Role of Charge Transfer and Spin-Orbit Coupling in Fluorescence Quenching. A Case Study with Oxonine and Substituted Benzenes[†]

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Fluorescence quenching of oxonine in methanol was investigated by means of a computerized dye laser flash spectrometer for the ΔG°_{et} dependence of the quenching rate constant (k_q) and the efficiencies of induced dye triplet formation (η_T), reduced dye radical formation (η_R), and induced internal conversion. A total of 34 substituted benzenes including 20 monohalogenated benzenes, toluenes, and anisoles were used as quenchers spanning a range of $-0.85 \leq \Delta G^\circ_{et} \leq 1.4$ eV for a possible photoelectron-transfer reaction with the dye singlet as electron acceptor. Induced internal conversion was the dominating channel in all cases. Free-radical formation was less than 2.0% throughout. Induced triplet formation was only detectable with heavy-atom-substituted quenchers and with $\Delta G^\circ_{et} \geq -0.13$ eV such that the free energy of the radical pair was not below the triplet energy of oxonine. In spite of a wide variation of k_q the efficiency η_T was almost constant for a set of quenchers with the same halogen substituent. The $\log k_q$ values were found to correlate with ΔG°_{et} , however, not in the well-known Rehm-Weller fashion with $\log k_q \propto -\Delta G^\circ_{et}/RT$ as the limiting behavior at positive ΔG°_{et} , but rather with a proportionality of $\log k_q$ to $-\log(\Delta G^\circ_{et})$. This type of correlation could be derived from an extended Rehm-Weller quenching model taking into account the charge-transfer character of the encounter complex prior to complete electron transfer. On the basis of this model we could also establish an almost linear correlation between the rate constant of induced triplet formation and the function $F_{HA} = C_X^2 \zeta_X^2 J(\Delta G^\circ_{et})$ which allows prediction of the pertinent rate constant over 6 orders of magnitude with an uncertainty of a factor of 2.2. In F_{HA} the parameter C_X^2 is an average spin density transferred to the halogen substituent X of the quencher in the case of full charge transfer, ζ_X is the atomic spin-orbit coupling constant of X, and $J(\Delta G^\circ_{et})$ is the thermally averaged charge-transfer character of the encounter complex multiplied by a factor proportional to its dissociation lifetime.

Introduction

The enhancement of spin-forbidden processes by heavy atoms has been a matter of considerable interest in molecular spectroscopy since 1949 when McClure¹ first established a correlation between the decay time of aromatic triplets and the spin-orbit coupling constants of halogen substituents. Of particular interest is the fact that for inducing or accelerating spin-forbidden transitions in a molecule it may be sufficient that heavy atoms are present in the surrounding medium (external heavy atom effect). The first systematic investigations of external heavy atom effects were reported by McGlynn and co-workers.²⁻⁴

The processes which have been influenced by external heavy atom effects are singlet-triplet absorption,^{2,5,6} radiative³ and nonradiative⁷ decay of excited triplets, phosphorescence depolarization,^{8,9} and fluorescence decay by induced triplet formation.⁴ Important applications of external heavy atom effects are the determination of triplet energies by $S_0 \rightarrow T_1$ absorption,⁶ the determination of triplet formation efficiencies by the technique suggested by Wilkinson and co-workers,¹⁰ and the control of certain photochemical reactions which yield different products from the excited S_1 and from the T_1 state.¹¹⁻¹³ The latter two applications are based on induced triplet formation. Avoiding of this process may be of considerable practical interest, e.g., in connection with the lightfastness of dyes,¹⁴ where triplet formation is often the primary step for undesired photodegradation.

Although it is obvious that spin-orbit coupling must be involved in some way in all of the above-mentioned effects, particularly in the case of the external heavy atom effect the mechanistic details are still a matter of debate. Usually the central question is, if (a) the heavy atom in the perturber P merely enhances the in-

tramolecular coupling of the pertinent states in the excited molecule A, or if (b) indirect coupling via intermediate states $^1(A \cdots P)^*$, $^3(A \cdots P)^*$ is involved with the further problem of assessing the nature of the intermediate state either as a locally excited perturber state ($(A \cdots P)^* = A \cdots P^*$) or as a charge transfer (CT) state ($(A \cdots P)^* = (A^+ \cdots P^-)$ or $(A^- \cdots P^+)$).

Another point important for understanding the external heavy atom effect is the question of complex formation between excited molecule and external perturber. If there is a bonding interaction between them this will extend the contact time of the pair¹⁵ and will obviously increase its susceptibility to a heavy atom effect. On the other hand it is possible that the stabilizing interaction responsible for the bonding may enhance the efficiency of the heavy atom effect by its very nature. Among the interactions

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discussed in this regard, charge-transfer (CT) interaction may support intersystem crossing even without any heavy atom present,^{16,17} but it may also provide an efficient mechanism for an internal conversion process in fluorescence quenching via fast forward and backward electron transfer.¹⁸ Thus the simultaneous presence of CT and heavy atom interactions will cause an intriguing situation with respect to their mutual interplay. A number of experimental studies have contributed information on the mechanisms of external heavy atom effects. Since in the present work we are concerned with fluorescence quenching we will briefly review some of the work pertaining to this particular process.

It has been demonstrated by quenching experiments with Xe^{10c} and with Cs^+ ions¹⁹ that the external heavy atom effect does not require obvious contributions from CT states or low-lying locally excited states of the perturber. Recently it was also shown in molecular beam experiments²⁰ that van der Waals complexes of aromatic molecules with Kr and Xe exhibit faster electronic decay than the isolated aromatics.

A correlation of the fluorescence quenching constant of several aromatic compounds with the energy gap between S_1 and the next situated lower or, if thermally accessible, higher triplet state has been demonstrated in a series of papers by Dreeskamp and co-workers²¹⁻²³ using alkyl iodides as quenchers. Their findings reflect the importance of the Franck-Condon factor in the heavy-atom-induced intersystem crossing process. Since the same energy gap determines the purely intramolecular process (k_{ISC}) in the fluorescer one might also expect a correlation of the quenching rate constant with k_{ISC} . Such relations have been indeed reported for Cs^+ ¹⁹ and Ag^+ ²⁴ as quenchers.

The particular problem of interference between CT and heavy atom effect has been addressed in a paper by Schulte-Frohlinde and Hermann²⁵ who investigated the fluorescence quenching of various 9,10-substituted anthracenes by 1,4-substituted benzenes carrying one electron donating or accepting substituent and one Cl or Br substituent. The induced formation of triplets was qualitatively confirmed in some experiments and the quenching process was discussed as being exclusively due to induced triplet formation. It was attempted to increment the quenching rate constant for CT and heavy atom contributions whereby it was concluded that, as a rough approximation, both contributions could be considered as additive effects.

Quenching experiments of acridinium fluorescence by Bendig et al.,²⁶ who applied a series of bromo and iodo hydrocarbons as quenchers, furnished linear correlations between $\log k_q$ and the ionization potentials of the quenchers, though with different slopes for the bromo and iodo compounds. The rate constants of the corresponding iodo quenchers were consistently higher by a factor of about 20. This provided evidence that the quenching was due to induced triplet formation. CT and heavy atom effect were concluded to be multiplicative effects.

Gutierrez and Whitten compared the efficiencies of fluorescence quenching and induced cis-trans photoisomerization (which served as an indicator of the degree of induced triplet formation) in the quenching of singlet excited 1,2-bis(pyridyl)ethylenes by aromatics and heteroaromatics¹¹ and by aliphatic halogen compounds.¹² From their results they concluded that CT quenching and induced

triplet formation should be considered as distinct and separate processes, whereby CT interaction determines the quenching rate and the heavy atom effect the amount of induced triplet formation. A further conclusion was that systems with the CT state energy between S_1 and T_1 of the quencher were most efficient in induced triplet formation.

The present systematic investigation of fluorescence quenching of oxonine by various benzene derivatives including those carrying an additional halogen substituent was undertaken in order to complement the picture which had emerged from two previous

$$E(S_1) = 2.07 \text{ eV} \quad E(T_1) = 1.67 \pm 0.08 \text{ eV}$$

$$E_{\text{OxH}^+/\text{OxH}} = -0.35 \text{ V (vs. SCE)}$$

studies of our groups. In the first one²⁷ we had investigated the branching between radical formation by electron transfer and induced T_1 - S_0 intersystem crossing in thionine triplet quenching by the complete series of monohaloanilines. The conclusions from this work, which were also corroborated by analogous investigations with oxonine and selenine triplets,²⁸ were that the quenching could be conceived as a sequential process of (i) electron transfer by which a triplet exciplex was formed, this process determining the rate constant of quenching, and (ii) the decay of the triplet exciplex by dissociation into free radicals or by heavy-atom-induced spin-inverted electron back-transfer regenerating the dye ground state. A marked positional dependence of the heavy atom effect was found which paralleled the unpaired spin density transferred to the heavy atom substituent in the quencher radical cation.

In the second work²⁹ the efficiency of radical formation versus induced internal conversion was studied in the fluorescence quenching of oxonine by aromatic amines and methoxy compounds covering a wide range of oxidation potentials which corresponded to a range of free enthalpy change ΔG°_{et} of electron transfer from -1.56 to -0.12 eV. This investigation furnished a linear relationship between the log of the radical yield and ΔG°_{et} . The radical yield was appreciable (0.45) at the lower limit and decreased to almost vanishing values at the upper limit where, however, the quenching was still close to diffusion-controlled.

