)\phi_{\text{FL}}^{\text{DCA}}(1)\}$

Contrary to the situation with DCA, the quantum yield of fluorescence of air-saturated toluene solutions of BA at 40 °C are found to be concentration independent over the measured range of 2×10^{-4} - 2×10^{-2} M. The results are presented in Table 5.

TABLE 5

Pressure dependence of the quantum yield of fluorescence of BA in air-saturated toluene

<i>p</i> (bar)	200	400	600	1000
$\phi_{\text{FL}}^{\text{BA}}(p)/\phi_{\text{FL}}^{\text{BA}}(1)$	1.09 ₅	1.19	1.29	1.47
Error	± 0.01	± 0.02	± 0.02	± 0.04

$T = 40$ °C; $\lambda_{\text{exc}} = 365$ nm; $[\text{BA}] = 2 \times 10^{-4}$ - 2×10^{-2} .

In eqn. (2) only α and $\phi_{\text{T}}^{\ddagger}$ are pressure-independent quantities [16]. Therefore a variation of pressure only results in

$$\frac{I_{\text{ch}}(p)}{I_{\text{ch}}(1)} = \frac{k_{\text{th}}(p)\rho(p)\phi_{\text{ET}}(p)\phi_{\text{FL}}^{\text{acc}}(p)}{k_{\text{th}}(1)\rho(1)\phi_{\text{ET}}(1)\phi_{\text{FL}}^{\text{acc}}(1)} \quad (3)$$

Herein ρ is the pressure-dependent density of the solvent. After rearrangement one obtains for the pressure dependence of the yield of energy transfer

$$\ln \left\{ \frac{\phi_{\text{ET}}(p)}{\phi_{\text{ET}}(1)} \right\} = \ln \left\{ \frac{I_{\text{ch}}(p)}{I_{\text{ch}}(1)} \right\} - \ln \left\{ \frac{k_{\text{th}}(p)}{k_{\text{th}}(1)} \right\} - \ln \left\{ \frac{\rho(p)}{\rho(1)} \right\} - \ln \left\{ \frac{\phi_{\text{FL}}^{\text{acc}}(p)}{\phi_{\text{FL}}^{\text{acc}}(1)} \right\} \quad (4)$$

The pressure dependences of the intensities of chemiluminescence and the quantum yields of fluorescence are already listed in Tables 3, 4 and 5. The pressure dependences of the density of toluene at 40 °C and of the rate constant for the thermal decomposition of TMD at 60 °C were published earlier [16]. Thus the yield ϕ_{ET} of energy transfer can be calculated as a function of pressure and acceptor concentration for BA and DCA using eqn. (4). A small systematic error may be introduced if $k_{\text{th}}(p)/k_{\text{th}}(1)$ is temperature dependent. However, this error is then concentration independent. The values for the pressure and acceptor concentration dependences of the yields of energy transfer are summarized in Tables 6 and 7.

TABLE 6

Pressure and BA concentration dependences $\ln \{ \phi_{\text{ET}}(p)/\phi_{\text{ET}}(1) \}$ of the yield ϕ_{ET} of energy transfer

<i>p</i> (bar)	<i>c</i> _{BA} (M)				Error
	2×10^{-4}	1×10^{-3}	5×10^{-3}	2×10^{-2}	
200	-0.09	-0.08	-0.02	+0.03	± 0.05
400	-0.22	-0.19	-0.09	+0.02	± 0.05
600	-0.33	-0.30	-0.16	+0.01	± 0.06
1000	-0.56	-0.50	-0.30	-0.02	± 0.07

TABLE 7

Pressure and DCA concentration dependences in $\{\phi_{ET}(p)/\phi_{ET}(1)\}$ of the yield ϕ_{ET} of energy transfer

p (bar)	c_{DCA} (M)				Error
	2×10^{-4}	1×10^{-3}	5×10^{-3}	2×10^{-2}	
200	-0.10	-0.08	-0.02	+0.04	± 0.05
400	-0.21	-0.19	-0.07	+0.04	± 0.05
600	-0.31	-0.28	-0.12	+0.04	± 0.06
1000	-0.54	-0.48	-0.24	+0.02	± 0.07

Discussion

The energy levels involved in the energy transfer from T_1 acetone to BA are shown in Fig. 1. The levels of the S_1 , T_1 and T_2 states of DCA are nearly identical with those of BA. Therefore the scheme depicted in Fig. 1 may be taken as representative of the energy transfer to both acceptors. The T_1 state of the donor acetone is $27\,300\text{ cm}^{-1}$ higher in energy than the potential acceptor levels of the anthracene derivatives, *i.e.* the S_1 , T_1 and T_2 states. The deactivation of T_1 acetone in the absence of BA or DCA is determined by the rate constant $k_{\text{dea}}^{\text{TA}}$.

