1 H, CH=N); IR (film) 1660, 1635 cm^{-1}; MS, *m/e* (relative intensity) 354 (M$^+$, 0.2), 339 (2), 237 (31), 105 (23), 91 (100), 77 (18). The product was unstable and gave unreliable microanalytical data.

Reaction of 1a with Water. A solution of **1a** (1 g, 4.0 mmol) in ether saturated with water (100 mL) was set aside for 1 week. After this time a white crystalline product had deposited. This was removed by filtration, and the product (0.85 g, 94%) was identified as benzylammonium benzoate by comparison with an authentic sample.

Reaction of 1a with Methanol. A solution of **1a** (1 g, 4 mmol) in methanol (80 mL) was refluxed for 1 h. The solvent was removed and the residual oil was distilled under reduced pressure. [In all the experiments, with the exception of that for **1c**, NMR spectroscopy of the crude showed that the reaction had gone to 100% completion forming the fragmentation products exclusively.] The fraction collected at 25 °C (0.1 mmHg) was methyl benzoate, and the fraction at 35 °C (0.1 mmHg) was identified as *N*-benzyl-2-methylpropanimine (**2**). Proof of identity was obtained by comparison with an authentic sample prepared by the method of Tiollais.[15]

Reaction of 1b with Methanol. A solution of **1b** (1.7 g, 8 mmol) in methanol (0.5 mL) was refluxed for 8 h. Distillation of the crude yielded a fraction at 95 °C identified as *N*-isopropyl-2-methylpropanimine (**3**) by comparison with an authentic sample prepared by the method of Tiollais[15] and a fraction at 100 °C (80 mmHg) identified as methyl benzoate.

Reaction of 1c with Methanol. A solution of **1c** (1 g, 4 mmol) in methanol (80 mL) was refluxed for 8 h. The solvent was removed, and the residual oil was distilled under reduced pressure. The fraction at 25 °C (0.1 mmHg) was identified as methyl benzoate, and the ^{1}H NMR spectrum of the residue showed a complex pattern of signals.

Reaction of 1d with Methanol. A solution of **1d** (1 g, 3 mmol) in methanol (60 mL) was refluxed for 8 h. The solvent was removed, and the residual oil was distilled under reduced pressure. The fraction collected at 100 °C (80 mmHg) was methyl benzoate, and the residue was identified as *N*-(diphenylmethyl)-2-methylpropanimine (**4**) by comparison with a pure sample synthesized by the method of Tiollais.[15]

Reaction of 1a with Benzylamine. A mixture of **1a** (1 g, 4 mmol) and benzylamine (5 mL, 46 mmol) was refluxed for 30 min. The benzylamine was removed by distillation under reduced pressure, and the crude was washed with hexane. The residual oil crystallized from *n*-pentane yielding 0.35 g (41%) of *N,N'*-dibenzylformamidine (**10**), mp 75 °C (lit.[16] mp 75.5–77.5 °C). Evaporation of hexane from the organic layer yielded 0.61 g (68%) of *N*-benzyl-2-methyl-1-phenylpropanimine (**11**). Both **10** and **11** were identified by comparison with pure samples synthesized by the methods of Taylor et al.[16] and Pérez-Ossorio et al.,[17] respectively.

Reaction of 12 with Benzylamine. A mixture of **12** (0.44 g, 1.2 mmol) and benzylamine (3 mL, 28 mmol) was refluxed for 30 min. The crude was treated as described before, yielding 0.23 g (83%) of **10** and 0.26 g (88%) of **11**.

Reaction of 15 with Benzylamine. A mixture of **15** (175 mg, 0.4 mmol) and benzylamine (3 mL, 28 mmol) was refluxed for 30 min. After this time workup yielded the unchanged imine.

Reaction of 16 with Benzylamine. A mixture of **16** (1 g, 4 mmol) and benzylamine (5 mL, 46 mmol) was refluxed for 30 min. After removal of the benzylamine, the crude was washed with hexane. The residual solid was recrystallized from hexane/ethanol, giving 0.72 g (86%) of *N*-benzylbenzamide (**18**) as white needles, mp 105–106 °C (lit.[18] mp 105–106 °C). Evaporation of hexane from the organic layer yielded 0.68 g (72%) of **11**.