In the present work the applied quenchers cover a range of ΔG°_{et} values in the positive and weakly negative region where the CT state is localized above S_1 or between S_1 and T_1 of the dye. Thus induced triplet formation that we had previously been able to detect with allylthiourea and other quenchers³⁰⁻³² was possible. In the present investigation special experimental effort was made to obtain precise values of the yields of induced triplet formation, radical formation, and induced internal conversion for a closely related series of quenchers in order to reveal the possible relation between CT and heavy atom interaction in the quenching process.

Experimental Section

1. Chemicals. Oxonine was synthesized according to the method of Kehrmann and Saager³³ with the modification that 3,7-dinitrophenoxazine was reduced to leucooxonine by Pt-catalyzed hydrogenation which led to considerable yield improvement.

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Figure 1. Setup of the laser flash spectrometer: DL, dye laser; XBO, probe light source; PS, probe light shutter; FC, flow-through cuvette; MV, magnetic valve; GM, grating monochromator with step motor; PM, photomultiplier; PD, photodiode; EM, energy meter; BS, beam splitter; A, apertures; F, filters; L, lenses; M, mirrors.

The dye was purified by column chromatography.

The compounds used as fluorescence quenchers and listed below were obtained from various suppliers: EGA/Aldrich (E), Fluka (F), Merck or Merck Schuchard (M), Riedel de Haen (R). Purification procedures applied are abbreviated as d (distillation), dv (distillation in vacuo), sv (sublimation in vacuo), r (recrystallization). The following is a list of the quenchers in alphabetical order: aniline (M, reagent grade, dv), anisole (M, 99%, d), 4-bromoacetanilide (E, >99.9%), 4-bromoacetophenone (E, >98%, sv), 4-bromoaniline (F, >99%), 2-bromoanisole (E, 99%, d), 3-bromoanisole (E, 99%, d), 4-bromoanisole (E, 99%, 2× d), bromobenzene (M, 99%, 2× d), 4-bromobenzonitrile (E, 98%, sv), 4-bromochlorobenzene (E, 99%, sv), 4-bromofluorobenzene (E, 97%, 2× d), 4-bromonitrobenzene (E, 99%, sv and r from methanol), 4-bromophenol (F, >99%), 2-bromotoluene (F, >98%, d), 3-bromotoluene (F, >99%), 4-bromotoluene (F, >99%), 4-chloroanisole (E, >99%), chlorobenzene (F, 99.5%), 4-chlorotoluene (F, >99%), fluorobenzene (F, >99.5%), 2-iodoanisole (F, 98%, 2× dv), 3-iodoanisole (R, 98%, 2× dv), 4-iodoanisole (F, 98%, sv), iodobenzene (M, >98%, 2× dv), 2-iodotoluene (F, 98%, 2× dv), 3-iodotoluene (F, 98%, 2× dv), 4-iodotoluene (F, 98%, sv), potassium bromide (M, >99.5%), potassium iodide (M, >99.5%). The solvent used for the experiments was methanol (M, reagent grade).

2. Apparatus. Absorption spectra were recorded on a Zeiss DMR 10 spectrophotometer. Fluorescence measurements were performed with a Fluorispec SF1, using a perpendicular arrangement of fluorescence excitation and observation. Oxonine fluorescence was excited at 540 nm. Fluorescence spectra were not corrected since only relative fluorescence intensities were to be compared in the quenching experiments.

Induced triplet formation was monitored by triplet-triplet absorption spectroscopy using a computer-controlled laser flash spectrometer. The setup of this instrument is depicted in Figure 1. The sample is photolyzed in a 1 cm flow-through cuvette by the pulse of a flash-lamp-pumped dye laser (Lambda Physik FL 3000). A wavelength of 590 nm was used with rhodamine 6G as the laser dye. The laser pulse width limiting the time resolution was about 1 μs, and pulse energies up to 14 mJ were available. The probe light source was a 150-W xenon high-pressure lamp (OSRAM XBO 150 W/1) pulsed for millisecond intervals with an electrical power of 4 kW. To make optimum use of the energy of the narrow laser beam, probe light and exciting beams were crossed in the cuvette at a very low angle (4.4°). At maximum laser energy the energy density over the cross section of the probe beam in the cuvette (ca. 3 mm²) amounted to 0.35 J cm⁻² (1.7 × 10⁻⁶ E cm⁻²). Since the exciting energy flux is distributed over a fairly long period of ca. 1 μs the stationary concentration of excited singlet remains low during a pulse and two-photon processes are largely avoided. Furthermore, the long pulse duration is very favorable in that excited molecules which were not converted to triplets in the quenching process can be excited many times during the same laser pulse so that the measured triplet signals are greatly enhanced, which extends the detection limits for efficiencies of induced triplet formation to values of about 0.05%. A step-motor-controlled grating monochromator (Ja-

SCHEME I

rell-Ash 82-410) was used for wavelength selection of the probe light which was monitored by an EMI 9659 QB photomultiplier with extended S20 photocathode. The signals from the photomultiplier and a photodiode monitoring the laser flash time profile were recorded on a two-channel Datalab 922 digitizer, the time resolution of the detection system being 50 ns. An independent reading of the integrated laser pulse energy was also taken by use of an energy meter (Laser Precision Rk 3230 with a pyroelectric detector RkP-335). Data acquisition and operation of the system was completely under microcomputer control (Texas Instruments TM 990) which allowed for a signal repetition frequency of 10 s⁻¹. Before investigations the solutions were flushed with high-purity nitrogen (O₂ content less than 6 ppm) for 30 min. Exchange of probe solution in the cuvette was achieved by means of a flow system driven by a slight pressure of N₂ and controlled by the microcomputer through a magnetic valve, so that the solution could be kept at rest during signal recording. Furthermore, a computer-controlled shutter restricted exposure times of the sample solution to the probe light to a minimum period necessary for signal recording.

The computer control allowed various modes of operation and data processing. For the present work the modes of signal averaging of complete kinetic traces and of transient spectra recording were applied. In the latter mode the optical density of the transients is recorded at several selected delay times for each signal. During the measurement the monochromator is stepped through the wavelength interval of interest whereby signal averaging over a selected spectral width is applied continuously. As a result of this mode one obtains a simultaneous on-line recording of several transient spectra at various delay times. For details of the laser spectrometer cf. ref 34. Another mode of operation especially suited for the detection of magnetokinetic effects has been described previously.³⁵

Procedures for Determining Rate and Efficiency Parameters

1. General Kinetics. The reactions considered in this investigation and the pertinent rate and efficiency parameters are presented in Scheme I. The excited dye and the quencher are denoted as A* and D in order to express their roles as electron acceptors and donors, respectively. The singlet excited dye ¹A* decays with a rate constant *k*₀, whereby the excited state ³A* is formed with an efficiency of *η*_T⁰ and *η*_G⁰ = (1 - *η*_T⁰) is the sum of the efficiencies of fluorescence and internal conversion. Singlet quenching by the donor takes place with a rate constant *k*_q, and *η*_R, *η*_T, *η*_G are the efficiencies of radical formation, induced triplet formation, and induced internal conversion, respectively, in the bimolecular quenching process (*η*_R + *η*_T + *η*_G = 1).

The rate constant *k*_q was obtained from measuring stationary fluorescence intensities *I* and applying the Stern-Volmer relation

$$I_0/I = 1 + k_0^{-1}k_q[D] \quad (1)$$

The efficiency parameters *η*_i were obtained from [D]-dependent quantum yields Φ_i determined by transient absorption measurements with the laser flash spectrometer.

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Figure 2. Transient absorption spectra recorded in the "spectral control mode" of the laser flash spectrometer with a solution of 2×10^{-5} M oxonine and 0.225 M iodobenzene in methanol, oxygen free. The spectra are recorded by sampling the transient signals at intervals of $9 \mu\text{s}$ starting $5 \mu\text{s}$ after the laser flash. The time window for sampling of each data point was $3 \mu\text{s}$. For each of the three wavelength sections displayed the monochromator was stepped by 0.2 nm per laser pulse. Every point plotted in the spectra represents an average of 50 single-shot data, corresponding to an effective spectral width of 10 nm . The horizontal lines represent the control of constancy of the laser energy corresponding to an absolute energy input of 0.13 J cm^{-2} per pulse into the sample. For convenience of presentation only the absolute value of ΔE is plotted. Actually ΔE is negative in the region between about 500 and 600 nm . For reasons of clearness, signal traces 11–20 have been omitted in the middle part of the figure.

According to Scheme I the quantum yield Φ_T of dye triplet formation depends on the donor concentration as follows:

$$\Phi_T = (\eta_T^0 k_0 + \eta_T k_q [D]) / (k_0 + k_q [D]) \quad (2)$$

This may be rearranged to the following expression:

$$(\Phi_T - \eta_T^0)^{-1} = (\eta_T - \eta_T^0)^{-1} (1 + k_0 k_q^{-1} [D]^{-1}) \quad (3)$$

which allows η_T and k_q to be evaluated from slope and intercept of a straight line if η_T^0 and k_0 are known. Alternatively η_T may be determined by comparing absorption and fluorescence measurements directly, i.e., by combining eqs 1 and 2:

$$\Phi_T = \eta_T - (\eta_T - \eta_T^0) I / I_0 \quad (4)$$

Relations analogous to eqs 2–4 also hold for the radical yield, however, with the simplification that a corresponding term from the monomolecular process is zero.

2. Absolute Quantum Yields. Three quantities must be determined for obtaining absolute quantum yields: the absolute light intensity applied to the sample, the fraction of light absorbed, and the amount of products formed. The first item has been dealt with in the Experimental Section. The second one is not a trivial matter of applying Lambert–Beer's law because the concentrations of dye ground state and transients, competing in light absorption with the ground state, change during the laser flash. Furthermore, in the quasi-collinear arrangement of laser and probe-light beam the concentrations are not constant along the optical path length. The third of the above items requires the knowledge of the extinction coefficients of the transients in order to assess their absolute concentrations. We will deal with the latter problem first.

