J. Am. Chem. Soc. 1989, 111, 6983–6987

are calculated to have very small barriers associated with deprotonation and, therefore, are unlikely to be observable in the gas phase.

(6) No stable equilibrium structures were found for the tetracation analogues of $C_3H_3^+$, namely $H_3N_3^{4+}$, CH_3NO^{4+}, and $C_2H_3F^{4+}$.

Acknowledgment. We are grateful for the generous allocation of computer time on the Fujitsu FACOM VP-100 of the Australian National University Supercomputer Facility.

Influence of Heavy Atoms on the Deactivation of Singlet Oxygen ($^1\Delta_g$) in Solution

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Abstract: A very sensitive infrared emission spectrometer and very low excitation powers were used to determine $^1O_2$ lifetimes (τ_Δ) directly from phosphorescence decays in various chlorine-, bromine-, or iodine-substituted perfluorinated solvents. Laser-pulsed excitation was employed for measurement of τ_Δ in various halogen-substituted benzenes and perdeuterobenzenes. From the data the influence of heavy-atom-substituted solvents on radiationless $^1O_2$ deactivation has been studied. Radiationless deactivation occurs by collisional E → V energy transfer from $^1O_2$ to single oscillators X–Y of the solvent molecule. If the heavy atom is part of the energy accepting oscillator X–Y, a strong increase of intercombination probability is observed correlating with the square of the spin–orbit interaction energy of the heavy atom. If the heavy atom is not part of X–Y, only a very weak external heavy-atom effect on the collisional $^1O_2$ deactivation takes place. A model describing collisional $^1O_2$ deactivation by solvent molecules yields τ_Δ values for a large variety of solvents, which excellently agree with experimental data over the entire range of 4.5 orders of magnitude.

The lifetime (τ_Δ) of singlet oxygen ($^1\Delta_g$, $^1O_2$) in solution is extremely sensitive to the nature of the solvent and varies over a wide range from 4 to 100 000 μs.[1,2] Deactivation of $^1O_2$ in most solvents is largely radiationless by collisional electronic to vibrational (E → V) energy transfer from $^1O_2$ to a single oscillator of a solvent molecule.[2,3] The most probable energy-accepting oscillator of the solvent molecule is that terminal atom pair with the highest fundamental vibrational energy.[2]

Radiative deactivation of $^1O_2$ by phosphorescence emission at 1275 nm plays only a minor role since the emissive $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition is highly forbidden. A very low phosphorescence quantum yield of $Q_P = 4.7 \times 10^{-5}$ in benzene has recently been calculated by us from corrected emission spectra, using an infrared luminescence spectrometer with known spectral sensitivity.[4] Q_P depends like τ_Δ very strongly on solvent. In the weakly deactivating solvent freon-113 ($C_2F_3Cl_3$), two independent methods gave $Q_P = 0.15$, a maximum value.[4,5]

Radiationless deactivation of $^1O_2$ by $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ intersystem crossing (isc) is expected to be of no importance in solution. The Franck–Condon (FC) factor of the $^1\Delta_g$ ($v = 0$) → $^3\Sigma_g^-$ ($v = 5$) transition can be extrapolated from literature data to be on the order of 10^{-13}.[2,6] However, this transition is still exergonic by 337 cm^{-1}, and thus this estimate appears even to be an upper limit value for the FC factor of isoenergetic isc.[7] $^1O_2$ lifetimes of about 10 s have been determined in emission experiments at reduced pressure in the gas phase.[8] Since these values are 100 times larger than the maximum value of τ_Δ in solution, it is clear that even in weakly deactivating solvents isc does not contribute to the deactivation of $^1O_2$.

As deactivation of $^1O_2$ demands a change of multiplicity, an acceleration due to spin–orbit coupling can be expected under the influence of heavy atoms. However, preliminary results of Hurst and Schuster[3] indicate only a small and $^1O_2$ lifetime-dependent heavy-atom effect on τ_Δ. To get more insight into this puzzling problem, we determined lifetimes of $^1O_2$ for a variety of highly purified halogenated solvents of very different deactivating power using low excitation energies. The evaluation and discussion of the results in context with data obtained already earlier in this laboratory actually reveals a subtle but strong effect of heavy atoms on the radiationless $^1O_2$ deactivation process.

Experimental Section

The solvents used were benzene (C_6H_6), spectroscopic grade from Merck, and fluorobenzene (C_6H_5F, 99%), chlorobenzene (C_6H_5Cl, 99+%), bromobenzene (C_6H_5Br, 99+%), iodobenzene (C_6H_5I, 99%), benzene-d_6 (C_6D_6, 99.5%), bromobenzene-d_5 (C_6D_5Br, 99+%), hexafluorobenzene (C_6F_6, 99%), chloropentafluorobenzene (C_6F_5Cl, 95%), bromopentafluorobenzene (C_6F_5Br, 99%), iodopentafluorobenzene (C_6F_5I, 99%), fluorotrichloromethane ($CFCl_3$, 99+%), dibromotetrafluoroethane ($C_2F_4Br_2$), and perfluorohexyliodide ($C_6F_{13}I$, 99%) from Aldrich. All solvents were purified by column chromatography with neutral Al_2O_3 (Woelm). With C_6F_5Cl, which was originally only of 95% purity, this procedure was performed three times, 5,10,15,20-Tetraphenylporphine (TPP) (Aldrich gold label), methylene blue (MB) (Fluka, puriss.), and D_2O (Merck, Sharp, & Dohme, 99.96%) were used without further purification. H_2O was distilled twice. Rubicene (RUB) was prepared by the procedure described by Clar.[9] All solutions were air saturated, and the experimental temperature was about 22 °C.