Acknowledgment. We thank the British Council, The Ministerio de Educación y Ciencia of Spain, and the Comisión Asesora de Investigación Científica y Técnica for financial support.

Registry No. **1a**, 86537-64-6; **1b**, 108344-34-9; **1c**, 108344-35-0; **1d**, 108365-39-5; **2**, 22483-21-2; **3**, 28916-24-7; **4**, 62740-71-0; **10**, 2304-00-9; **11**, 101583-56-6; **12**, 108344-36-1; **15**, 108344-37-2; **16**, 41169-42-0; **18**, 1485-70-7; benzylammonium benzoate, 34243-68-0; methyl benzoate, 93-58-3.

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Electron Transfer on the Photodehalogenation of 2-(4-Chlorophenyl)benzoxazole Assisted by Amines

Suzanne Fery-Forgues, Dominique Lavabre, and Nicole Paillous*

Laboratoire des IMRCP, UA au CNRS no. 470, Université Paul Sabatier, 31062 Toulouse Cedex, France

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The photochemical reactivity of 2-(4-chlorophenyl)benzoxazole in the presence of a series of amines has been investigated. A fluorescence quenching study provides evidence for the formation of an exciplex between the singlet excited state of the benzoxazole derivative and the amine in its ground state. This exciplex gives rise to a charge-transfrer complex (CTC). The quenching fluorescence date can be fitted by a Weller–Marcus system, thus leading to large reorganization energies. The measurement of dehalogenation, which is drastically increased in the presence of amines, allowed us to estimate the reactivity of the CTC. In the case of tertiary amines, 1% of the CTC formed via the singlet state leads to the dehalogenation. For secondary amines a hydrogen transfer between the amine and the excited triplet state of the chloro compound is also postulated.

Electron transfers between the excited state of light-absorbing molecules and electron-rich or electron-poor substrates have been extensively investigated in the last 2 decades.[1] Only a few reports have focussed on the involvement of such a process during the dehalogenation reactions of aromatic compounds. Chlorides of the benzene,[2,3] naphthalene,[2,4] biphenyl[2,5] and anthracene[5]

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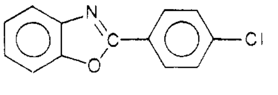
Table I. Fluorescence Quenching Rate Constants in Methanol and Ionization Potentials of Amines

no.	amine	$k_2\tau^1$ (M^{-1})	k_2 (M^{-1} s^{-1})	k_2/k_{diff}	ln ($k_2/k_{diff} - k_2$)	$\Sigma\sigma^*$	IP (eV)
1	diazabicyclooctane	18.00 ± 1.11	1.33×10^{10}	0.78	1.279		7.61[c]
2	*N*-ethyldiisopropylamine	19.15 ± 0.64	1.42×10^{10}	0.83	1.623	−0.44[a]	7.18[d]
3	tributylamine	14.31 ± 0.81	1.06×10^{10}	0.62	0.504	−0.39[b]	7.24[d]
4	tripropylamine	15.07 ± 0.44	1.11×10^{10}	0.65	0.632	−0.35[b]	7.29[d]
5	triethylamine	11.79 ± 0.45	8.73×10^{9}	0.51	0.054	−0.30[b]	7.35[d]
6	*N*-methylpyrrolidine	8.65 ± 0.48	6.40×10^{9}	0.37	−0.504	−0.26[b]	7.40[d]
7	*N*-ethylpiperidine	8.47 ± 0.37	6.27×10^{9}	0.36	−0.537	−0.28[b]	7.37[d]
8	*n*-butylmethylamine	3.80 ± 0.20	2.81×10^{9}	0.16	−1.619	+0.46[a]	8.28[d]
9	diethylamine	2.90 ± 0.19	2.15×10^{9}	0.12	−1.932	+0.29[b]	8.07[d]