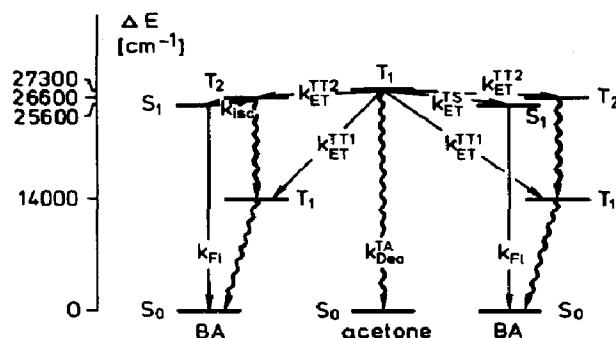


Fig. 1. Scheme for the energy transfer from T_1 acetone to BA.

On the right-hand side of the scheme presented in Fig. 1 the spin-forbidden direct TS energy transfer is shown. This transfer occurs by a long range mechanism during which the molecules do not need to approach each other to within their collisional diameters [17]. Turro and Steinmetzer [2] showed that such a mechanism prevails in a solid matrix with DBA as acceptor. The rate constant for the direct energy transfer from T_1 acetone to the S_1 state of the acceptor was estimated by both authors to be about $10^9\text{ M}^{-1}\text{ s}^{-1}$. Because of the smaller heavy atom effect for BA and DCA one can assume $k_{\text{ET}}^{\text{TS}} < 10^9\text{ M}^{-1}\text{ s}^{-1}$. Because $k_{\text{ET}}^{\text{TS}}$ is a rate constant for a long range process, it may be expected to be pressure independent.

Competing with the direct excitation of the S_1 state, either the T_1 or the T_2 level of the acceptor can be populated via a TT energy transfer. Both processes are spin-allowed and exothermic. Their rate constants k_{ET}^{TT1} and k_{ET}^{TT2} should be diffusion controlled. According to Debye's relation (eqn. (1)) a value of about $1.4_5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ can be expected. Thus the excitation of the triplet states should be much faster than the direct population of the S_1 levels. k_{ET}^{TT1} and k_{ET}^{TT2} should be pressure dependent corresponding to the reciprocal viscosity of the solvent, which is given in Table 8 [1, 18 - 20].

TABLE 8

Pressure dependence of the viscosity of toluene at 40 °C

p (bar)	200	400	600	1000
$\eta(p)/\eta(1)$	1.150	1.310	1.486	1.874

Interpolated data according to Bridgman [21].

Since each excited acetone molecule can only be quenched once and since $k_{ET}^{TS} \ll k_{diff}$, the total rate of quenching of T_1 acetone in solution is expected to be diffusion controlled and independent of the number of potential acceptor levels. The acceptor molecule will then be excited to its S_1 , T_1 or T_2 states, depending on the mechanism involved*.

An excitation of the T_1 state of the acceptor does not lead to an emission of light under the given circumstances. Furthermore, if one assumes that an excitation of the T_2 state is followed by a deactivation through internal conversion to the T_1 state, then direct spin-forbidden TS energy transfer to the S_1 acceptor level is the only remaining contribution to the indirect chemiluminescence. In this case the yield of energy transfer from T_1 acetone to the S_1 state of the acceptor can be expressed by

$$\phi_{ET}^{TS} = \frac{k_{ET}^{TS} [\text{acc}]}{k_{diff}^{acc} [\text{acc}] + k_{dea}^{TA}} \quad (5)$$

where [acc] represents the concentration of acceptor and k_{diff}^{acc} is the diffusion-controlled rate constant for the quenching of T_1 acetone by the acceptor and is much greater than k_{ET}^{TS} .