In Figure 2 is shown the time evolution between 5- and $185\text{-}\mu\text{s}$ delay times of transient spectra in a typical experiment. In the long-wavelength region the spectrum is typical of the triplet and closely resembles that of related dyes as thionine³⁶ and selenine.^{28,37} Whereas the decay in this wavelength region is uniform this is not the case in the short-wavelength region where a long-lived band persists after $185 \mu\text{s}$. This band is mainly due to the semioxonine radical formed in the quenching either of the excited singlet or

of triplet by the electron donor (iodobenzene in this case). Thus the absorption in the long-wavelength region is due to the triplet alone whereas in the short-wavelength region triplet and semioxonine radical have overlapping absorption. The spectral change in the region between about 500 and 610 nm is negative and is mainly due to the bleaching of the dye ground state.

The assumption that only three types of species, i.e., dye triplet [$T = {}^3A^+$], radicals [$R = (A^+ + D^{\bullet+})$], and ground state [$G = A^+$], have to be considered in the reaction scheme³⁸ can be corroborated by establishing linear correlations of spectral changes with any set of three wavelengths x, y, z :

$$\Delta E_x = a \Delta E_y + b \Delta E_z \quad (5)$$

The coefficients a and b depend on the extinction coefficients of the pertinent species at the wavelengths considered. If one wavelength, say y , is chosen in a spectral region where only the triplet absorbs we may express ΔE_x as follows:

$$\Delta E_x = a' \Delta E_y + b' (\Delta E_z - c' \Delta E_y) \quad (6)$$

The reason of introducing eq 6 is that the extinction coefficients of radical and triplet, ϵ_R and ϵ_T , are separated in the primed coefficients:

$$a' = \frac{(\epsilon_T - \epsilon_G)_x}{\epsilon_{T,y}} \quad (7a)$$

$$b' = \frac{(\epsilon_R - \epsilon_G)_x}{(\epsilon_R - \epsilon_G)_z} \quad (7b)$$

$$c' = \frac{(\epsilon_T - \epsilon_G)_z}{\epsilon_{T,y}} \quad (7c)$$

The relation with the unprimed coefficients is

$$a = a' - b' c' \quad (8a)$$

$$b = b' \quad (8b)$$

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(38) This scheme describes the phenomena detectable on the microsecond time scale. Since, due to the duration of the laser pulse, time resolution was restricted to about $1 \mu\text{s}$ there was no need to take short-lived species as exciplexes or radical pairs explicitly into account in the kinetics, since their quasi-stationary concentrations are by at least 3 orders of magnitude below that of dye triplet and free radicals (cf. ref 35).

Figure 3. Correlation of laser-induced transient absorbance at three different wavelengths for a solution of 2×10^{-5} M oxonine and 0.09 M 2-iodoanisole in oxygen free methanol. A, Y, Z are traces observed at 568, 760 and 403 nm, respectively. X was calculated as ΔE_x according to eq 5. S is the calculated contribution of semioxonine to the absorbance at $\lambda = 403$ nm and corresponds to the term $\Delta E_z - c'\Delta E_y$ in eq 6.

Using one wavelength from each of the three spectral regions shown in Figure 2 ($x = 568$ nm, $y = 760$ nm, $z = 403$ nm) corresponding to spectral maxima or being as close to them as avoiding of laser stray light (590 nm) allowed, it was found that for all systems investigated in this work eq 5 holds well with

$$a = -1.82 \quad \text{and} \quad b = -2.35$$

Since a and b did not significantly depend on the donor used it may be concluded that the absorbance of the radical cation contributes little at the wavelengths considered or that it is very similar at least for those quenchers where radical formation is considerable (e.g., 2-iodoanisole). A demonstration of the validity of eq 5 is given in Figure 3.

In order to determine the coefficients a' and b' which are specific for triplet and semioxonine, respectively, some additional information on the relative concentrations of the two species is needed. It can be obtained by experiments where KI is added in a concentration which is sufficient for rapid triplet quenching but still avoids competition in singlet quenching with the electron donor. Previous experiments with thionine have shown that triplet quenching by I^- occurs without radical formation.³⁹ The same will be assumed for oxonine triplet. Then the difference $\Delta_I(\Delta E_i)$ in parallel experiments with and without I^- observed at delay times where the triplet is still present in the I^- free experiment are only due to a change of the triplet contribution, i.e.

$$\Delta_I(\Delta E_z) = c'\Delta_I(\Delta E_y) \quad (9a)$$

$$\Delta_I(\Delta E_x) = a'\Delta_I(\Delta E_y) \quad (9b)$$

Thus a' and c' can be obtained. Equation 8a represents an independent criterion to check whether the assumption underlying eqs 9a,b are justified. In fact this turned out to be the case. The best values for a' and c' were

$$a' = -2.43; \quad c' = 0.26$$

The relations 7a–c may be used for obtaining absolute $\Delta\epsilon$ values at different wavelengths if $\epsilon_{T,760}$ is known. To obtain this quantity the limiting value of ΔE_{760} at high laser energies was accurately determined for the case of oxonine fluorescence quenching by 9.5

TABLE I: Molar Extinction Coefficients^a Used for Determining Product Yields from Transient Absorption Signals

absorbing state	$\epsilon(403 \text{ nm})$	$\epsilon(568 \text{ nm})$	$\epsilon(590 \text{ nm})^b$	$\epsilon(760 \text{ nm})$
OxH ⁺ (S ₀)	1400	70650	73700	0
OxH ⁺ (T ₁)	7700	12000	6200	24100
OxH ⁺ (D ₀)	26500 ^c	12000 ^c	16800 ^c	0

^a In units of $M^{-1} \text{ cm}^{-1}$. ^b For obtaining the absorbance values at 590 nm, the usual laser wavelength, the laser was tuned to 582.5 nm. ^c These values may include contributions (<4000) from donor cation radicals.

Figure 4. Absorption spectra of triplet (1) and radicals (2) evaluated from transient spectra obtained with a solution of 2×10^{-5} M oxonine and 0.055 M 2-iodoanisole in oxygen-free methanol. For details of the spectral separation cf. text. Spectrum 3 represents the absorption spectrum of oxonine in the ground state.

$\times 10^{-2}$ M 4-iodotoluene. Assuming complete conversion⁴⁰ of the dye into triplet or radical under these conditions, we obtained

$$\epsilon_{T,760} \geq 23400 \text{ M}^{-1} \text{ cm}^{-1}$$

which is a lower bound to the actual value, the equality being valid in the case that no radicals are formed ($\eta_R/\eta_T = 0$).

Substituting $\epsilon_{T,760}$ into eqs 7a and 7c yields $(\epsilon_T - \epsilon_G)_{568}$ and $(\epsilon_T - \epsilon_G)_{403}$, respectively. In order to fix the corresponding $\Delta\epsilon$ values for the radicals we made use of the observation that when oxonine triplet is quenched by aniline, which is known²⁸ to yield radicals with an efficiency of 1.0, the absorbance at 568 nm does not change during the process where radicals are formed from the triplet. Hence

$$(\epsilon_T - \epsilon_G)_{568} \approx (\epsilon_R - \epsilon_G)_{568} \quad (10)$$

which allows one to determine $(\epsilon_T - \epsilon_G)_{403}$ from eq 7b

$$(\epsilon_T - \epsilon_G)_{403} = \epsilon_{T,760} a' / b' \quad (11)$$

Using this value it can be estimated that in the quenching of oxonine singlet by 4-iodotoluene the ratio η_R/η_T is about 1/30 which can be used to obtain an improved $\epsilon_{T,760}$ and correct also the other $\Delta\epsilon$ values. The molar extinction coefficients finally used in the analysis of product formation efficiencies are listed in Table I.

Knowing the absolute extinction coefficients at two wavelengths is sufficient to construct the absolute $\Delta\epsilon$ spectra for triplet and radicals from two ΔE spectra corresponding to different triplet/radical ratios. The ϵ_T and ϵ_R spectra thus obtained are shown in Figure 4.

To obtain the quantum yields of product formation Φ_T and Φ_R in experiments with specific donor concentrations the transient absorption signals observed at 760, 568, and 403 nm were fitted

(40) At the highest laser energy applied every dye molecule can be excited more than 50 times during the laser pulse so that the assumption will be justified even if the sum of the efficiencies of triplet and radical formation in a single quenching event is only 34% as finally determined.