The infrared luminescence spectrometer, which could be modified either to record spectra or to determine $^1O_2$ lifetimes ($\tau_\Delta \geq 7$ ms), has been described.[2] In lifetime measurements the excitation pulses were produced from a stationary excitation source by means of a chopper. Pulse energy amounted to <20 μJ, and pulse power, to <2 mW. The excitation wavelengths for the sensitizers TPP, RUB, and MB were chosen in each experiment to be outside the absorption range of the purified solvents. In order to prevent quenching of $^1O_2$ the sensitizers were used in very low concentrations in the weakly deactivating solvents, i.e. 0.6×10^{-6}–6×10^{-6} M depending on sensitizer and solvent. For

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(1) Rodgers, M. A. J. *J. Am. Chem. Soc.* **1983**, *105*, 6201–6205.

(2) Schmidt, R.; Brauer, H.-D. *J. Am. Chem. Soc.* **1987**, *109*, 6976–6981.

(3) Hurst, J. R.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 5756–5760.

(4) Schmidt, R. *Chem. Phys. Lett.* **1988**, *151*, 369–374.

(5) Schmidt, R.; Seikel, K.; Brauer, H.-D. *J. Phys. Chem.* **1989**, *93*, 4507–4511.

(6) Halmann, M.; Laulicht, I. *J. Chem. Phys.* **1965**, *43*, 438–448.

(7) Herzberg, G. *Spectra of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1950; p 560.

(8) Clark, I. D.; Wayne, R. P. *Proc. R. Soc. London, A* **1969**, *314*, 111.

(9) Clar, E.; Willicks, W. *J. Chem. Soc.* **1958**, 942–946.

0002-7863/89/1511-6983$01.50/0

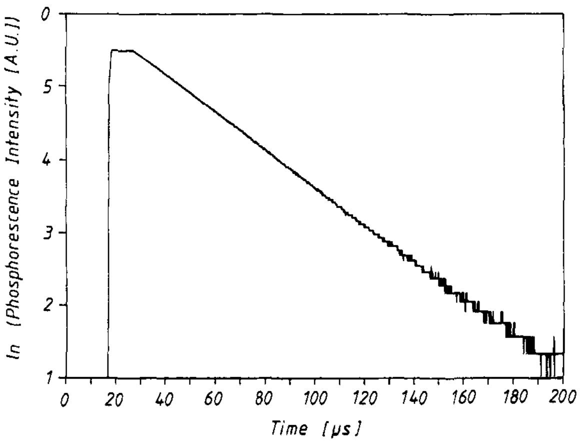

Figure 1. Semilogarithmic plot of $^1O_2$ phosphorescence emission decay. [TPP] = 2.8×10^{-5} M in C_6H_5I: excitation wavelength, 514 nm; pulse energy, 12.5 mJ; $\tau_\Delta = 39.3$ µs.

lifetime measurements in the range $\tau_\Delta \leq 7$ ms a pulsed dye laser FL 3002 from Lambda Physics (pulse width < 20 ns) was employed, which was pumped by an EMG 200 E excimer laser from Lambda Physics. In these experiments MB (D_2O) and TPP (rest of the solvents) were employed as sensitizers. The optical density of these sample solutions amounted to about 0.5 (TPP) or 0.1 (MB) at the laser wavelength 514 nm, corresponding to concentrations of [TPP] $\approx 3 \times 10^{-5}$ M and [MB] $\approx 3 \times 10^{-5}$ M. $^1O_2$ quenching by sensitizers did not take place in these experiments. The excitation pulse energy was varied for each solution between 0.18 and 12.5 mJ. The area (1×3.5 cm^2) of the entire rectangular sample cell was illuminated by the defocused laser beam. Consequently, in these experiments the number of absorbing molecules was 200 to 3 times (TPP) and 10 times (MB) larger than the number of absorbed photons. Emission of $^1O_2$ was detected in right-angle arrangement to the exciting beam by a liquid N_2 cooled EO817P Ge diode (rise time 300 ns) from North Coast. A 5-mm-thick Si disk and a 1270-nm interference filter from Schott were used to suppress stray exciting radiation and sensitizer fluorescence. The preamplified detector signal was fed into a Gould 4072 transient recorder (8-bit resolution). The $^1O_2$ decay curves were transferred to an IBM AT3 microcomputer and stored on disk.

Results

Figure 1 shows an example of the decay of $^1O_2$ emission following laser pulse excitation of TPP in C_6H_5I. Strictly monoexponential behavior was observed as in all measurements.