Should the indirect chemiluminescence not originate from the energy transfer through the TS mechanism, then the S_1 state of the acceptor can only be reached by a two-step process according to a TT mechanism. In this case the energy is transferred from T_1 acetone to the T_2 level of the acceptor in a diffusion-controlled process. From there the S_1 state, which is susceptible to fluorescence, can be reached by ISC with a yield of ϕ_{ISC}^{TS} . As a competitor

*The possibility that the total rate of quenching depends on the number of acceptor levels for the diffusion-controlled transfer was not totally excluded in a previous publication [1]. Current investigations involving further anthracene derivatives indicate, however, that such a speculation is incorrect.

to T_2 excitation, only energy transfer to the T_1 level is conceivable. This does not lead to indirect chemiluminescence. The yield ϕ_{ET}^{TTS} of the energy transfer from T_1 acetone to the S_1 level of the acceptor, following the TT mechanism, can then be described by

$$\phi_{ET}^{TTS} = \frac{0.5k_{diff}^{acc} [acc] \phi_{ISC}^{TS}}{k_{diff}^{acc} [acc] + k_{dea}^{TA}} \quad (6)$$

assuming that excitation of the T_1 and T_2 states occurs with equal probability. From the ratio SL/INT obtained from the plot of $1/I_{ch}$ versus $1/c_{acc}$ at constant TMD concentration, one can derive the equation

$$SL/INT = k_{dea}^{TA}/k_{diff}^{acc} \quad (7)$$

which holds for both alternative mechanisms.

From relation (8) involving the Stern–Volmer constant $K(acc)$ for the quenching of the indirect chemiluminescence by 2,4-hexadiene,

$$K(acc) = \frac{k_q}{k_{dea}^{TA} + k_{diff}^{acc} [acc]} \quad (8)$$

the determination of k_{dea}^{TA} and k_{diff}^{acc} relative to k_q , which is the rate constant of quenching of T_1 acetone by hexadiene, is possible. The following values of SL/INT for the acceptors DBA, BA and DCA

$$K(DBA) = 200 \text{ M}^{-1}, \quad [DBA] = 10^{-3} \text{ M}, \quad SL/INT = 1.82 \times 10^{-3} \text{ M} [1]$$

$$K(BA) = 190 \text{ M}^{-1}, \quad [BA] = 1.07 \times 10^{-3} \text{ M}, \quad SL/INT = 2.14 \times 10^{-3} \text{ M}$$

$$K(DCA) = 176 \text{ M}^{-1}, \quad [DCA] = 1.3 \times 10^{-3} \text{ M}, \quad SL/INT = 1.87 \times 10^{-3} \text{ M}$$

enable the calculation of the subsequent data correlations of k_{diff}^{acc} and k_{dea}^{TA} :

$$k_{diff}^{DBA} = 1.8 \times k_q \text{ M}^{-1} \text{ s}^{-1}, \quad k_{dea}^{TA} = k_q/310 \text{ s}^{-1}$$

$$k_{diff}^{BA} = 1.6 \times k_q \text{ M}^{-1} \text{ s}^{-1}, \quad k_{dea}^{TA} = k_q/285 \text{ s}^{-1}$$

$$k_{diff}^{DCA} = 1.8 \times k_q \text{ M}^{-1} \text{ s}^{-1}, \quad k_{dea}^{TA} = k_q/299 \text{ s}^{-1}$$

It is known that diene compounds quench the T_1 state of acetone at a diffusion-controlled rate [15]. Therefore, substituting k_{diff} for k_q , the former being calculated according to eqn. (1) to be equal to $1.45 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, one obtains*

$$k_{diff}^{DBA} = 2.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}, \quad k_{diff}^{BA} = 2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{diff}^{DCA} = 2.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}, \quad k_{dea}^{TA} = 5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$

The value for the deactivation of T_1 acetone in air-saturated toluene of $5 \times 10^7 \text{ s}^{-1}$ is essentially greater than that in other solvents, e.g. in benzene $k_{dea}^{TA} = 1 \times 10^7 \text{ s}^{-1}$ [22]. Apparently energy transfer to the T_1 state of the

*The assumption $k_q = k_{diff}$ is confirmed by the observation that k_q shows a pressure dependence proportional to the reciprocal viscosity of the solvent.

solvent, which lies only 1600 cm^{-1} higher in energy, reduces the lifetime of T_1 acetone. However, participation of toluene in the energy transfer process from T_1 acetone to the different acceptors could not be detected [1].

The rate constants for the diffusion-controlled quenching of T_1 acetone by DBA, BA and DCA are equal within experimental errors. The deviation from the value of k_q for hexadiene, which was taken as the reference value, is not surprising if one considers the differences in the structures of the quenchers.