TABLE II: Reaction Parameters for Fluorescence Quenching of Oxonine

quencher	ΔG°_{et} , ^a eV	k_q , 10 ⁸ M ⁻¹ s ⁻¹	η_T , %	η_R , %
4-bromonitrobenzene	1.4	7.0	<i>b</i>	<i>b</i>
3-bromobenzotrifluoride	1.2	1.0	<i>b</i>	<i>b</i>
4-bromobenzonitrile	1.2	1.4	<i>b</i>	<i>b</i>
4-bromoacetophenone	1.0	2.5	<i>b</i>	<i>b</i>
fluorobenzene	0.7	0.4	<i>b</i>	<i>b</i>
chlorobenzene	0.7	0.6	0.06	<i>b</i>
bromobenzene	0.56	1.25	1.2	<0.03
iodobenzene	0.40	3.3	24	0.44
4-bromofluorobenzene	0.62	1.3	0.6 ± 0.3	<i>f</i>
4-bromochlorobenzene	0.63	1.5	1.2 ± 0.6	<i>f</i>
4-chlorotoluene	0.32	0.94	0.08	<0.02
2-bromotoluene	0.41	1.4	1.4	0.13
3-bromotoluene	0.44	1.3	1.4	≤0.05
4-bromotoluene	0.30	2.0	1.4	<0.02
2-iodotoluene	0.25	6.0	25	0.7
3-iodotoluene	0.24	5.0	30	1.0
4-iodotoluene	0.13	9.1	34	0.5
anisole	0.04	40 ^c	<i>b</i>	<i>f</i>
4-chloroanisole	0.00	46	0.08	<0.1
2-bromoanisole	0.08	8.5	2.3	0.14
3-bromoanisole	0.08	3.1	2.0	0.12
4-bromoanisole	-0.02	61	2.2	0.06
2-iodoanisole	0.03	45	36	2.0
3-iodoanisole	0.03	16	30	0.9
4-iodoanisole	-0.07	102	24	0.3
1,3-dimethylbenzene	0.16	0.63 ^d	<i>b</i>	<i>f</i>
1,4-dimethylbenzene	0.14	1.0 ^d	<i>b</i>	<i>f</i>
4-bromophenol	-0.11	120	<i>b</i>	<i>b</i>
4-bromoacetanilide	-0.13	59	0.9	<0.03
1,2-dimethoxybenzene	-0.27	100 ^e	<i>b</i>	0.8 ^g
1,3-dimethoxybenzene	-0.23	100 ^e	<i>b</i>	<i>f</i>
1,4-dimethoxybenzene	-0.38	110 ^e	<i>b</i>	1.0 ^g
aniline	-0.85	100	<i>b</i>	<i>b</i>
4-bromoaniline	-0.83	170	<i>b</i>	<i>b</i>

^aStandard free enthalpy of (OxH[•]D^{•+}) radical pair formation according to eq 16 with data from Table III. ^bNot detectable. ^cFrom ref 43. ^dFrom ref 44. ^eFrom ref 53. ^fLow values, but not quantitatively determined. ^gFrom ref 29.

by integrating the following phenomenological equations for triplet and radical concentration and computing the resultant time profiles of absorption by using the extinction coefficients given in Table I.

$$\dot{C}_T(x,t) = \Phi_T I_{absG}(x,t) - k_1 C_T(x,t) - k_2 C_T^2(x,t) \quad (12)$$

$$\dot{C}_R(x,t) = \Phi_R I_{absG}(x,t) + \Phi_R' k_1 C_T(x,t) \quad (13)$$

$$C_T(x,t) + C_R(x,t) + C_G(x,t) = C_0 \quad (14)$$

Here $I_{absG}(x,t)$ is the rate per volume at which laser photons are absorbed by the ground state and k_1 and k_2 are effective first- and second-order rate constants of triplet decay, respectively. In eqs 12 and 13 singlet quenching and corresponding product formation are treated as instantaneous processes on the time scale of the experiment. Φ_R' is the actual yield of radical formation in the triplet quenching process.

The rate of photons absorbed and the changes in concentration of the three species considered decrease along the optical path in the cuvette. Since second-order decay of the triplets and screening of the ground state due to transient absorption at the laser wavelength had to be taken into account, it was not possible to separate spatial and temporal integration. Thus we applied a numerical method with finite differences in x and t .³⁴ Increments of $\Delta x = 0.1$ cm and $\Delta t = 5$ ns were usually sufficient to achieve a relative accuracy of Φ_T better than 1%.

By fitting the parameters in eqs 12 and 13 the experimental curves at the three wavelengths could be satisfactorily reproduced and Φ_T and Φ_R were uniquely determined. Furthermore, these values were confirmed by additional experiments applying triplet quenching by I⁻ ions at a concentration such that radical formation from the triplet is suppressed ($\Phi_R' = 0$) but the singlet quenching by the donor is not affected.

TABLE III: Ionization Potentials IP and Polarographic Half-Wave Oxidation Potentials $E_{1/2}$ Used for Estimation of ΔG°_{et}

quencher	IP, ^a V	$E_{1/2}$, ^b V
4-bromonitrobenzene	9.92 ^c	
4-bromobenzonitrile	9.7 ^c	
3-bromobenzotrifluoride	9.68 ^c	
4-bromoacetophenone	9.47 ^d	
benzene	9.24	2.43 ^e
fluorobenzene	9.2, 9.19 ^f	
chlorobenzene	9.07, 9.06 ^f	2.42 ^e
bromobenzene	8.98, 9.05 ^f	2.28, ^g 2.33 ^e
iodobenzene	8.73	2.12 ^e
4-bromofluorobenzene	8.99	
4-bromochlorobenzene	9.0 ^f	
toluene	8.82	2.33 ^e
2-chlorotoluene	8.83	
3-chlorotoluene	8.83	
4-chlorotoluene	8.69	
2-bromotoluene	8.78	
3-bromotoluene	8.81	
4-bromotoluene	8.67	
3-iodotoluene	8.62	
3-iodotoluene	8.61	
4-iodotoluene	8.50	
1,2-dimethylbenzene	8.56	1.87 ^h
1,3-dimethylbenzene	8.58	1.88, ^h 1.91 ⁱ
1,4-dimethylbenzene	8.44	1.86, ^h 1.77 ⁱ
phenol	8.51	1.70 ^j
4-bromophenol	8.31 ^j	
anisole	8.21, 8.3 ^j	1.76, ^k 1.77 ⁱ
4-chloroanisole		1.72 ⁱ
2-bromoanisole	8.6 ^m	
3-bromoanisole	8.6 ^m	
4-bromoanisole	8.5 ^f	1.70 ⁱ
2-iodoanisole		1.75 ^m
3-iodoanisole		1.75 ^m
4-iodoanisole		1.65 ⁱ
1,2-dimethoxybenzene		1.45 ^k
1,3-dimethoxybenzene		1.49 ^k
1,4-dimethoxybenzene		1.34 ^k
aniline	7.7	0.87 ⁱ
4-bromoaniline		0.89 ⁱ
4-bromoacetanilide	8.39 ^c	
<i>N,N</i> -dimethylaniline	7.12	0.79 ^k
<i>N,N</i> -diethylaniline	6.99	0.76 ^k

^aFrom ref 45 unless otherwise stated. ^bIn acetonitrile vs SCE. ^cValue of unbrominated compound from ref 45. ^dValue of chlorinated compound from ref 45. ^eReference 11. ^fFrom a photoelectron spectrum in ref 46. ^gReference 47. ^hReference 48. ⁱReference 49. ^jReference 50. ^kReference 51. ^lReference 52. ^mEstimated according to eq 18.

From these values of Φ_T and Φ_R as functions of the donor concentration the efficiency parameters η_T and η_R were determined according to eq 4.

Results

The reaction parameters k_q , η_T , and η_R determined for the quenching of oxonine fluorescence by a series of potential electron donors are listed in Table II. Also given are the standard free enthalpy ΔG°_{et} of radical pair formation by the electron-transfer process

The value of ΔG°_{et} was obtained by using the relation¹⁸

$$\Delta G^\circ_{et} = F(E_{D^+/D} - E_{A/A^-}) - E_{0,0}(^1A^*) + \Delta G_c \quad (16)$$

where F is the Faraday constant, $E_{D^+/D}$ the standard oxidation potential of the electron donor, E_{A/A^-} the standard reduction potential of the electron acceptor and $E_{0,0}(^1A^*)$ the purely electronic excitation energy of the electron acceptor. The quantity ΔG_c , denoting the Coulomb energy of the radical pair, is zero for the present systems since we deal with a neutral acceptor radical (OxH[•]) and a neutral donor.

The value of $E_{0,0}(^1\text{OxH}^{\bullet+})$ was determined as 2.07 eV from the intersection point of absorption and fluorescence spectra, both

Figure 5. Plot of $\log k_q$ versus the standard free enthalpy ΔG°_{et} of radical pair formation by electron transfer from the quenchers listed in Table II to singlet excited oxonine: ● (O) quenchers with (without) Cl, Br, or I substituents. The strike-through symbol indicates cases where no induced triplet formation was observed. The solid line was calculated according to the Rehm-Weller model, the dashed curves according to the exciplex model for various values of β given in units of $\lambda = 0.435$ eV (cf. text).

normalized to the same maximum value. The standard reduction potential $E_{\text{OxH}^+/\text{OxH}^\bullet}$ of oxonine was obtained from potentiometric data of Michaelis and Granick.⁴¹ Correcting for the change in solvation energy between water and methanol by use of the Born equation results in a value of -0.35 V vs SCE for methanol.³⁴

For the standard oxidation potential of the quenchers the polarographic half-wave potentials in acetonitrile were used where available (cf. Table III). In other cases $E_{D^+/D}$ was estimated from published ionization potentials which are known to correlate linearly with the former.⁴² From the data in Table III for compounds where both $E_{1/2}$ and IP are available one obtains

$$E_{1/2} \text{ (vs SCE)} = \text{IP} - 6.7 \pm 0.1 \text{ V} \quad (17)$$

No literature data were available for the 2- or 3-substituted bromo- and iodoanisoles. Therefore, the required values for these were estimated by analogy with the behavior of the corresponding toluenes:

$$\text{IP(ortho)} \approx \text{IP(meta)} \approx \text{IP(para)} + 0.1 \text{ V} \quad (18)$$

For lack of more direct data in the case of bromo compounds 1–4 of Table II the ionization potentials of the corresponding H or Cl derivatives were used which might overestimate the actual values by 0.1–0.2 V.