Table I lists the $^1O_2$ lifetimes determined with our two different experimental setups. τ_Δ values determined by pulsed-laser excitation were found to be independent of the excitation pulse energy (0.18, 0.65, 2.3, and 12.5 mJ) with the exception of C_6D_5Br and C_6F_5I. In C_6D_5Br τ_Δ was found to be independent of pulse energy from 0.18 to 2.3 mJ. Only with 12.5-mJ excitation, a reduced lifetime of $\tau_\Delta = 1210$ µs was obtained. Consequently, this value was omitted in averaging. In C_6F_5I throughout the employed range of pulse energy lifetimes were found ranging from 4300 (0.18) to 2500 µs (12.5 mJ). The reason for power-dependent $^1O_2$ lifetimes is probably the photochemical production of $^1O_2$ quenchers during the laser pulse, as already Hurst and Schuster pointed out.[3] In C_6F_5I therefore the τ_Δ determination was carried out also with the experimental setup using low-energy excitation (<20 µJ), yielding a power-independent value of $\tau_\Delta = 15\,100$ µs. All τ_Δ values determined by this method did not depend on excitation power in the investigated range (<2 mW). Consequently, the lifetime data of the left column of Table I, which are average values of 5–9 individual decays, are not subject to the uncertainty of extrapolation. In contrast, the literature τ_Δ values listed in the right column are at least partially extrapolated and may therefore be of less accuracy.

Only the lifetimes determined in C_6H_6, C_6H_5I, and C_6D_6 agree satisfactorily. Especially, the literature value given for C_6F_6 is much too low. Probably this is a result of different solvent purity and elevated excitation powers used. At first sight the influence of heavy-atom substitution on τ_Δ is rather puzzling and weak. In the benzene and perdeuterobenzene series the replacement of H (or D) by a halogen atom results in an increase of τ_Δ. However, in the perfluorobenzene and the perfluoroalkane series a distinct decrease of $^1O_2$ lifetime with heavy-atom substitution is noted that is stronger for the weakly deactivating perfluoroalkanes. Nevertheless, the reduction of τ_Δ by a factor of 2.6 upon substitution of one fluorine by one iodine atom in C_6F_{14} is a surprisingly small effect.

Table I. Lifetimes τ_Δ of $^1O_2$ in Different Solvents

solvent	τ_Δ, µs	
C_6H_6	30.9 ± 0.6^a	32^f
C_6H_5F	42.7 ± 2^a	49^f
C_6H_5Cl	43.3 ± 1^a	51^f
C_6H_5Br	42.4 ± 1^a	50^f
C_6H_5I	39.3 ± 1^a	35^f
C_6D_6	790 ± 20^a	700^f
C_6D_5Br	1360 ± 20^b	812^f
C_6F_6	$25\,000 \pm 1000^d$	3900^f
C_6F_5Cl	$24\,500 \pm 2000^c$	
C_6F_5Br	$21\,900 \pm 1000^c$	
C_6F_5I	$15\,100 \pm 1000^c$	
C_6F_{14}	$96\,000 \pm 3000^d$	
$CFCl_3$	$110\,000 \pm 10\,000^c$	
$C_2F_3Cl_3$	$99\,000 \pm 3000^d$	
CCl_4	$87\,000 \pm 3000^d$	
$C_2F_4Br_2$	$49\,700 \pm 2000^c$	
$C_6F_{13}I$	$36\,500 \pm 2000^c$	
D_2O	67.8 ± 2^e	
H_2O	4.2 ± 0.5^e	

[a] Laser-pulsed excitation, 0.18 mJ ≤ pulse energy ≤ 12.5 mJ. [b] Laser-pulsed excitation, 0.18 mJ ≤ pulse energy ≤ 2.3 mJ. [c] Excitation with pulse formed from continuous irradiation by chopping, pulse energy < 20 µJ. [d] Method c, values from ref 2. [e] Laser-pulsed excitation, pulse energy = 12.5 mJ. [f] Laser-pulsed excitation; most τ_Δ values are extrapolated to the limit of zero laser power from laser pulse power dependent data; data from ref 3.

Discussion

Rodgers[1] and Hurst and Schuster[3] were the first who realized that second-order rate constants k_D of $^1O_2$ deactivation by strongly deactivating solvents can be composed additively from incremental rate constants. Hurst and Schuster proposed eq 1 in which k_{XY}

$$k_D = \sum_{XY} N_{XY} k_{XY} \qquad (1)$$

represents the rate constant of $^1O_2$ deactivation by a terminal bond X–Y (X–Y = C–H, C–D, O–H, and O–D) and N_{XY} is the number of times that particular X–Y occurs per solvent molecule.

Recently, we discovered a strong linear correlation between ln k_{XY} and E_{XY}, the energy of highest frequency fundamental vibration of X–Y.[2] The correlation could be interpreted quantitatively by a model presented originally by Hurst and Schuster,[3] which describes the deactivation of $^1O_2$ by the solvent molecule as a spin-forbidden collisional energy transfer from $^1O_2$ to a single oscillator X–Y of the solvent molecule. This process occurs by coupling of the highest fundamental vibrational mode of X–Y with an electronic and vibronic transition of $^1O_2$. Several single reaction channels, which differ only by the vibrational quantum number m of the product state of O_2, are in competition according to eq 2. The off-resonance energy E_m depends only on m and E_{XY} (eq 3). E_Δ and $E_{\Sigma,m}$ are the energies of O_2 in the educt state and

$$O_2\,(^1\Delta_g, v = 0) + \text{X–Y}\,(v = 0) \xrightarrow{k_{XY}^m} O_2\,(^3\Sigma_g^-, v = m) + \text{X–Y}\,(v = 1) + E_m \qquad (2)$$

$$E_m = E_\Delta - E_{\Sigma,m} - E_{XY} \qquad (3)$$

the product state of eq 2. The single-channel rate constant k_{XY}^m is given by eq 4 where C is a normalization constant, P is the

$$k_{XY}^m = CPFF_mR_m \qquad (4)$$

intercombination probability, F and F_m are the FC factors for the 0 → 1 transition of X–Y and the $^1\Delta_g\,(v = 0) \rightarrow {}^3\Sigma_g^-\,(v = m)$ transition of O_2, and R_m is the off-resonance factor describing the probability of that coupled transition in dependence of E_m.