The rate constant $k_{\text{dea}}^{\text{TA}}$ for the deactivation of T_1 acetone is pressure independent over the pressure range employed [1]. Since $k_{\text{diff}}^{\text{acc}}$ should show a pressure dependence proportional to the reciprocal viscosity of the solvent, one expects a plot of $(k_{\text{dea}}^{\text{TA}}/k_{\text{diff}}^{\text{acc}})(p) \times \eta(1)/\eta(p)$ versus pressure to be parallel to the abscissa. As can be seen from Figs. 2 and 3 this is indeed the case for BA and DCA as it was for DBA.

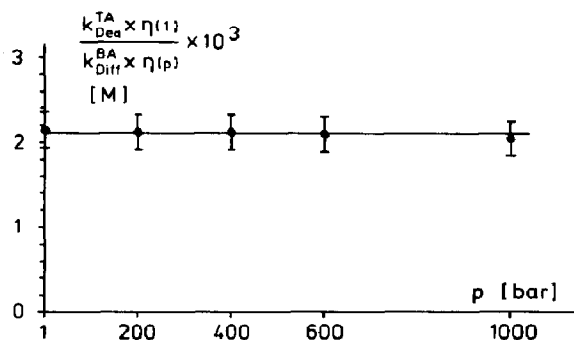


Fig. 2. Pressure dependence of $k_{\text{dea}}^{\text{TA}}$ using data with BA as acceptor.

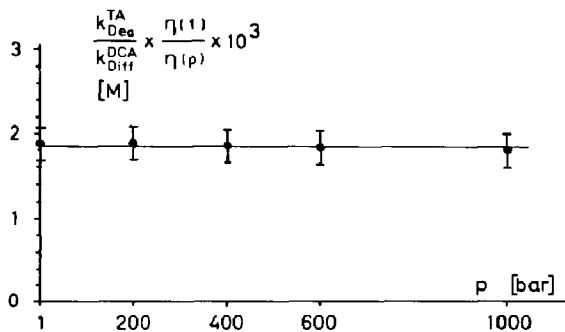


Fig. 3. Pressure dependence of $k_{\text{dea}}^{\text{TA}}$ using data with DCA as acceptor.

The orders of magnitude and pressure dependences of the rate constants $k_{\text{ET}}^{\text{TS}}$, $k_{\text{diff}}^{\text{acc}}$ and $k_{\text{dea}}^{\text{TA}}$ relevant for the energy transfer are known. Thus the pressure dependence of the yield $\phi_{\text{ET}}^{\text{TS}}$ of energy transfer following the TS mechanism can be estimated. From relation (5) a pressure independence follows for $\phi_{\text{ET}}^{\text{TS}}$ at low acceptor concentrations with $k_{\text{diff}}^{\text{acc}}[\text{acc}] \ll k_{\text{dea}}^{\text{TA}}$, whereas at high acceptor concentrations, i.e. with $k_{\text{diff}}^{\text{acc}}[\text{acc}] \gg k_{\text{dea}}^{\text{TA}}$, the yield should

increase with pressure in proportion to the increase in viscosity of the solvent. Figure 4 shows the experimentally obtained pressure and concentration dependences of the yield ϕ_{ET} of energy transfer from acetone to BA.

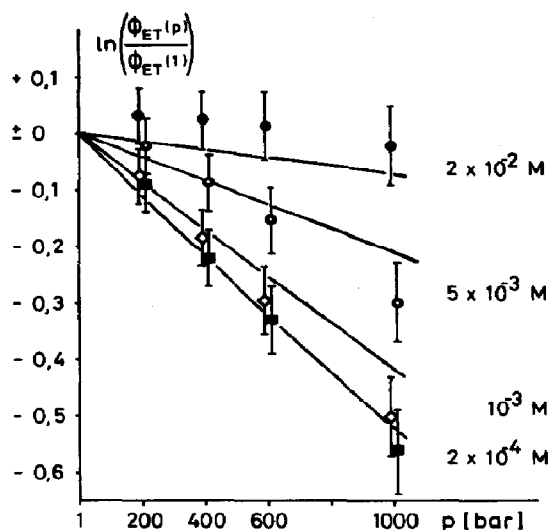


Fig. 4. Pressure and BA concentration dependences of the yield of energy transfer ϕ_{ET} .

An inspection of Fig. 4 reveals that the expectations outlined above are not confirmed by the experimental data. Instead of an increase in ϕ_{ET} with pressure at high BA concentrations one observes an almost pressure-independent behaviour, and instead of pressure independence at low acceptor concentrations a definite decrease in ϕ_{ET} with increasing pressure is found. Therefore the direct energy transfer to BA in solution cannot play a major role.