The k_q values obtained from the Stern-Volmer constants are based on a k_0 value of $2.94 \times 10^8 \text{ s}^{-1}$.³⁷ In Figure 5 $\log k_q$ is plotted versus the standard free enthalpy ΔG°_{et} of radical pair formation by electron transfer. Also shown is the correlation line established by Rehm and Weller¹⁸ to apply for the electron-transfer quenching

SCHEME II

mechanism of aromatic compounds in acetonitrile solution. The data points of our experiments do not in general follow the Rehm-Weller correlation. However, this curve obviously represents a borderline marking the lowest k_q to be found as a function of ΔG°_{et} . The significance of the dashed curves in Figure 5 will be discussed below.

The quantum yield η_T^0 of spontaneous triplet formation of oxonine was measurable with the highest absorbed laser energy of 10^{-3} einsteins L^{-1} only, yielding a value of $\eta_T^0 = 0.06\%$. This figure also marks the detection limit of efficiencies η_T for induced triplet formation. No such process was observed with quenchers, though brominated, in the ΔG°_{et} range ≥ 1.0 eV. One should note that these quenchers also will be discussed as a special case below.

Induced triplet formation is found in the ΔG°_{et} region between 0.8 and -0.1 eV for practically all quenchers carrying halogen substituents, 4-bromophenol being the only exception. The values for the chlorinated quenchers are on the same order of magnitude as spontaneous triplet formation. The results for the brominated compounds range between 1 and 2%, those for the iodinated quenchers between 24 and 35%.

At strongly negative ΔG°_{et} values (4-bromoaniline $\Delta G^\circ_{et} = -0.83$ eV) induced triplet is not detectable. It must be pointed out, however, that for $\Delta G^\circ_{et} < -0.4$ eV the energy of the radical pair is below the oxonine triplet ($E(^3\text{OxH}^\bullet) = 1.67 \pm 0.08$ eV)³⁰ so that the rate constant of triplet quenching approaches that of singlet quenching which severely hampers the observation of induced triplet formation since in this case the triplet decays almost as fast as it is formed.

The efficiencies η_R of the radical formation are all very low and in no case greater than 2%. Precise determinations were carried out, however, only in those cases where induced triplet formation was detectable. It turned out that in all cases η_R was smaller than η_T by at least 1 order of magnitude.

Discussion

A Quantitative Model of the Quenching Process. As one of the main conclusions from the results presented in Table II we note that, of the three deactivation channels, i.e., radical formation by electron transfer, induced triplet formation, and induced internal conversion, the latter is clearly dominating (>65%). Induced triplet formation requires the presence of a heavy atom substituent but even in the most prominent case (2-iodoanisole) does not exceed the efficiency of induced internal conversion. Formation of free radicals is practically negligible with the quenchers investigated. The observed low order of magnitude of η_R is consistent with the ΔG°_{et} correlation established by Iwa et al.²⁹

What is the mechanism of the dominating induced internal conversion process? Since it is this mode of deactivation which largely determines the value of k_q we may learn something about it from the correlation between k_q and ΔG°_{et} shown in Figure 5. From the deviations of many of the data points from the Rehm-Weller (RW) correlation line it is clear that the RW mechanism cannot generally apply to our systems. According to this mechanism (cf. Scheme II) the quenching rate constant is expressed as¹⁸

$$k_q = \frac{k_d}{1 + \frac{k_{-d}}{k_{et}} \left(1 + \frac{k_{-et}}{k_g^{IP}} \right)} \quad (19)$$

with k_{et} given by

$$k_{et} = k_{et}^0 \exp(-\Delta G^\circ_{et}/RT) \quad (20)$$

Thus one obtains

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$$k_q = \frac{k_d}{1 + \frac{k_d}{k_{et}^0} \left(\exp(\Delta G_{et}^*/RT) + \frac{k_{et}^0}{k_g^{rp}} \exp(\Delta G_{et}^0/RT) \right)} \quad (21)$$

The standard free enthalpy of activation ΔG_{et}^* is a monotonic function of ΔG_{et}^0 and adopts the limiting values $\Delta G_{et}^* = 0$ for $\Delta G_{et}^0 \rightarrow -\infty$ and $\Delta G_{et}^* = \Delta G_{et}^0$ for $\Delta G_{et}^0 \rightarrow +\infty$. Furthermore for systems of the type investigated by Rehm and Weller the relations

$$k_{et}^0 = k_g^{rp} = 4k_d \quad (22)$$

can be applied. They were also found to be valid in the case of thionine triplet quenching by a series of aromatic quenchers in methanolic solution.⁵⁴

The essential feature of the RW mechanism is that only pure charge-localized states, i.e., the encounter complex ($A^{\bullet} \cdots D$) with $p_{CT} = 0$ and the radical pair ($A^{\bullet} \cdots D^{\bullet}$) with $p_{CT} = 1$ are considered, whereby irreversible decay (rate constant k_g^{rp}) occurs exclusively in the latter. In terms of a reaction energy diagram (cf. Figure 6) where the adiabatic energy of educt and product state is plotted as a function of the relevant collective nuclear coordinate the Rehm-Weller view corresponds to a situation with almost negligible electronic interaction between the educt and the product state. The only effect of the interaction, which may be represented by a resonance integral β , is to allow the system to change from one potential curve to the other at the crossing point. Thus the rate of quenching is kinetically determined by the barrier crossing.

In order to explain the $\log k_q$ (ΔG_{et}^0) relation observed in the present investigation we suggest modifying the RW model by allowing a finite β to become effective already in the region well before the crossing point which is tantamount to considering the effect of exciplex formation on the quenching rate. The wave function of the locally excited encounter complex (${}^1LE = (A^{\bullet} \cdots D)$) and the contact radical pair (${}^1CT = {}^1(A^{\bullet} \cdots D^{\bullet})$) are mixed through the interaction to form the exciplex state (1EX)

$$\Psi({}^1EX) = a\Psi({}^1LE) + b\Psi({}^1CT) \quad (23)$$

whereby a lowering of the educt and product minima is achieved and the activation barrier is rounded off (cf. Figure 6a). Furthermore the encounter complex adopts some CT character already before the barrier crossing. Accordingly, a corresponding propensity to undergo the same type of irreversible decay as the pure CT state in the RW model is transferred to it.

On the basis of such considerations we suggest a kinetic model that is described by Scheme III. It is characterized by reversible exciplex formation in an encounter (rate constants k_{ex} and k_{-ex}) and by irreversible exciplex decay to the ground state (k_g^{ex}) and to the locally excited triplet state of A (k_t^{ex}). Since in all cases investigated here induced triplet formation was found to be less efficient than that of induced internal conversion, the former may be neglected in the discussion of the general ΔG_{et}^0 dependence of k_q . The rate parameters of the exciplex model will be related to those of the RW model by setting⁶¹

$$k_g^{ex} = f \langle b^2 \rangle_q k_g^{rp} \quad (24)$$

and

$$k_{-ex} = k_d \langle \exp(-E_{stab}/RT) \rangle_q \quad (25)$$

Here the symbol $\langle \rangle_q$ denotes thermal averaging over the reaction coordinate q . The square of b corresponds to the CT character of the exciplex and

$$E_{stab}(q) = E({}^1LE) - E({}^1EX) \quad (26)$$

is the stabilization energy of the encounter complex due to adiabatic CT interaction.

The factor f is a proportionality constant, the value of which shall be chosen such that in the limits $\Delta G_{et}^0 \rightarrow \pm\infty$ the exciplex

Figure 6. (a) Energy profiles over reaction coordinate q of electron transfer. Parameters: $\beta = 0$ (---), $\beta = 0.2\lambda$ (—). $\Delta G_{et}^0 = 0.5\lambda$ (curves 0 and 1), 0.25λ (curve 2), 0.0λ (curve 3), and -0.25λ (curve 4). (b) CT character b^2 weighted by thermal probability density p_{therm} as a function of reaction coordinate q . Parameters corresponding to those in (a).

SCHEME III

model yields the same behavior for k_q as the RW model. From Scheme III the quenching rate constant is obtained as

$$k_q(EX) = k_{ex} / (1 + k_{-ex} / k_g^{ex}) \quad (27)$$

In the limit $\beta \rightarrow 0$ and $\Delta G \rightarrow +\infty$ we assume

$$\langle b^2 \rangle_q \approx \exp(-\Delta G_{et}^0/RT)$$

while $E_{stab} = 0$, so that $k_{-ex} \gg k_g^{ex}$ and

$$\lim_{\substack{\beta \rightarrow 0 \\ \Delta G_{et}^0 \rightarrow +\infty}} k_q(EX) \approx k_{ex} f \frac{k_g^{rp}}{k_d} \exp(-\Delta G_{et}^0/RT) \quad (28)$$

For the RW model one obtains from eq 21

$$\lim_{\Delta G_{et}^0 \rightarrow +\infty} k_q(RW) = 2k_d \exp(-\Delta G_{et}^0/RT) \quad (29)$$

In the limit $\Delta G_{et}^0 \rightarrow -\infty$ we have $k_{-ex} \ll k_g^{ex}$ so that

$$\lim_{\Delta G_{et}^0 \rightarrow -\infty} k_q(EX) = k_{ex} \quad (30)$$

whereas

$$\lim_{\Delta G_{et}^0 \rightarrow -\infty} k_q(RW) = k_d / 1.25 \quad (31)$$

From a comparison of eqs 28, 29, 30, and 31 and adopting $k_g^{rp}/k_d = 4$ from eq 22 we obtain $f = 0.625$ and $k_{ex} = k_d / 1.25$.