Equation 4 deviates from a corresponding equation given by Hurst and Schuster[3] by the inclusion of P and by the consideration of only the highest fundamental vibrational mode of X–Y. That simplification followed from the strong correlation between $\ln k_{XY}$ and E_{XY} (vide supra).[2] CP was regarded to be constant for non-heavy-atom-containing oscillators, and in a first approximation F was assumed to be independent of X–Y. F_m values have been taken from the literature,[6] and for the energy dependence of R_m the following exponential relations were proposed by us

$$E_m > 0 \qquad R_m = e^{-\alpha E_m} \tag{5}$$

$$E_m \leq 0 \qquad R_m = e^{E_m/RT} \tag{6}$$

with α a proportionality constant, R the gas constant, and T the temperature. Since for a given reaction channel m E_m is only a function of E_{XY}, the single-channel rate constant $k_{XY}{}^m$ depends according to eq 3–6 only on E_{XY}. As all possible single reaction channels are in competition, the overall rate constant of energy transfer is then given by:

$$k_{XY} = CPF\sum_m F_m R_m \tag{7}$$

With eq 7 it was actually possible to describe the linear correlation between $\ln k_{XY}$ and E_{XY} by a two-parameter fit with $CPF = 6.4 \times 10^9$ M^{-1} s^{-1} and $\alpha = 5 \times 10^{-3}$ cm.[2]

Thus it is useful to calculate from the collected data rate constants k_{XY} in order to investigate the heavy-atom effect on the radiationless deactivation of $^1O_2$. In weakly deactivating solvents like $C_2F_3Cl_3$ $^1O_2$ phosphorescence contributes significantly to the deactivation of $^1O_2$.[4] For these solvents therefore eq 8 has to be used for the calculation of k_D with [S], the molarity of the solvent, and k_P, the $^1O_2$ phosphorescence rate constant.

$$k_D = (1/\tau_\Delta - k_P)/[S] \tag{8}$$

As was demonstrated in a previous report[5] a solvent-independent mean value of $k_P = 1.3 \pm 0.6$ s^{-1} was found in C_6H_6, CH_3CN, $CHCl_3$, CS_2, CCl_4, and $C_2F_3Cl_3$. This average applies also for the majority of weakly deactivating solvents of Table I.[10] Since k_P is at least seven times smaller than $1/\tau_\Delta$ for each of the solvents of Table I, only a negligible error is introduced if k_D is calculated by eq 8 using the average value of $k_P = 1.3$ s^{-1}. The present value of k_P differs significantly from the earlier employed too large $k_P = 7.1$ s^{-1}.[2] Therefore, slight deviations from earlier published values of k_{XY} occur for X–Y = C–Cl, C–F and C=S. From k_D values of solvents X_nY_m containing only one kind of oscillator X–Y rate constants k_{XY} are easily obtained by division through N_{XY}. For solvents containing two different kinds of oscillators the larger k_{XY} value is calculated by subtracting from k_D the smaller k_{XY} value as many times as the corresponding oscillator occurs in the solvent molecule. Afterward the difference is divided by N_{XY} corresponding to the faster deactivating oscillator. Table II lists the results.

In Figure 2 the values of $\ln k_{XY}$ are plotted against the highest fundamental vibrational energies E_{XY} of the corresponding oscillators X–Y. The curve drawn in Figure 2, describing the dependence of $\ln k_{XY}$ on E_{XY} for non-heavy-atom-containing oscillators, results as a two-parameter fit from eq 7 and was already given in ref 2. Despite its approximative character, the above-discussed collisional energy-transfer model reproduces quite well the experimental data for oscillators consisting only of light atoms. The deactivating power of oscillators X–Y decreases exponentially with E_{XY} until a minimum value is reached for C–F$_{al}$. With further decreasing E_{XY}, however, an increase in k_{XY} is observed in the series C–F$_{al}$, C–Cl$_{al}$, C–Br$_{al}$, and C–I$_{al}$, which is not reproduced by the fitted curve.

Table II. Second-Order Rate Constants k_{XY} of Energy Transfer from $^1O_2$ to Oscillators X–Y