[a] Data from Hull, L. A.; Davis, G. T.; Rosenblatt, D. H.; Mann, C, K. *J. Phys. Chem.* **1969**, *73*, 2142. [b] Data from Hall, H. K., Jr. *J. Am. Chem. Soc.* **1957**, *79*, 5441. [c] Data from Nelsen, S. F. *Isr. J. Chem.* **1979**, *18*, 45. [d] Calculated from the equation IP = (1.229 ± 0.071)$\Sigma\sigma^*$ + (7.718 ± 0.036), corr coeff = 0.98, from the method given in Hull, L. A.; Davis, G. T.; Rosenblatt, D. H. *J. Am. Chem. Soc.* **1969**, *91*, 6247.

series have in particular been studied. However, the nature of the excited state involved remains a much debated question. In a recent paper[6] dealing with the photolysis of 2-(4-halophenyl)benzoxazoles, we reported that the photodehalogenation rate of the chloro compound was



strongly enhanced in the presence of *cis*-piperylene, which could not be explained by energy transfer, the triplet excited state of the 2-(4-chlorophenyl)benzoxazole being slightly higher than the triplet state of *cis*-piperylene. With the same behavior being observed with triethylamine, a well-known electron donor, an electron-transfer reaction was postulated.

Mechanism I proposed by Ohashi[3] and Bunce[2] could account for this photoreduction:

$$\mathrm{BzCl} \xrightarrow{I_a} {}^1\mathrm{BzCl}$$

$${}^1\mathrm{BzCl} \xrightarrow{k_1} \mathrm{BzCl} + h\nu$$

$${}^1\mathrm{BzCl} \xrightarrow{k_d} \mathrm{BzCl}$$

$${}^1\mathrm{BzCl} + \mathrm{D} \xrightarrow{k_2} (\mathrm{BzCl}\text{- - -}\mathrm{D})^*$$

$$(\mathrm{BzCl}\text{- - -}\mathrm{D})^* \xrightarrow{k_3} \mathrm{BzCl} + \mathrm{D}$$

$$(\mathrm{BzCl}\text{- - -}\mathrm{D})^* \xrightarrow{k_4} \mathrm{Bz}^{\bullet} + \mathrm{Cl}^- + \mathrm{D}^{\bullet +}$$

In an attempt to establish the involvement of such a mechanism in our case, the interactions between the singlet state of the benzoxazole derivative and a series of tertiary and secondary amines was investigated on the basis of spectroscopic and thermodynamic date. In a first step, evidence was given for the formation of an exciplex, evolving toward a charge-transfer complex (CTC). In a second part, the reactivity of the CTC was considered and measurements of the dehalogenation rate have been used to demonstrate the involvement of the CTC in the photodehalogenation process.

Formation of a Charge-Transfer Complex

As previously reported 2-(4-chlorophenyl)benzoxazole fluoresces in oxygen-free solution at room temperature with a quantum yield of 0.57 ± 0.03.[6] Its fluorescence was systematically quenched by added amines. In each case, we observed that the quenching increased with the amine concentration following the Stern–Volmer equation (eq 1),

$$I_0/I = 1 + k_2\tau^1[\mathrm{D}] \qquad (1)$$

where I_0 and I are the relative fluorescence intensities in the absence and presence of quencher (D), respectively, k_2 is the bimolecular quenching rate constant, and τ^1 is the fluorescence lifetime. This result was in agreement with the mechanism of fluorescence quenching that has been described as an exciplex-induced decay. From plots of I_0/I vs. [D], $k_2\tau^1$ could be extracted. τ^1 was measured by multifrequency phase-modulation fluorometry and found to be 1.35×10^{-9} s either in acetonitrile or in methanol. The k_2 values thus obtained for each amine in methanol are given in Table I. These values may be compared to the diffusion rate constant k_{diff}.