For calculating k_q values with the exciplex model we assumed a quadratic dependence of the zero-order potentials of 1LE and 1CT on the reaction coordinate q (cf. Figure 6)

$$E({}^1LE) = \lambda q^2 \quad (32)$$

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$$E(^1\text{CT}) = \Delta G^\circ_{\text{et}} + \lambda(1 - q)^2 \quad (33)$$

Here λ is the nuclear reorganization energy after electron transfer according to the Marcus theory.⁵⁵ A major contribution to λ is due to solvent reorganization. For numerical calculations we used a value of $\lambda = 0.435$ eV which is in best accord with the original Rehm–Weller data and with the above-mentioned data on triplet quenching of thionine by benzene derivatives in methanol.⁵⁴ If the difference $E(^1\text{CT}) - E(^1\text{LE})$ is denoted as e , the energy of the lower state (^1Ex) obtained after introducing the resonance interaction β is

$$E(^1\text{Ex}) = \frac{1}{2}e + \lambda q^2 - (e^2/4 + \beta^2)^{1/2} \quad (34)$$

The CT character of ^1Ex as an implicit function of q is given by

$$b^2(q) = E_{\text{stab}}^2/(\beta^2 + E_{\text{stab}}^2) \quad (35)$$

The thermal averages entering into eqs 24 and 25 were calculated by numerical integration of the corresponding function over q using the weight factor

$$w = \exp(-E(^1\text{Ex})/RT) \quad (36)$$

and normalizing the integrals by the partition function $\int_{-\infty}^{\infty} w \, dq$.

The $\Delta G^\circ_{\text{et}}$ -dependent curves obtained for k_q from the exciplex model are shown in Figure 5 for various values of β . As can be noted in the positive $\Delta G^\circ_{\text{et}}$ region, all data points except for quenchers 1–4 fall between the lines corresponding to $\beta = 0.05$ (0.022 eV) and 0.2 (0.087 eV) whereby a lower value of $\beta = 0.1$ (0.043 eV) still bounds most of the data points. This finding provides strong evidence for the assumed quenching mechanism with partial CT from the quencher to the excited dye.

Since quenchers 1–4 involve strongly electron-accepting substituents it seems possible that the particular behavior of this group of compounds can be explained by involving also reverse CT contributions with the quencher acting as an electron acceptor.

The order of magnitude to be adopted for the resonance energy appears quite reasonable. Values used in theoretical work in typical exciplexes range about 0.15 eV.⁵⁶

The theoretical curves in Figure 5 show that even smaller electronic interactions in the encounter complex may cause significant deviations from the Rehm–Weller curve. At present it is difficult to explain the variations of such small β values in terms of the chemical structure of the systems. Certainly β will depend on the distance of closest approach which may be related to specific interactions between certain regions of the reactants and on their specific solvation.

Comparing the $\Delta G^\circ_{\text{et}}$ dependence of $k_q(\text{Ex})$ with the Rehm–Weller curve we note that, except for the most obvious difference in the behavior for $\Delta G^\circ_{\text{et}} \rightarrow +\infty$, there is also a different curvature at $\Delta G^\circ_{\text{et}} \approx 0$. In the case of the exciplex model the change of the slope is more abrupt which, however, fits the bulk of our data points even better than the Rehm–Weller curve. To understand the differences between $k_q(\text{Ex})$ and $k_q(\text{RW})$ one has to analyze the effects of thermally averaging the CT character and of taking exciplex bonding into account.

For $\Delta G^\circ_{\text{et}} \rightarrow +\infty$ the bonding effect is negligible. However, as is borne out by Figure 6b, the CT character acquired by the exciplex at the potential minimum of the locally excited state is dominating over the contribution from the minimum of the CT state. This feature determines the behavior of $k_q(\text{Ex})$ in the more positive $\Delta G^\circ_{\text{et}}$ region. A detailed analysis shows that for $\Delta G^\circ_{\text{et}} \rightarrow +\infty$ $\log k_q(\text{Ex}) \propto -\log \Delta G^\circ_{\text{et}}$ whereas for the Rehm–Weller model one has $\log k_q(\text{RW}) \propto -\Delta G^\circ_{\text{et}}/RT$.

Before $\log k_q(\text{Ex})$ turns to its limiting behavior in the more positive $\Delta G^\circ_{\text{et}}$ region it parallels the Rehm–Weller curve in the weakly positive $\Delta G^\circ_{\text{et}}$ region. The onset of the divergence from

the Rehm–Weller behavior shifts to lower k_q as $\beta \rightarrow 0$ in which limit the two models can be made convergent.

The higher value of $k_q(\text{Ex})$ at $\Delta G^\circ_{\text{et}} \approx 0$ is caused by an increasing influence of the exciplex binding energy as $\Delta G^\circ_{\text{et}}$ is lowered and by the increasing contribution of CT character from the CT minimum of the exciplex potential curve (cf. Figure 6b). In our model thermal equilibrium distribution is assumed over the complete q domain, whereas implicit in the Rehm–Weller model is the assumption that equilibrium distribution is established only up to the top of the barrier and barrier crossing becomes rate determining for the quenching process in the $\Delta G^\circ_{\text{et}} \approx 0$ region. In fact it would be possible to incorporate also the latter feature into the exciplex model. It is not of importance, however, in the more positive $\Delta G^\circ_{\text{et}}$ region where our main concern has been located, when specifying the exciplex model.

Induced Triplet Formation. As noted above, induced triplet formation is only observable with halogen substituents in the quenchers. However, even with these the process of induced internal conversion is always the dominating one. For a more quantitative analysis we will particularly consider the donors of the halogenated series of benzene, toluene, and anisole. The most striking feature concerning the efficiency of η_T of induced triplet formation in this series of donors is the constancy of η_T for a given halogen substituent while there is considerable variation of $\Delta G^\circ_{\text{et}}$ and k_q : Cl ($\eta_T = 0.065$ – 0.08% , $k_q = (0.6$ – $46) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), Br ($\eta_T = 1.3$ – 2.3% , $k_q = (1.25$ – $61) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), I ($\eta_T = 24$ – 36% , $k_q = (3.3$ – $102) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$).

According to Scheme III we may express η_T as

$$\eta_T = k_i^{\text{ex}}/k_0^{\text{ex}} \quad (37)$$

Here $k_0^{\text{ex}} = k_g^{\text{ex}} + k_i^{\text{ex}}$ is largely determined by k_g^{ex} which was demonstrated to obey a characteristic $\Delta G^\circ_{\text{et}}$ dependence. Thus we may conclude from the observed constancy of η_T that for donors with the same halogen a similar $\Delta G^\circ_{\text{et}}$ dependence must also control k_i^{ex} . To show this in detail we evaluate the ratio $k_i^{\text{ex}}/k_{-\text{ex}}$ which must closely follow the $\Delta G^\circ_{\text{et}}$ dependence of k_i^{ex} at $\Delta G^\circ_{\text{et}} > 0$ where $k_{-\text{ex}}$ is close to its limiting value, since E_{stab} (cf. eq 35) is small. The ratio $k_i^{\text{ex}}/k_{-\text{ex}}$ can be directly obtained from experimental quantities. Using the quantity α

$$\alpha \equiv \frac{k_0^{\text{ex}}}{k_{-\text{ex}}} = \frac{k_q/k_{\text{ex}}}{1 - k_q/k_{\text{ex}}} \quad (38)$$

which may be calculated from k_q and its diffusion-controlled limit we obtain from eqs 37 and 38

$$k_i^{\text{ex}}/k_{-\text{ex}} = \eta_T \alpha \quad (39)$$

The values obtained for $\eta_T \alpha$ for the various donors inducing triplet formation are listed in Table IV. In Figure 7a $\log(\eta_T \alpha)$ is plotted versus $\Delta G^\circ_{\text{et}}$. Here we see that for each set of donors with the same halogen, $\eta_T \alpha$ decreases rather systematically with increasing $\Delta G^\circ_{\text{et}}$. The correlation lines shift to higher values in the series Cl, Br, I of substituents which parallels the increasing SOC strength of these atoms.

In order to account for this heavy atom effect more quantitatively we test the following assumption:

$$k_i^{\text{ex}} = c_{X,i}^2 \zeta_X^2 F(\Delta G^\circ_{\text{et}}) \quad (40)$$

i.e., we factorize the rate constant k_i^{ex} into a function $F(\Delta G^\circ_{\text{et}})$ which is independent of the halogen substituent X and a factor $c_{X,i}^2 \zeta_X^2$, where ζ_X is the atomic SOC constant of the halogen and $c_{X,i}$ is the Hückel coefficient of the halogen X, in the singly occupied π -MO at the electron donor D ($i \equiv \text{o-X-D}$, $m\text{-X-D}$, $p\text{-X-D}$).