X–Y[a]	X_nY_m	τ_Δ, μs	k_D, M^{-1} s^{-1}	k_{XY}, M^{-1} s^{-1}	$\ln k_{XY}$	E_{XY},[b] cm^{-1}
O–H	OH_2	4.2[c]	4290	2145	7.67	3400
C–H$_{ar}$	C_6H_6	30.9[c]	2880	480	6.17	3050
C–H$_{al}$	C_6H_{12}	23[d]	4680	390	5.97	2960
O–D	OD_2	68[c]	265	132	4.89	2500
C–D$_{ar}$	C_6D_6	790[c]	113	18.8	2.93	2270
C–D$_{al}$	$CDCl_3$	9400[e]	8.41	7.67	2.04	2250
C=S	CS_2	34 000[e]	1.69	0.85	−0.17	1520
C–F$_{ar}$	C_6F_6	25 000[e]	4.47	0.75	−0.29	1520
C–F$_{al}$	C_6F_{14}	96 000[e]	1.85	0.13	−2.03	1250
C–Cl$_{al}$	$C_2F_3Cl_3$	99 000[e]	1.05	0.22	−1.53	800
C–Cl$_{al}$	CCl_4	87 000[e]	0.98	0.25	−1.40	800
C–Cl$_{al}$				0.23[f]	−1.46[f]	800
C–Br$_{al}$	$C_2F_4Br_2$	49 700[c]	2.27	0.87	−0.14	660
C–I$_{al}$	$C_6F_{13}I$	36 500[c]	5.64	3.93	1.37	560

[a] ar = aromatic; al = aliphatic. [b] In liquid phase. [c] This work. [d] From ref 1. [e] From ref 2. [f] Average value.

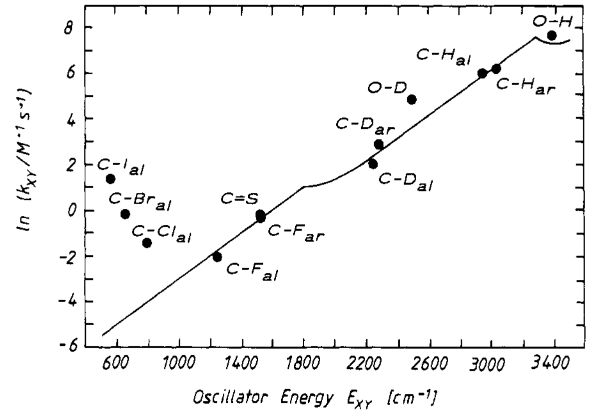

Figure 2. Semilogarithmic plot of the rate constant k_{XY} of E → V energy transfer from $^1O_2$ to oscillator X–Y against the energy E_{XY} of the highest fundamental vibration of X–Y. Data from Table II. Curve best fit according to eq 7 with $CPF = 6.4 \times 10^9$ M^{-1} s^{-1} and $\alpha = 5 \times 10^{-3}$ cm.

The calculated curve of Figure 2 allows the evaluation of the spin–orbit coupling dependent effects of oscillators C–HA on k_{XY}. Only the frequency dependence is contained in the fit. Each experimental value of k_{XY} consists according to eq 7 of a product of constants CF, of a frequency-dependent factor $\sum_m F_m R_m$, and a spin-orbit coupling dependent factor P. Thus for heavy-atom-containing oscillators the differences between $\ln (k_{XY})_e$, the experimental, and $\ln (k_{XY})_f$, the fitted values of $\ln k_{XY}$, at the corresponding E_{XY} are logarithmic measures for the increase of the intercombination probability in $^1O_2$ deactivation by C–HA due to spin–orbit coupling. Let P and P_{HA} be the intercombination probabilities for non-heavy- and heavy-atom-containing oscillators, respectively; then eq 9 may be used to calculate relative intercombination probabilities $P_R = P_{HA}/P$.

$$\ln (P_R) = \ln (k_{XY})_e - \ln (k_{XY})_f \tag{9}$$

From the values of $\ln (k_{XY})_f$ given in Table III and the corresponding experimental $\ln (k_{XY})_e$ data of Table II, values of P_R for different halogen-substituted oscillators C–HA are calculated, which are compared in Table III with relative rate constants of some mono- or bimolecular intercombination processes of heavy-atom-substituted compounds.

After having removed from k_{XY} the masking frequency effect, a very strong heavy-atom effect on the intercombination probability of collisional $^1O_2$ deactivation is revealed in Table III. P_R increases by 3 orders of magnitude if C–F as deactivating oscillator is replaced by C–I. The magnitude of the heavy-atom effect is about the same as the one found for isc and phosphorescence of naphthalene and for spin-forbidden bimolecular energy transfer from perylene to naphthalene. Consequently, the heavy-atom substituent interacts directly and to a similar extent with the electronic excited system in each of the regarded systems. Thus

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(10) Schmidt, R., to be submitted for publication.
(11) McClure, D. S. *J. Chem. Phys.* **1949**, *17*, 905–913.
(12) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970; p 264.
(13) Ermolaev, V. L.; Svitashev, K. K. *Opt. Spectrosc.* (*Engl. Transl.*) **1959**, *7*, 399.
(14) Zander, M.; Dreeskamp, H.; Koch, E. *Z. Naturforsch.* **1974**, *29A*, 1518–1519.

