Physical Triplet Quenching by Electron Donors

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Absolute radical yields, as determined by flash spectroscopy, are reported for the reaction of the thionine triplet $^3TH^+$ and its protonated form $^3TH_2^{++}$ with a variety of electron donors in methanolic solution. The different yields, extrapolated to infinite donor concentrations, are due to partial physical quenching of the triplets in the electron transfer reaction. The results are indicative of a triplet exciplex as an intermediate in the electron transfer reaction.

In the reactions of singlet excited molecules with electron donors the quantum yields of the electron transfer products are usually found to be considerably smaller than 1, even under conditions of complete fluorescence quenching[1]. This can be explained by the fact that the formation of free radicals, produced by separation of the initially generated radical pairs has to compete with a spin conserving geminate recombination, yielding the ground state products.

When considering triplet reactions, the geminate radical pair originates in a triplet spin state and the geminate recombination, yielding the ground state products, ought to be spin forbidden. Higher radical product yields are therefore to be expected than in the singlet case. Few data exist, however, for these yields in triplet state reactions.

The work presented here was stimulated by the results of our investigation of a catalytic effect in the photoreduction of the dye thionine. This effect could be satisfactorily explained by the different radical product yields of the two electron donors involved[2].

In the present work we report radical product yields of two acid-base conjugated thionine triplet forms in their reaction with different donors in methanolic solution as measured by kinetic flash spectroscopy.

The yields were determined from the maximum value of the optical density change due to the acid form of the semireduced thionine $TH_2^{\dot{+}}$. This species absorbs in the very long wavelength region, so the absorption of the aromatic radical cations does not interfere with the former. For the investigation of the reaction of the basic triplet form $^3TH^+$, a methanolic buffer of pH = 8.6 was used[3], giving a quantitative protonation of the semireduced thionine radicals produced by the electron transfer[4]. The investigations of the reaction of the acid triplet form $^3TH_2^{++}$ were carried out in methanolic solutions containing 0.1 M/l phosphoric acid.

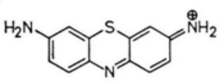
The numeric values of the total quenching constants (sum of the rate constants for physical quenching and radical formation) as well as the radical product yields extrapolated to infinite donor concentration are presented in Table 1.

Table 1.

Donors	Reaction with $^3TH^+$ [a]		Reaction with $^3TH_2^{++}$ [b]	
	$k_Q + k_R$ [c]	Φ_R [d]	$k_Q + k_R$ [c]	Φ_R [d]
9.10-Dimethylanthracene	3.5×10^9	0.80 ± 0.08	4.0×10^9	0.80 ± 0.08
Azulene	2.0×10^9	0.75 ± 0.08	4.0×10^9	0.85 ± 0.09
1.3-Diphenylisobenzofuran	4.5×10^9	0.80 ± 0.08	4.0×10^9	0.85 ± 0.09
4-Methoxydimethylaniline	5.0×10^9	0.80 ± 0.1	—	—
Hydroquinone	2.5×10^9 [e]	0.85 ± 0.09	2.5×10^9	0.80 ± 0.08
Diaza[2,2,2]bicyclooctane	8.0×10^8	0.85 ± 0.09	—	—
4-Bromoaniline	3.0×10^9	0.40 ± 0.05	4.0×10^9	0.45 ± 0.05
Bromobenzene	$< 4 \times 10^4$	—	$< 4 \times 10^4$	—
Thiourea	7.5×10^6	0.20 ± 0.03	8.0×10^8	0.16 ± 0.02
N-Allylthiourea	8.0×10^6	0.31 ± 0.03	7.0×10^8	0.30 ± 0.03
Selenourea	4.5×10^9	0.04 ± 0.01	3.5×10^9	0.10 ± 0.02

Solvent was methanol, oxygen-free.

a) $TH^+ =$



b) Produced with 0.1 m methanolic H_3PO_4.

c) Sum of rate constants for physical quenching (k_Q) and radical formation (k_R) dimension $1 \times mol^{-1} \times sec^{-1}$.

d) $\Phi_R = k_R / (k_Q + k_R)$.

e) Presumably hydrogen transfer reaction.

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It can be seen that many of the electron donor molecules, whose reactions with the thionine triplets have been studied, give very high radical product yields. The compounds showing considerable or even dominant physical quenching contain heavy atoms. The deviations from a value of 1 for the radical product yield cannot be explained in terms of static quenching effects: The absorption spectra ruled out complex formation in the ground state. Quenching of excited singlet states does not take place with the donor concentrations used in the experiments. Therefore the reduced radical yields result from a more or less efficient physical quenching of the triplet state.