The ratios k_2/k_{diff} were calculated with $k_{diff} = 1.7 \times 10^{10}$ M^{-1} s^{-1} in methanol at 20 °C (Table I). In all cases, these ratios showed that a single encounter is not efficient for deactivation of the excited state. Ratio values decreased from 0.83 for *N*-ethyldiisopropylamine to 0.12 for diethylamine, while the ionization potential of amines increased.

The method of Evans[7] can be used in order to establish the formation of a CTC from the exciplex. This kinetic method is based on a correlation between the quenching rate constant k_2 and the ionization potential of the electron donor.

Assuming that the reaction is controlled by diffusion,[8] the usual scheme for fluorescence quenching reaction could be replaced by a new expression:

$${}^1\mathrm{BzCl} + \mathrm{D} \underset{k_{-q}}{\overset{k_{diff}}{\rightleftharpoons}} ({}^1\mathrm{BzCl}/\mathrm{D}) \xrightarrow{k_r} (\mathrm{BzCl}^{\bullet -}\text{- - -}\mathrm{D}^{\bullet +})$$

which introduces an equilibrium and splits the formation of the CTC in two steps, the key step being the formation of a proximity pair. In this scheme k_{-q} is the rate constant for diffusion of the proximity pair out of the solvent cavity and k_r is the rate constant for the quenching reaction. This leads to a new Stern–Volmer equation (eq 2), which is close

$$I_0/I = 1 + (k_{diff}k_r/(k_{-q} + k_r))\tau^1[\mathrm{D}] \qquad (2)$$

to eq 1. Since (1) and (2) are of the same form, k_2 may be given by

$$k_2 = k_{diff}k_r/(k_{-q} + k_r)$$

which allows comparison of the exciplex with the proximity pair. This last expression is equivalent to

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$$k_r/k_{-q} = k_2/(k_{\text{diff}} - k_2)$$

where the right-hand side of the equation is already known. If we suppose that the rate constant for diffusion out of the solvent cavity, k_{-q}, is to a first approximation determined by only the properties of the solvent, then

$$\ln (k_r/k_{-q}) = \ln (k_2/(k_{\text{diff}} - k_2)) \propto \Delta G^\ddagger$$

where $\Delta G^\ddagger$ is the free energy of activation for the electron-transfer reaction. Since the fluorescer did not change when varying the nature of the amine, $\Delta G^\ddagger \propto \text{IP} + C$ where IP is the ionization potential of the donor and C accounts for the solvation of a pair of ions. In our case, the values $\ln [k_2/(k_{\text{diff}} - k_2)]$ (listed in Table I) were plotted vs. ionization potential for all the studied amines. A linear relationship was observed obeying the expression

$$\ln (k_2/(k_{\text{diff}} - k_2)) = (-2.40 \pm 0.76)\text{IP} + (18.01 \pm 5.74)$$

The assumptions of constant solvation terms and constant k_{-q} are thus verified. The link thereby established between the fluorescence quenching rate constant and the ionization potential of amines strongly indicates the existence of the CTC.

Thermodynamic Approach

A thermodynamic approach to the reaction was then undertaken. A correlation between the fluorescence quenching rate constant, k_2, and the free energy change (ΔG) involved in the electron-transfer process was examined. In order to have results consistent with the literature data required for this correlation (oxidation potential, etc.), the k_2 values used in this part were obtained from quenching experiments carried out in acetonitrile. The strong enhancement of the fluorescence quenching observed when changing from methanol to acetonitrile could be attributed to the differences of solvation.

The free energy change (ΔG) is given by the Weller equation[9] (eq 3), where E(D/D$^+$) is the oxidation potential

$$\Delta G = 96.50(E(\text{D/D}^+) - E(\text{A}^-/\text{A}) - e_0^2/a\epsilon) - \Delta E_{0,0} \qquad (3)$$

of the electron donor D, and E(A$^-$/A) is the reduction potential of the electron acceptor. The reduction potential of 2-(4-chlorophenyl)benzoxazole was measured by polarography and found to be −1.90 ± 0.02 V vs. the saturated calomel electrode in acetonitrile solution. $e_0^2/a\epsilon$ is the energy gained by bringing the two radical ions at the encounter distance a in a solvent of dielectric constant ϵ ($e_0^2/a\epsilon$ is assumed to be 0.06 eV in acetonitrile), and $\Delta E_{0,0}$ is the energy level of the fluorescent state[6] (370 kJ/mol). The free energy changes (ΔG) calculated for every amine are given in Table I. They vary from −126.82 kJ/mol for **1** to −66.02 kJ/mol for **9**, indicating the strong exothermicity of the electron-transfer process.