Table III. Influence of Spin–Orbit Coupling Due to Heavy-Atom Substituent on the Relative Intercombination Probability P_R of Collisional $^1O_2$ Deactivation and on Relative Rate Constants k_R of Mono- and Bimolecular Intercombination Processes

substituent	F	Cl	Br	I
$Z_{eff}{}^{a}$	2.26	2.93	3.73	4.38
ζ,^{b} cm^{-1}	272	587	2460	5060
ln $(k_{XY})_f{}^{c}$	−1.73	−3.98	−4.68	−5.18
$P_R{}^{d}$	0.74	12	94	700
$k_R{}^{isc\,e}$	1.3	7	105	900
$k_R{}^{P\,f}$	1.6	8	100	1360
$k_R{}^{ET\,g}$		9	135	1150

[a] Effective nuclear charge of halogen atom. [b] Spin–orbit interaction energy of halogen atoms, data from ref 11. [c] Calculated from eq 7 with $CPF = 6.4 \times 10^9$ M^{-1} s^{-1} and $\alpha = 5 \times 10^{-3}$ cm. [d] Calculated from eq 9. [e] Relative rate constants of $T_1 \rightarrow S_0$ isc of 1-substituted naphthalenes referred to the value for 1-methylnaphthalene, data from ref 12, original data from ref 13. [f] As for *d* but relative rate constants of phosphorescence. [g] Relative rate constants of S → T energy transfer from perylene to 1-substituted naphthalenes referred to the value for 1-chloronaphthalene and multiplied with 9, data from ref 14.

one observes an internal heavy-atom effect on the $^1O_2$ deactivation if the heavy atom is part of the deactivating oscillator X–Y. It follows that a partial penetration of the electron clouds of terminal atom Y and $^1O_2$ must occur in the deactivating collision. As $^1O_2$ deactivation requires no particular activation,[2,3,15,16] the partial overlap occurs on a repulsive potential surface already under the influence of the available thermal energy.

If the heavy atom is only a substituent of the solvent molecule but not part of the deactivating oscillator, only a very small heavy-atom effect takes place. This conclusion can be drawn from a comparison of the τ_D values of the halogenated benzenes of Table I. As k_{XY} values are much smaller for oscillators C–HA than for oscillators C–H$_{ar}$ (compare Table II), deactivation of $^1O_2$ by these solvents occurs exclusively by C–H$_{ar}$. The increase of τ_Δ in going from C_6H_6 to C_6H_5HA reflects directly the corresponding decrease of [C–H$_{ar}$]. Only the slight but significant smaller τ_Δ in C_6H_5I points to a very small external heavy-atom effect.

As result of a first-order perturbation calculation on the internal heavy-atom effect on the radiative intercombination probability in an atom or molecule, McClure[11] obtained eq 10 where the

$$P_{3,n} = P_{1,n}\left(\frac{\mathbf{H}_{13}}{\Delta E}\right)^2\left(\frac{\nu_3}{\nu_1}\right)^3 \tag{10}$$

contribution from only one perturbing state was considered. $P_{1,n}$ is the transition probability between perturbing singlet and the normal state, ν_1 and ν_3, are the energies of singlet and triplet state and ΔE is the energy difference between triplet and singlet. $\mathbf{H}_{13}$ is the matrix element of the spin–orbit operator between the corresponding states. According to McClure, one can approximate $\mathbf{H}_{13}$ by the spin–orbit interaction energy ζ of the respective atom, which is proportional to $Z_{eff}{}^4$. For a molecule McClure expected that the ζ value for the heaviest atom in the excited system of the molecule would be a reasonable approximation to the molecular $\mathbf{H}_{13}$ value. If one investigates the internal heavy-atom effect on an intercombination transition for a series of compounds, which vary only by the atomic number of substituent without changing the energies of the involved excited states, one can consider all variables of eq 10 with exception of $\mathbf{H}_{13}$ as constant. Consequently, the values of P_R and k_R of Table III should correlate with ζ^2 or $Z_{eff}{}^8$. In Figure 3 logarithmic plots of P_R, $k_R{}^{isc}$, $k_R{}^P$, and $k_R{}^{ET}$ against ζ and against Z_{eff} are given. The experimental data can be fitted quite well by straight lines either with slope 2.2, intercept −5.2, and correlation coefficient 0.99 (ζ) or with slope 10.2, intercept −3.7, and correlation coefficient 0.99 (Z_{eff}). Consequently, the empirical relations P_R, $k_R \propto \zeta^{2.2}$ and P_R, $k_R \propto Z_{eff}{}^{10}$ result. Although McClure's theory of the internal heavy-atom effect is

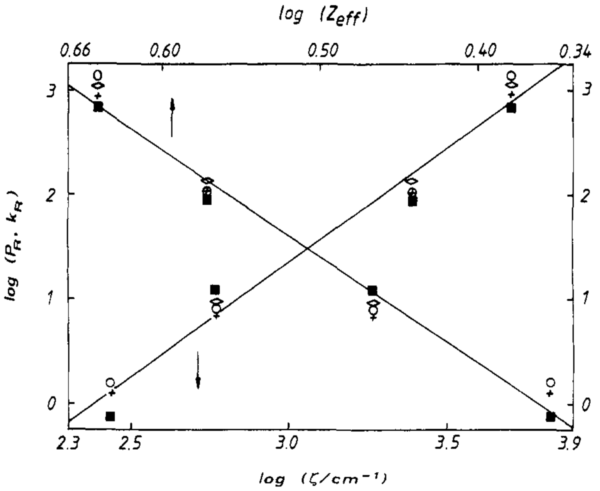

Figure 3. Logarithmic plots of relative intercombination probability P_R in collisional $^1O_2$ deactivation and of relative rate constants k_R of spin-forbidden processes vs spin–orbit interaction energy ζ and vs effective nuclear charge Z_{eff} of heavy-atom substituent. Data from Table III: (■) P_R, (+) $k_R{}^{isc}$, (O) $k_R{}^P$, (◇) $k_R{}^{TS}$. Straight lines according to linear least-square fits: slope 2.2, intercept −5.2, correlation coefficient 0.99 (ζ); slope 10.2, intercept −3.7, and correlation coefficient 0.99 (Z_{eff}).