Such an expression has been shown to account well for the substituent dependence of $T_1 \rightarrow S_0$ ISC rate constants in triplet exciplexes between thionine and haloanilines, i.e., systems similar to those considered in this work.²⁷ A theoretical justification of expression 40 is the relation of the factor $c_{X,i}^2 \zeta_X^2$ to one-center contributions of the heavy atom to the electronic matrix element of SOC appearing squared in the golden rule expression of radiationless transitions.^{27,58}

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TABLE IV: Analysis of Induced Triplet Formation Efficiency η_T for Halobenzenes and Derivatives as Quenchers of Singlet Excited Oxonine

donor	η_T	α^a	$\eta_T\alpha$	$c_{X,i}^{2b}$	$c_{X,i}^2\zeta_X^{2c}$	J^d
chlorobenzene	0.06	0.005	3.0×10^{-4}	0.045	0.059	0.007
bromobenzene	1.2	0.010	1.2×10^{-2}	0.087	2.0	0.010
iodobenzene	24	0.028	6.7×10^{-1}	0.210	21.0	0.016
4-chlorotoluene	0.08	0.008	6.4×10^{-4}	0.036	0.047	0.022
2-bromotoluene	1.4	0.012	1.7×10^{-2}	0.040	0.94	0.017
3-bromotoluene	1.4	0.011	1.5×10^{-2}	0.022	0.52	0.015
4-bromotoluene	1.4	0.017	2.4×10^{-2}	0.060	1.41	0.023
2-iodotoluene	25	0.053	1.3	0.094	9.4	0.029
3-iodotoluene	30	0.043	1.3	0.059	5.9	0.031
4-iodotoluene	34	0.082	2.8	0.120	12.0	0.073
4-chloroanisole	0.085	0.623	5.3×10^{-2}	0.025	0.032	2.17
2-bromoanisole	2.3	0.076	1.7×10^{-1}	0.024	0.56	0.18
3-bromoanisole	2.0	0.027	5.4×10^{-2}	0.008	0.19	0.18
4-bromoanisole	2.2	1.038	2.3	0.038	0.89	4.43
2-iodoanisole	36	0.603	2.2×10^1	0.047	4.7	0.78
3-iodoanisole	30	0.154	4.6	0.016	1.6	0.78
4-iodoanisole	24	5.510	1.3×10^2	0.068	6.8	28.0

^a $\alpha = k_q/(k_{ex} - k_q)$, $k_{ex} = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. ^b The Hückel coefficients $c_{X,i}$ of the halogens X in the HOMO π -orbital of the donor i were obtained by using the following parameters (α_X , β_{C-X}): Cl (2.0, 0.4), Br (1.5, 0.3), I (1.2, 0.25), CH_3 ($\alpha = -0.4$ for ring C), OCH_3 (O: 1.6, 0.8). ^c For ζ_X relative values ($\zeta_1^2 \equiv 100$) were used, based on the absolute SOC parameters from ref 57. $\zeta_{\text{Cl}}^2 = 587.3 \text{ cm}^{-1}$, $\zeta_{\text{Br}}^2 = 2456.7 \text{ cm}^{-1}$, $\zeta_{\text{I}}^2 = 5068.8 \text{ cm}^{-1}$. ^d Calculated according to eq 44 for $\beta = 0.2 \lambda$, $\lambda = 0.435 \text{ eV}$.

Figure 7. (a) log plot of $\eta_T\alpha$ and (b) log plot of $(\eta_T\alpha/c_{X,i}^2\zeta_X^2)$ versus ΔG_{et}° for the halobenzene derivatives of Table IV: O, chlorinated, ●, brominated, ○, iodinated quencher compounds.

Since k_{ex} should not be susceptible to SOC effects we expect that the quantity $\eta_T\alpha/c_{X,i}^2\zeta_X^2$ should exhibit a general correlation with ΔG_{et}° if eq 40 holds true. The values of $c_{X,i}^2$ and ζ_X^2 used to test this correlation are also listed in Table IV. Standard parameter sets were used in the Hückel calculation (cf. footnotes of Table IV). The parameters for iodine, where no standard parameters are available, were taken from our studies of triplet

exciplexes^{28,59} where they have been adjusted to fit the ISC rate constants of these triplet exciplexes. The iodine parameters thus obtained represent reasonable extrapolations of the Hückel parameters of Cl and Br.⁶⁰ The log plot of the reduced parameter $\eta_T\alpha/c_{X,i}^2\zeta_X^2$ versus ΔG_{et}° is shown in Figure 7b. It is evident that use of eq 40 in fact leads to a unified correlation for the complete set of donors listed in Table IV. In other words, the ratio $k_t^{ex}/(k_{ex}c_{X,i}^2\zeta_X^2)$ must be a rather well-defined universal function of ΔG_{et}° . We will show how this function can be related to the exciplex quenching model.

It is already an assumption implicit in the introduction of the halogen SOMO coefficient in eq 40 that the rate of the ISC process should be proportional to the unpaired spin density transferred to the halogen substituent by the CT process that accompanies exciplex formation. Thus, in order to complete this idea, we set

$$F(\Delta G_{et}^\circ) = A p_{CT}(\Delta G_{et}^\circ) \quad (41)$$

where A is a correlation constant and $p_{CT}(\Delta G_{et}^\circ)$ is the thermally averaged CT character $\langle b^2 \rangle_q$ (cf. eq 24). From eqs 25 and 39–41 we obtain

$$\begin{aligned} \eta_T\alpha &\equiv \frac{k_t^{ex}}{k_0^{ex}} = \frac{A c_{X,i}^2 \zeta_X^2 p_{CT}(\Delta G_{et}^\circ)}{k_d \langle \exp(-E_{stab}/RT) \rangle_q} \\ &\equiv B c_{X,i}^2 \zeta_X^2 J(\Delta G_{et}^\circ) \end{aligned} \quad (42)$$

(59) Waschi, H. P.; Steiner, U. E., to be published.

(60) In view of the problems in accounting for electronic properties of heavy atoms within the Hückel formalism no special effort was taken for fitting the iodine Hückel parameters to the present results, although some improvement of the correlation may be obtained. For example, with $\alpha_I = 1.0$ and $\beta_{CI} = 0.2$, the spin densities on iodine are increased by about a factor of 2 and the correlation data of eq 45 become $\log(\eta_T\alpha) = 0.02 + 1.01 \log(c_{X,i}^2\zeta_X^2)$, with $r = 0.986$ and $\sigma = \pm 0.25$.

(61) Note Added in Proof. Professor J. Mattay has drawn our attention to another quenching model⁶² invoking exciplex formation with partial charge transfer to account for a decreased slope of $\log(k_q)$ vs ΔG_{et}° as compared to the RW type behavior. In ref 62 as in other work^{63,64} it is assumed that the CT character of the exciplex is independent of ΔG_{et}° . With this assumption the theoretical relation between $\log(k_q)$ and ΔG_{et}° remains linear in the region of positive ΔG_{et}° , whereas in our case, with ΔG_{et}° -dependent CT character, $\log(k_q)$ approaches a proportionality to $-\log(\Delta G_{et}^\circ)$. In view of the scatter of experimental data points it may be difficult to distinguish between these theoretical results experimentally. From a theoretical point of view, however, our assumption appears to be the more consistent one.

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(63) Wagner, P. J.; Leavitt, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 3669–3677.

(64) Loutfy, R. O.; Dogra, S. K.; Yip, R. W. *Can. J. Chem.* **1979**, *57*, 342–347.

with

$$B = A/k_{-d} \quad (43)$$

$$J(\Delta G^\circ_{et}) = p_{CT}(\Delta G^\circ_{et}) / \langle \exp(-E_{stab}/RT) \rangle_q \quad (44)$$

The function J can be obtained without any further assumptions from the exciplex model as described above. It depends on the choice of the interaction matrix element β . It turned out that a change of β is mainly reflected as a constant scaling factor of $J(\Delta G^\circ_{et})$; i.e., the general shape of $J(\Delta G^\circ_{et})$ is rather insensitive to the choice of β . Thus we will confine our analysis to a fixed β value of 0.2λ (≈ 0.084 eV). The arbitrariness of the scaling factor thus introduced will enter into the value of the correlation constant B , the absolute value of which will not be of further concern here.

In order to test the correlation, suggested by eq 42, we plotted $\log(\eta_T\alpha)$ versus $\log(c_{X,i}^2\zeta_X^2J)$ in Figure 8a. As can be seen, there is a fairly good linear correlation over the complete range of data. A least-squares fit yields

$$\log(\eta_T\alpha) = 0.01 + 1.08 \log(c_{X,i}^2\zeta_X^2J) \quad (45)$$

with a correlation coefficient of $r = 0.972$ and a standard deviation of ± 0.35 . This means that from ΔG°_{et} and the substituent parameters $c_{X,i}$ and ζ_X the relative rate of ISC k_t^{ex}/k_{-ex} can be predicted with an accuracy of a factor of 2.2 over a range characterized by a ratio of about 10^6 between the highest and the lowest value. The slope of approximately unity in the log plot confirms the linear relation between k_t^{ex}/k_{-ex} and the "electronic term" $c_{X,i}^2\zeta_X^2J$ suggested in eq 44.

We will now discuss the significance of the correlation of k_t^{ex} with the Hückel coefficient $c_{X,i}$ of the halogen. In fact, the correlation of $\eta_T\alpha$ with $c_{X,i}^2\zeta_X^2J$ is much better than with ζ_X^2J only, which indicates that the coupling of spin density to the heavy atom is an important factor and leads to an enhancement of the differences between the halogen substituents that would arise from the SOC constants only. On the other hand, as is documented in Table IV, the $c_{X,i}$ coefficients exhibit a pronounced dependence on the position of the substituent X. Such a position dependence is not borne out in the experimental values of η_T , however.

Therefore we have also investigated the correlation of $\log(\eta_T\alpha)$ with $\log C_X^2\zeta_X^2$, where C_X is independent of position and donor (cf. Figure 8b). Using for C_{Cl} the average of the $c_{Cl,i}$ in Table IV (0.035) the best correlation is obtained with $C_{Br} = 0.080$ and $C_I = 0.32$, yielding

$$\log(\eta_T\alpha) = 0.102 + 0.916 \log(C_X^2\zeta_X^2J) \quad (46)$$

with $r = 0.985$ and $\sigma = \pm 0.26$.

This correlation is slightly superior to that with the position-dependent $c_{X,i}$ for individual donors and the slope is somewhat less than 1.0. Nevertheless, it must be pointed out that the factors C_X^2 obtained from an unbiased fit of the data follow the averages of c_{p-X-D}^2 over the various donors ($c_{p-Br-D}^2 = 0.062$, $c_{p-I-D}^2 = 0.132$). Thus the concept of spin density transferred to the halogen by π -charge transfer in the exciplex definitely has some experimental basis.