With the aim of comparing our values with a general theory of electron transfer, the well-known Weller–Marcus system was used. Rehm and Weller[9] have derived an empirical equation for the electron-transfer fluorescence quenching rate constant, k_2 (eq 4). ΔG is calculated from

$$k_2 = \frac{2 \times 10^{10}\ \text{M}^{-1}\ \text{s}^{-1}}{1 \times 0.25[\exp(\Delta G^\ddagger/RT) + \exp(\Delta G/RT)]} \qquad (4)$$

eq 3 and $\Delta G^\ddagger$, the activation free enthalpy, is assumed to be a monotonic function of ΔG (eq 5). $\Delta G_0^\ddagger$, the activation

$$\Delta G^\ddagger = [(\Delta G/2)^2 + (\Delta G_0^\ddagger)^2]^{1/2} + \Delta G/2 \qquad (5)$$

free energy at $\Delta G = 0$, is experimentally fixed at 10.04 kJ/mol. An alternative expression for ΔG was derived by Marcus[10] (eq 6). With $\Delta G_0^\ddagger = 10.04$ kJ/mol, the two

$$\Delta G^\ddagger = \Delta G_0^\ddagger\ [1 + (\Delta G/4\Delta G_0^\ddagger)]^2 \qquad (6)$$

theories are in good agreement with experimental data for electron-transfer fluorescence quenching of neutral molecules when $\Delta G > -62.7$ kJ/mol. For more exothermic reactions, the Marcus equation leads to a decrease in k_2, namely the Marcus inverted region. If the fluorescence quenching rate constant k_2 is plotted vs. the free energy ΔG for our system, it becomes obvious that neither the Weller curve nor the Marcus one fit our experimental data when $\Delta G_0^\ddagger = 10.04$ kJ/mol. With the kinetic treatment having demonstrated the possibility of an electron-transfer process, our system could be described by a curve based upon the Weller or Marcus theory. If we allow $\Delta G_0^\ddagger$ to vary, a rather good fit could be obtained with the one condition that the $\Delta G_0^\ddagger$ optimized value from least-squares fits be equal to 17.75 kJ/mol using the Weller theory and 38.09 kJ/mol in the Marcus case.

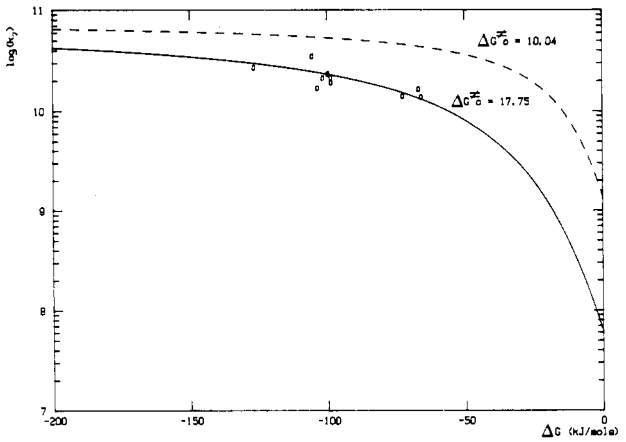

Figure 1. Plot of log k_2 (from fluorescence quenching) vs. ΔG (from eq 3): curve based on the Weller equation (eq 4 and 5) with $\Delta G_0^\ddagger = 10.04$ kJ/mol (dashed line) and $\Delta G_0^\ddagger = 17.75$ kJ/mol (straight line).