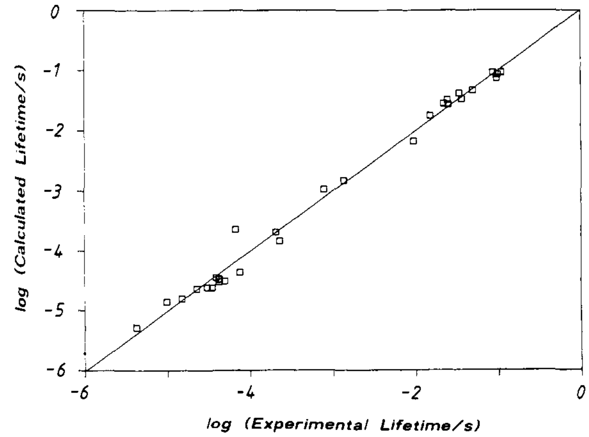

Figure 4. Logarithmic plot of calculated vs experimental $^1O_2$ lifetimes for the 19 solvents of Table I and the 10 solvents given below. Straight line according to linear least-squares fit: slope 1.00, intercept 0.00, correlation coefficient 0.99. Equations 1 and 8 and $k_{OH} \approx 1737$, $k_{CH}{}^{ar} = 614$, $k_{CH}{}^{al} = 391$, $k_{OD} = 39.3$, $k_{CD}{}^{ar} = 13.9$, $k_{CD}{}^{al} = 11.4$, $k_{CN} \approx 11.4$, $k_{CO} = 2.16$, $k_{CS} = 0.68$, $k_{CF}{}^{ar} = 0.68$, $k_{CF}{}^{al} = 0.18$, $k_{CCl} = 0.23$, $k_{CBr} = 0.87$, $k_{CI} = 3.93$ M^{-1} s^{-1} were used for calculation. Additional solvents (own experimental τ_Δ (μs)): CH_3CN (75), CH_3OH (9.8), C_2H_5OH (15.2), acetone (50), CH_2Cl_2 (96), $CHCl_3$ (207), $CDCl_3$ (9400), CS_2 (34 000), n-C_5H_{12} (35.4), cyclohexane (23).

rather approximative, it describes the experimental results satisfactorily.

The question could arise why C–Cl exerts a distinct internal heavy-atom effect on $^1O_2$ deactivation but not C=S, as one can infer from Figure 2. However, the similarity in atomic weights of Cl and S leads to wrong speculations. The important parameter is Z_{eff} amounting 2.62 for S and 2.93 for Cl. On the basis of the above found experimental correlation between P_R and Z_{eff}, one calculates for C=S $P_R = 3.8$ compared to $P_R = 12.4$ for C–Cl. Thus, it follows that the deviation of ln k_{XY} from the fitted curve in Figure 3 caused by spin–orbit interaction should not be similar but much smaller for C=S than for C–Cl. That experimentally even a smaller deviation results is certainly a consequence of the simplifications of the collisional energy-transfer model. For example, the supposition of a constant *FC* factor for the fundamental transition of oscillators X–Y could be a good approximation for oscillators with single bonds but fail for oscillators with double bonds like C=S.

Although it is a rather simple concept to consider a $^1O_2$ deactivating solvent regardless of its specific molecular structure

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(15) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423–3430.

(16) Gorman, A. A.; Hamblett, I.; Lambert, C.; Spencer, B.; Standen, M. C. *J. Am. Chem. Soc.* **1988**, *110*, 8053–8059.

as a purely additive composite of single terminal oscillators, it is striking to see its good description of experimental τ_Δ values. Taking the empirical values k_{XY} of the heavy-atom-containing oscillators C–Cl, C–Br, and C–I for aromatic and aliphatic solvent molecules and for the rest of oscillators k_{XY} values resulting from the corresponding E_{XY} and from the fitted curve of Figure 2, it is possible to calculate τ_Δ values using eq 1 and 8. The linear least-squares fit of a logarithmic plot of calculated vs experimental $^1O_2$ lifetimes shown in Figure 4 results in slope 1.00, intercept 0.00, and a correlation coefficient of 0.99. The only value deviating considerably (by a factor of 3) is τ_Δ measured in D_2O. Thus the excellent quantitative description of the experimental $^1O_2$ lifetimes by the collisional E → V energy-transfer model is demonstrated.

The fitted curve of Figure 2 and the above-mentioned empirical values of k_{XY} can of course be used to calculate approximative $^1O_2$ lifetimes for solvents not included in Figure 4. For that purpose it is only necessary to take from the fit ln k_{XY} values using literature data on E_{XY} for the desired oscillators X–Y (e.g., $E_{C=O}$ = 1750 cm^{-1}). Since τ_Δ values have been measured in highly purified solvents using low irradiation powers, the estimated lifetimes are only realistic in weakly deactivating solvents under corresponding conditions.