So far our kinetic analysis according to the exciplex model has demonstrated that in the deactivation of the exciplex the rate constants of both, IC and ISC, are intimately related to its CT character. It must be pointed out, however, that the statistical scatter on the correlations established separately for k_g^{ex}/k_{-ex} and k_t^{ex}/k_{-ex} would not allow one to explain the remarkable independence of η_T within each donor series with the same halogen.

The linear correlations established through the log plots may be expressed in explicit form as

$$\alpha \equiv \frac{k_0^{ex}}{k_{-ex}} = aJ^{1-\epsilon} \quad (47)$$

$$\eta_T\alpha \equiv \frac{k_t^{ex}}{k_{-ex}} = bC_X^2\zeta_X^2J^{1-\epsilon'} \quad (48)$$

From the logarithmic regression lines, with $J(\Delta G^\circ_{et})$ calculated for $\beta = 0.2\lambda$, one obtains $a = 0.34$ and $b = 1.26$. The parameters

Figure 8. Double log plot of $\eta_T\alpha$ (a) versus $(c_{X,i}^2\zeta_X^2J)$ and (b) versus $(C_X^2\zeta_X^2J)$. Whereas the $c_{X,i}$ are the individual Hückel coefficients of the halogen in the HOMO of the various donors (cf. Table IV) C_X is a constant for each halogen. For the definition of C_X cf. text. The assignment of the data point symbols is the same as in Figure 7.

ϵ and ϵ' signifying the deviation from linearity are 0.22 and 0.07, respectively. The physical interpretation of a and b has to be sought in terms of Franck-Condon (FC) factors of the corresponding processes and the existence of correlations 47 and 48 implies that throughout the series of quenchers listed in Table IV the FC factors of IC and ISC, respectively, remain rather constant. There are of course individual deviations of the FC factors with the various quenchers from the average value a or b .

Individual "FC factors" may be defined as

$$a_{X,i} = \alpha/J^{1-\epsilon}|_{X,i} \quad (49)$$

$$b_{X,i} = \eta_T\alpha/(C_X^2\zeta_X^2J^{1-\epsilon'})|_{X,i} \quad (50)$$

Their statistical distribution can be characterized by mean and relative standard deviation: $\bar{a}_{X,i} = 0.40 \pm 55\%$ and $\bar{b}_{X,i} = 0.81 \pm 67\%$. It is now of interest to note that, although individually scattered, pairs of $a_{X,i}$ and $b_{X,i}$ are correlated. We find

$$a_{X,i} = 0.46b_{X,i} \pm 0.1 \quad (51)$$

with a correlation coefficient of $r = 0.89$. This correlation follows directly from the remarkable constancy of $\eta_T = k_t^{ex}/k_0^{ex}$ within each set of quenchers with the same halogen substituent, which contrasts with the wide variation of the individual rate constants k_t^{ex} and k_0^{ex} within the set.

Thus we see that IC and ISC in the adiabatically formed exciplex are processes closely coupled not only by means of their common relation to the CT character of the exciplex as measured through the function J but also by the similar trends in their FC factors. We take this as an indication that the FC factors of both

IC and ISC processes in the exciplex are governed by the same type of accepting modes.

Conclusions

In the present investigation the rate constant of fluorescence quenching (k_q) and the efficiencies of induced ISC (η_T), radical formation by electron transfer (η_R), and induced IC (shown to equal $1 - \eta_T - \eta_R$) have been systematically investigated as a function of the free enthalpy change ΔG°_{et} of electron transfer. It was found that, even with heavy atom substituents in the quencher, the induced IC pathway of quenching is the dominating one.

The observed correlation of k_q with ΔG°_{et} proves the importance of charge transfer in the quencher complex for inducing an IC process. Induced triplet formation is only found with quenchers of heavy-atom-enhanced spin-orbit coupling. However, this process, too, is coupled to the CT character of the quencher complex. Thus, with the present systems the heavy atom effect on the rate constant of induced ISC does not appear as an additive contribution to the quenching constant but is proportional to the rate of the induced IC process.

By the term "quencher complex" we understand an exciplex formed reversibly and activationless in the encounter of excited dye and quencher. This complex may acquire partial CT character, the degree of which is determined by ΔG°_{et} and by the interaction matrix element β . Our exciplex quenching model is shown to represent a generalization of the Rehm-Weller mechanism of fluorescence quenching by electron transfer, which is contained in our model as the limiting case for $\beta = 0$. Whereas in the Rehm-Weller model charge transfer is a discontinuous process occurring during passage of the system over the activation barrier, in the exciplex model charge delocalization occurs continuously and adiabatically as the reaction system moves along the reaction coordinate and the onset of CT-induced IC and ISC processes lies well before the activation barrier that separates the potential wells of radical pair and encounter complex.

It is of interest to note that in the case of triplet quenching with compounds similar to those of the present investigation⁵⁴ the $\log k_q/\Delta G^\circ_{et}$ diagram is clearly of Rehm-Weller type. This difference between singlet and triplet quenching behavior can be readily explained within the exciplex quenching model. In the triplet case the same degree of CT character should be acquired in the encounter complex for the same ΔG°_{et} value if the CT interaction is the same which can be assumed if S_1 and T_1 are of the same orbital origin. However, the difference between triplet and singlet case lies in the efficiency of irreversible decay channels available

to the encounter complex. The IC process which is the dominant one in the singlet case does not exist in the triplet case. As for the ISC process, in the triplet case this has to cope with a larger energy gap than the corresponding process connecting S_1 and T_1 in the singlet case. Therefore, it is much slower and even in the presence of heavy atoms it can hardly compete with the rapid dissociation of the encounter complex. Thus, in the triplet case efficient irreversible decay of the excited state requires transformation of the encounter pair to the radical pair (as is characteristic of the Rehm-Weller mechanism) from where it may dissociate to form free radicals or undergo spin-inverted electron back transfer, particularly if heavy atoms are present to enhance spin-orbit coupling.²⁷

As a final remark we point out that in this paper the term exciplex has been used to express the presence of CT character in the encounter complex. Likewise one might express the fact that, through the same kind of interaction, the contact radical ion pair acquires some locally excited character by designating it an "exciplex". It was in this sense that the term has been used in our previous work on triplet quenching. Both types of exciplex states are separated by the energy barrier of the electron-transfer reaction proper. Thus the ambiguity of the term "exciplex" arises from the double minimum potential characterizing the situation of $-\lambda \leq \Delta G^\circ_{et} \leq \lambda$. Probably a lot of misunderstandings in the literature result from not clearly distinguishing between the two exciplex minima. In order to avoid future confusion we suggest to use the terms encounter type exciplex (ENCT exciplex) and radical pair type exciplex (RPT exciplex) for the corresponding species.

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Registry No. 4-BrC₆H₄NO₂, 586-78-7; 3-BrC₆H₄CF₃, 401-78-5; 4-BrC₆H₄CN, 623-00-7; 4-BrC₆H₄COCH₃, 99-90-1; PhF, 462-06-6; PhCl, 108-90-7; PhBr, 108-86-1; PhI, 591-50-4; 4-BrC₆H₄F, 460-00-4; 4-BrC₆H₄Cl, 106-39-8; 4-ClC₆H₄CH₃, 106-43-4; 2-BrC₆H₄CH₃, 95-46-5; 3-BrC₆H₄CH₃, 591-17-3; 4-BrC₆H₄CH₃, 106-38-7; 2-IC₆H₄CH₃, 615-37-2; 3-IC₆H₄CH₃, 625-95-6; 4-IC₆H₄CH₃, 624-31-7; PhOMe, 100-66-3; 4-ClC₆H₄OMe, 623-12-1; 2-BrC₆H₄OMe, 578-57-4; 3-BrC₆H₄OMe, 2398-37-0; 4-BrC₆H₄OMe, 104-92-7; 2-IC₆H₄OMe, 529-28-2; 3-IC₆H₄OMe, 766-85-8; 4-IC₆H₄OMe, 696-62-8; 1,3-Me₂C₆H₄, 108-38-3; 1,4-Me₂C₆H₄, 106-42-3; 4-BrC₆H₄OH, 106-41-2; 4-BrC₆H₄NHAc, 103-88-8; 1,2-(MeO)₂C₆H₄, 91-16-7; 1,3-(MeO)₂C₆H₄, 151-10-0; 1,4-(MeO)₂C₆H₄, 150-78-7; PhNH₂, 62-53-3; 4-BrC₆H₄NH₂, 106-40-1; oxonine, 53669-98-0.

Photochlorination of Simple Alkanes in Cryogenic Solids

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Photochemical reactions have been induced by laser photolysis of amorphous binary solids composed of chlorine mixed with propane, *n*-butane, isobutane, *n*-pentane, cyclopentane, *n*-hexane, or cyclohexane at 10–150 K. In each case, the laser dissociates the chlorine into atoms which react with the alkane to form HCl and the corresponding chloroalkane. Quantum yields for these reactions are in most cases less than or approximately unity. The results are consistent with a radical recombination reaction mechanism. There is some evidence for the existence of short chain reactions in samples of *n*-hexane and chlorine which produce up to 5 product molecules per absorbed laser photon. At 10 K, chlorine atoms react with primary, secondary, or tertiary H atoms. However, at temperatures near the melting points of the solids, reaction to form the lowest energy radical is strongly preferred. The dependence of photochlorination yields on photolysis wavelength shows that chlorine atoms, not electronically excited chlorine molecules, are responsible for initiating the reaction.

Introduction

Photochemistry of disordered molecular solids represents a convenient method of inducing transient or irreversible changes

in the chemical composition of a wide variety of materials utilizing the high spatial, temporal, and wavelength selectivity of lasers. Potential applications include photolithography, optical data storage and processing, photosensitization and solar energy conversion, and laser-induced detonation of explosives or propellants.

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