The Weller equation is much more suited than is the Marcus equation for treatment of the fluorescence data in our system. Weller curves for $\Delta G_0^\ddagger = 10.04$ kJ/mol (dashed lines) and for $\Delta G_0^\ddagger = 17.75$ kJ/mol (continuous line) are shown in Figure 1. If we refer to the literature, Ballardini et al.[11] have already related small variations of $\Delta G_0^\ddagger$ around the 10.04 kJ/mol value, using aliphatic amines as electron donors. As pointed out by Eberson,[12] large $\Delta G_0^\ddagger$ values might have been expected in certain systems, and some important variations were found in reactions involving at least one charged species.[13] In particular, the reduction of alkyl halides by inorganic salts or aromatic radical anions leads to $\Delta G_0^\ddagger = 48.12$ kJ/mol. In the case of benzoxazole chloride, the large $\Delta G_0^\ddagger$ value derived with the two theories could mainly be attributed to solvent reorganization due to the formation of ionic species from neutral molecules. The magnitude of $\Delta G_0^\ddagger$ could also account for some bond reorganization energies in the transition state.

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Table II. Fluorescence Quenching Rate Constants in Acetonitrile, Half-Wave Oxidation Potentials, and Free Energy of Electron Transfer (ΔG) and Charge Recombination (ΔG_{cr}) Reactions

no.	amine	$k_2\tau^1$ (M^{-1})	k_2 (M^{-1} s^{-1})	$E^{1/2}$, SCE (V)	$-\Delta G$ (kJ·mol^{-1})	$-\Delta G_{cr}$ (kJ·mol^{-1})
1	diazabicyclooctane	36.59 ± 4.40	2.71×10^{10}	0.68[a]	126.82	254.91
2	*N*-ethyldiisopropylamine	47.46 ± 2.83	3.51×10^{10}	0.90[a]	105.59	276.00
3	tributylamine	22.86 ± 2.23	1.69×10^{10}	0.92[a]	103.66	277.92
4	tripropylamine	28.38 ± 4.31	2.13×10^{10}	0.94[a]	101.73	279.85
5	triethylamine	31.59 ± 1.55	2.34×10^{10}	0.96[a]	99.80	281.78
6	*N*-methylpyrrolidine	28.93 ± 1.17	2.14×10^{10}	0.97[b]	98.83	282.74
7	*N*-ethylpiperidine	25.64 ± 0.40	1.90×10^{10}	0.97[b]	98.83	282.74
8	*n*-butylmethylamine	19.11 ± 0.55	1.41×10^{10}	1.24[a]	72.78	308.80
10	diisopropylamine	22.36 ± 2.44	1.65×10^{10}	1.30[a]	66.99	314.69
9	diethylamine	18.73 ± 0.79	1.38×10^{10}	1.31[a]	66.02	315.55

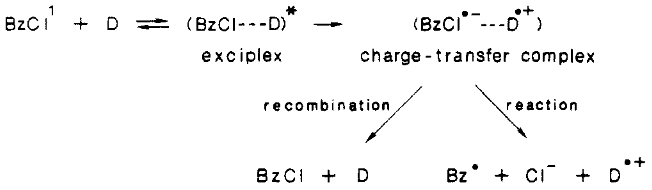
[a] Data from Mann, D. K.; Barnes, K. K. *Electrochemical Reactions in Non-Aqueous Systems*; Marcel Dekker: New York, 1970. Obtained from half-wave oxidation potential vs. Ag/Ag$^+$ 0.10 M in acetonitrile by adding 0.30 V. [b] Calculated from the equation $E = (0.388 \pm 0.036)\Sigma\sigma^* + (0.779 \pm 0.014)$, corr coeff = 0.98, from the method given in ref d, Table I, and addition of 0.30 V.