Conclusions

The radiationless deactivation of $^1O_2$ by solvent molecules occurs under partial penetration of the electron clouds as a collisional E → V energy transfer from $^1O_2$ to single oscillators X–Y (=terminal atom pairs) of the solvent molecule. Its rate constant k_{XY} correlates exponentially with the energy of the maximum vibrational quantum, which X–Y can accept. Consequently, a mass dependence results and solvents with light-atom oscillators like C–H deactivate $^1O_2$ much stronger than solvents with oscillators C–F. Since $^1O_2$ deactivation includes an intercombinational transition, a strong internal heavy-atom effect takes place if a heavy atom is part of the deactivating oscillator. However, as heavy-atom substitution in X–Y results in a decrease of vibrational frequency of X–Y, the actual spin–orbit interaction dependent effect on k_{XY} is weakened and operates only in the range of small rate constants k_{XY}. That is the reason why a clear heavy-atom effect on τ_Δ is observed only in weakly deactivating solvents but not in hydrogen-containing solvents. The magnitude of the internal heavy-atom effect is described quantitatively by the theoretical model on spin–orbit interaction developed by McClure. The external heavy effect exerted from heavy-atom-substituted solvents on radiationless deactivation of $^1O_2$ is very weak.

Acknowledgment. I thank Prof. Dr. H.-D. Brauer for numerous fruitful discussions and generous support. I gratefully acknowledge financial assistance by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie.

Sonoluminescence from Nonaqueous Liquids: Emission from Small Molecules

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Received April 6, 1989

Abstract: Sonoluminescence spectra from nonaqueous liquids under a variety of gases are presented. Ultrasonic irradiation of alkanes under Ar leads to emission from C_2, C_2H, and CH. When nitrogen is present, emission is seen from CN. When oxygen is present, emission from CO_2, CH, and OH is observed. Ultrasonic irradiation of tetrachloroethylene or CCl_4 leads to emission from Cl_2. The intensity of sonoluminescence decreases as the liquid vapor pressure increases. The properties of the dissolved gas also influence the sonoluminescence observed. Sonoluminescence is caused by chemical reactions of high energy species formed during cavitational collapse. It is a form of chemiluminescence. The principal source of sonoluminescence is *not* blackbody radiation or electrical discharge.

Ultrasonic irradiation of liquids can produce light. This phenomenon, known as sonoluminescence (SL), was first observed from water in 1934 by Frenzel and Schultes[1] and from organic liquids in 1937 by Chambers.[2] Although sonoluminescence from aqueous solutions has been studied in some detail,[3,4] little work on sonoluminescence from nonaqueous liquids has been reported. We present here sonoluminescence spectra from several nonaqueous liquids in the presence of various gases. We conclude that sonoluminescence from organic liquids is caused by emission from small free radicals and molecules, such as C_2, CN, CO_2, and Cl_2. A preliminary report[5] of this work has been published.

There has been some dispute over the mechanism of sonoluminescence.[3] All of the theories of SL invoke acoustic cavitation[6] (the formation, growth, and implosive collapse of bubbles in solution), as the source of the phenomenon. Noltink and Neppiras proposed SL was from blackbody emission[7] of the heated cavity. Electrical discharge[8] inside the bubble has been proposed several times as the source of SL, most recently by Margulis.[8d] Vaughan and Leeman have recently proposed a shock-wave model,[9] where SL is caused by a shock-wave from the collapsing bubble wall. In the hot-spot chemiluminescence model,[10,11] which is the best

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(1) Frenzel, H.; Schultes, H. *Z. Phys. Chem.* **1934**, *27b*, 421.

(2) Chambers, L. A. *J. Chem. Phys.* **1937**, *5*, 290.

(3) Verrall, R. E.; Sehgal, C. M. In *Ultrasound: its Chemical, Physical, and Biological Effects*; Suslick, K. S., Ed.; VCH Publishers: New York, 1988.

(4) Walton, A. J.; Reynolds, G. T. *Adv. Phys.* **1984**, *33*, 595.

(5) Suslick, K. S.; Flint, E. B. *Nature (London)* **1987**, *330*, 553.

(6) (a) Atchley, A. A.; Crum, L. A. In *Ultrasound: its Chemical, Physical, and Biological Effects*; Suslick, K. S., Ed.; VCH Publishers: New York, 1988. (b) Neppiras, E. A. *Phys. Rep.* **1980**, *61*, 159.

(7) Noltink, B. E.; Neppiras, E. A. *Proc. Phys. Soc.* **1950**, *63B*, 674.

(8) (a) Harvey, E. N. *J. Am. Chem. Soc.* **1939**, *61*, 2392. (b) Frenkel, Ya. I. *Russ. J. Phys. Chem.* **1940**, *14*, 305. (c) Degrois, M.; Baldo, P. *Ultrasonics* **1974**, *14*, 25. (d) Margulis, M. A. *Ultrasonics* **1985**, *23*, 157.

(9) Vaughan, P. W.; Leeman, S. *Ultrason. Int. Conf. (Proc.)* **1987**, 297.

(10) Fitzgerald, M. E.; Griffing, V.; Sullivan, J. *J. Chem. Phys.* **1956**, *25*, 926.

(11) (a) Suslick, K. S.; Hammerton, D. A.; Cline, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 5641. (b) Suslick, K. S.; Hammerton, D. A.; Cline, R. E. *IEEE Trans. Ultrason., Ferroelectr., Freq Control* **1986**, *UFFC-33*, 143. (c) Suslick, K. S.; Cline, R. E.; Hammerton, D. A. *IEEE Ultrason. Symp.* **1985**, 1116.

0002-7863/89/1511-6987$01.50/0