Triplet-triplet energy transfer can be excluded as a substantial cause of triplet deactivation: When using azulene ($E_T = 38.6$ kcal/mol[5]), the donor which probably has the lowest triplet energy and a short triplet life time, the radical yield is high. There may, however, be a small influence of triplet-triplet energy transfer: The conditions for triplet-triplet energy transfer are more favourable in the case of the basic thionine triplet ($E_T = 39 \pm 1.5$ kcal mol[6]) than for the acid triplet form ($E_T = 30 \pm 2.5$ kcal/mol[6]). In fact a slightly higher radical yield is found with the latter.

The measured lifetimes of the semireduced thionine being very long (in all cases longer than 1 msec), a recombination of free radicals during the first 20 μsec after flash triggering can also be excluded as a possible cause of reduced radical product yields.

The results, presented in Table 1, suggest that electron transfer reaction and quenching reaction are not independent. This fact is demonstrated by comparing the reactivity of p-bromoaniline and bromobenzene. (There is no quenching or radical formation with the latter compound up to concentrations of 1 mol/l.) Even stronger evidence for an interrelation between electron transfer and the physical quenching reaction is given by the reactivity of thiourea and allylthiourea towards the different protolytic triplet forms. For these donors the radical yields with the different triplet forms are the same, though the reaction with the acid triplet form is about 100 times faster than with the basic form[7]. This means that the rate constants for both radical formation and physical quenching are increased by a factor of 100, which fact strongly suggests that the physical quenching follows the electron transfer step, the latter being rate determining. In order to explain the physical quenching, one should therefore discuss an intersystem crossing process in the primarily formed electron transfer product, which competes with the formation of free radicals. As primary products of electron transfer we will discuss an exciplex or a radical pair (designated as 'geminate' radical pair in contrast to radical pairs formed by diffusive encounters of free radicals).

Very recently it has been demonstrated by the magnetic field dependence of fast triplet formation from geminate radical pairs, produced by electron transfer from aromatic amines to singlet excited pyrene, that intersystem crossing in radical pairs can be due to the hyperfine coupling between electronic and nuclear spins[8, 9]. The same mechanism might be operative in the intersystem crossing of radical pairs, originally formed in the electronic triplet state, making a recombination to singlet products possible.

High rate constants would be expected for the recombination of the semithionine with the oxidized donor radicals due to the negative free enthalpy of these reactions[10]. The long lifetime observed for the semithionine radicals is not consistent with such a high recombination rate constant of counter radicals, however, unless it is assumed that the concentration of the oxidized counter radicals is diminished by some other process (e. g. with the solvent). Such a process might be fast enough to prevent the recombination of freely diffusing radicals, but slow enough not to interfere with the geminate recombination phase of the radicals.

The reported yields of geminate recombination products due to hyperfine induced intersystem crossing are about 10%[8]. They are comparable to the small physical quenching yields of the donors in the upper half of Table 1. It is doubtful, however, whether the hyperfine mechanism can account for the large intersystem crossing yields which we have observed with some donors. The radicals of the thioureas and selenourea are expected to contribute less to the hyperfine coupling than the aromatic donor cations, as the radical electron is localized at atoms (S or Se) having nuclear spin zero for the major part of their natural isotopes. Furthermore in the radical pairs of our systems the diffusive separation in the radicals is not hindered by Coulomb attraction. In order to obtain more conclusive information, experiments are in progress to test the magnetic field dependence of the radical yield in our systems.

Recent investigations of radical formation in electron transfer reactions with excited singlet states indicate that an exciplex may be formed as an intermediate even in solvents as polar as methanol[8, 11]. Therefore this mechanism of radical formation should also be considered in the case of triplet reactions. Intersystem crossing processes in the exciplex are often faster than in the excited single component. This may be due to the fact that symmetry conditions are less restrictive for the intermolecular spin-orbit coupling matrix elements. Enhanced spin-orbit coupling should be expected when heavy atoms are introduced. An exciplex model for the electron transfer reaction in our systems would explain the smaller radical yield with p-bromoaniline as compared to the other aromatics and of selenourea as compared to the thioureas.

We think that our results are in favour of an exciplex mechanism, thus demonstrating that the investigation of the mechanism of physical triplet quenching by electron donors may provide information on the mechanism of electron transfer as well.

Acknowledgements

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