Table III. Comparison of $k_2\tau^1$ Values Obtained by Fluorescence Quenching Study and Dehalogenation Measurements for Tertiary and Secondary Amines

amine	slope	intercept	$k_2\tau^1$, M^{-1} (dehal)	$k_2\tau^1$, M^{-1} (fluorescence)	ϕ_{dehal}[a]
tertiary					
triethylamine[b]	3.71	73.8	20	11.8	2.25×10^{-3}
DABCO[b]	3.28	72.0	21.9	18.0	2.49×10^{-3}
secondary					
piperidine[c]	76.77	4239.0	56.4	15.6	8.50×10^{-5}
n-butylmethylamine[b]	1.10	143.5	130	3.8	3.93×10^{-3}
histamine[b]	1.12	135.9	121	10.6	4.03×10^{-3}

[a] Dehalogenation quantum yields for a concentration of amine [D] = 0.01 M. [b] Methanol solutions. [c] Cyclohexane solutions.

Scheme I



Reactivity of the CTC

Once formed, the CTC can either return to the ground state or lead to the separation of the radical ions. The charge recombination enthalpy is given by expression (7) derived from the Weller[9] equation. It has been calculated

$$-\Delta G_{cr} = 96.50(E(A^-/A) - E(D/D^+) + e_0^2/a\epsilon) \quad (7)$$

for every amine studied (Table II) and shows that the exothermicity of the reaction increases with the $E^{1/2}$ of amine. In spite of the high exothermicity of the charge recombination reaction, a small amount of CTC could lead to the separation of charged species. Thus, the decomposition of the radical anion BzCl$^{\bullet-}$ could generate the formation of 2-phenylbenzoxazole by hydrogen abstraction from solvent and give rise to the departure of the halogen atom as a chloride anion (Scheme I). In order to measure the importance of this process, photodechlorination assisted by amines was studied. The experiments were carried out in methanol with two tertiary amines (triethylamine and diazabicyclooctane) and two secondary amines (*n*-butylmethylamine and piperidine, the latter being used in cyclohexane solution). 2-(4-Chlorophenyl)benzoxazole (1.2×10^{-3} M) was irradiated from 1 to 2 h at 300 nm in the presence of amines (from 5×10^{-2} to 5×10^{-3} M). The formation of 2-phenylbenzoxazole and the disappearance of the chloro derivative were measured by HPLC and no secondary addition could be detected. The dehalogenation quantum yield in methanol in absence of amine is concentration dependent. It is equal to 2.38×10^{-6} for a 1.2×10^{-3} M concentration of substrate. For all the photolyses carried out in the presence of amines in methanol, the photodehalogenation was strongly enhanced. From mechanism I it can be seen that the quantum yield of dehalogenation is given by eq 8. If we

$$\phi_r^{-1} = \left(1 + \frac{k_3}{k_4}\right)\left(1 + \frac{1}{k_2\tau^1[D]}\right) \quad (8)$$

plot the reciprocal of the quantum yield of dehalogenation, ϕ_r^{-1}, vs. the reciprocal of the electron-donor concentration, $[D]^{-1}$, a linear variation was obtained for all the amines studied. The ratio intercept/slope thus gives us the $k_2\tau^1$ value (Table III). $k_2\tau^1$ can therefore be obtained by two independent ways, the fluorescence quenching estimating only the reactivity of the first excited state, whereas dehalogenation measures the total reactivity. In the case of tertiary amines, a good fit between the $k_2\tau^1$ values obtained with the two methods confirms the proposed mechanism given above. The efficiency of CTC in dehalogenation is given by

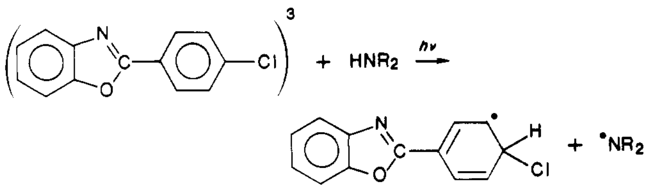
$$\gamma = \frac{k_4}{k_4 + k_3}$$

which can also be written

$$\frac{1}{\gamma} = \frac{k_4 + k_3}{k_4} = 1 + \frac{k_3}{k_4}$$

The fraction of CTC that leads to charge separation is thus the reciprocal of the intercept, namely, 0.013 ± 0.010 for TEA and 0.014 ± 0.008 for DABCO. This result means that only 1% of the CTC leads to dehalogenation and that the activation energy involved in the product formation might be twice as large as the deactivation energy. In the case of secondary amines, piperidine was used in cyclohexane. The high $k_2\tau^1$ value obtained by fluorescence can be attributed to the low solvent polarity which stabilizes the exciplex. On the other hand, this polarity might be insufficient to induce the formation of the CTC, thus explaining the very low dehalogenation rate. The efficiency