Consequently, the energy transfer following the indirect TT mechanism should be dominant. This can be confirmed through the satisfactory description of the data by the curves drawn in Fig. 4. These curves were calculated from eqn. (6) using the following data:

$$k_{\text{det}}^{\text{TA}} = 5 \times 10^7 \text{ s}^{-1}, \quad p \text{ independent}$$

$$k_{\text{diff}}^{\text{BA}} = 2.3 \times 10^{10} \times \eta(1)/\eta(p) \text{ M}^{-1} \text{ s}^{-1}$$

$$[\text{acc}] = [\text{acc}] \times \rho(p)/\rho(1), \quad \phi_{\text{ISC}}^{\text{TS}} = p \text{ independent}$$

This way it was shown that the energy transfer from T_1 acetone to BA follows the same mechanism as in the case of DBA as acceptor. A comparison of Tables 6 and 7 reveals that the pressure and concentration dependences of energy transfer to BA and to DCA are practically identical. Obviously the indirect TT mechanism dominates also for energy transfer from T_1 acetone to DCA.

As demonstrated in Table 1, the rates $k_{\text{ISC}}(0)$ of isoenergetic ISC from S_1 to T_2 are different for DBA as compared with BA and DCA. This can be explained by the inner heavy atom effect which originates from the halogen

substituents [4, 23]. If the reverse exothermic ISC from T_2 to S_1 involves no activation energy, then the yield of this process should reflect a similar difference to that for $k_{ISC}(0)$.

The intercept of a plot of $1/I_{ch}$ versus $1/c_{acc}$ is a relative measure of ϕ_{ISC}^{TS} , and its reciprocal value $I_{ch}(\infty)$ represents the extrapolation of the intensity of chemiluminescence to infinitely high acceptor concentrations. $I_{ch}(\infty)$ can be expressed by the following equation, derived from eqns. (2) and (6):

$$I_{ch}(\infty) = ak_{th}[TMD]\phi_{FL}^T\phi_{FL}^{acc} \times 0.5 \times \phi_{ISC}^{TS} \quad (9)$$

Since all investigations with DBA, BA and DCA were made under identical conditions and since the emission of fluorescence from these compounds covers the same spectral region, a comparison of the intercepts and a knowledge of the quantum yields of fluorescence permits the calculation of relative ϕ_{ISC}^{TS} values.

In air-saturated toluene solutions at 40 °C the following quantum yields of fluorescence were obtained:

$$\phi_{FL}^{DBA} = 0.116, \quad \phi_{FL}^{BA} = 0.027, \quad \phi_{FL}^{DCA} = 0.42$$

In combination with the $I_{ch}(\infty)$ values of

$$I_{ch}^{DBA}(\infty) = 150 [1], \quad I_{ch}^{BA}(\infty) = 18.6 \text{ (Table 2)}, \quad I_{ch}^{DCA}(\infty) = 34.6 \text{ (Table 2)}$$

subsequently the ϕ_{ISC}^{TS} values were calculated:

$$\text{DBA: } \phi_{ISC}^{TS} = 0.4; \quad \text{BA: } \phi_{ISC}^{TS} = 0.21; \quad \text{DCA: } \phi_{ISC}^{TS} = 0.025$$

In this sequence ϕ_{ISC}^{TS} for DBA was estimated from the result of Wilson *et al.* [15], *i.e.* $\phi_{ET} = 0.2$ for indefinitely high DBA concentration. Although the latter value carries some uncertainty, one can observe that the sequence of ϕ_{ISC}^{TS} values shows a similar trend to that for $k_{ISC}(0)$. This in turn supports the assumption that the ISC process from T_2 to S_1 for these compounds does not involve an activation energy.

DBA, BA and DCA are known as compounds with very high yields of ISC from S_1 to T_2 . Apart from the fluorescence emission, ISC is assumed to be the only important deactivation process of the S_1 state. At the same time reverse ISC from T_2 to S_1 has been shown here to be very efficient. As a consequence, for all three compounds in the photostationary state there exists an equilibrium between the S_1 and T_2 states during which the S_1 state can also be deactivated by emission (k_{FL}) and the T_2 state by internal conversion (k_{IC}).

From the result that the energy transfer, which gives rise to the indirect chemiluminescence with DCA as acceptor, proceeds according to the TT mechanism, despite the small yield of ISC from T_2 to S_1 ($\phi_{ISC}^{TS} = 0.025$), one can draw the conclusion that the rate constant of the direct spin-forbidden TS energy transfer is also influenced by the inner heavy atom effect to a major extent.

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