Scheme II



of n-BMA in inducing dehalogenation is similar to that of tertiary amines. However, the $k_2\tau^1$ value obtained by dehalogenation measurements is 35 times higher than that obtained from fluorescence. Mechanism I can be ruled out since the reactivity of the singlet state cannot explain alone the dehalogenation rate. The involvement of another excited state, probably the triplet state, must be considered. If an exciplex is formed between amines and the triplet excited state of the benzoxazole compound, the free energy change involved in the electron-transfer process is given by eq 9, where the triplet-state energy has been spectroscopically estimated as 260.9 kJ/mol. ΔG was found to be 36.32 kJ/mol for n-BMA and 43.07 kJ/mol for diethylamine. With the reaction being slightly endothermic, this triplet pathway may be dismissed. It is more probable that hydrogen transfer occurs between the amine and the triplet excited state of the chlorinated compound. The mechanism in Scheme II, could therefore be proposed, where return to aromaticity favors the departure of a chlorine radical. To test this hypothesis, a dehalogenation reaction was undertaken using histamine. It has been shown that the related amino acid, histidine, reacts with the triplet state of flavine mononucleotide by transfering one of the hydrogen atoms of the nitrogenous ring.[14] The difference between the $k_2\tau^1$ values obtained by the two methods using histamine was similar to that calculated for the two secondary amines (Table II), which confirms quantitatively the hydrogen-transfer assumption. This result is also consistent with the literature data that have shown that secondary amines generally can give a hydrogen atom to an aromatic molecule in its triplet excited state.

$$\Delta G_{\mathrm{et}} = 96.50(E(\mathrm{D}/\mathrm{D}^+) - E(\mathrm{A}^-/\mathrm{A}) - e_0^2/a\epsilon) - E_\mathrm{T} \qquad (9)$$

Conclusion

The whole set of our data demonstrates that the enhancement of the photodehalogenation of 2-(4-chlorophenyl)benzoxazole in the presence of amine results from an electron transfer. In the case of tertiary amines, the electron transfer involves mainly an exciplex between the singlet state of the benzoxazole and the ground state of the amine. In the case of secondary amines, another mechanism may also take place.

Experimental Section

Starting Materials. 2-(4-Chlorophenyl)benzoxazole was prepared and purified as described before.[15] DABCO (Fluka, purum) and histamine (Aldrich, >99%) were used as supplied. Other amines (Fluka, puriss) were distilled before use. Acetonitrile, methanol, and cyclohexane (Merck) were of spectroscopic grade and used without further purification.

Fluorescence Quenching Studies. UV spectra were determined with Beckman 5260 UV-vis spectrophotometer. Fluorescence experiments were carried out with a thermostated Aminco SFP 500 spectrofluorometer. Aliquots (2 mL) of a solution of 2-(4-chlorophenyl)benzoxazole (1.65×10^{-6} M) in the proper solvent were poured in a quartz cell. Degassing was achieved by bubbling with argon for 3 min. Amines do not absorb at the chosen excitation wavelength (λ_{ex} = 320 nm). The emission wavelength is set at 350 nm. The fluorescence intensity F_0 of the benzoxazole derivative is monitored and a known weight of amine is added. The fluorescence intensity F is then noted.

Correction for Inner Filter Effects. Because of the presence of the benzoxazole derivative, the optical density of the solution was slightly higher than 0.05 at the excitation wavelength. As it was necessary to correct the inner filter effects, we used the method of Lutz and Luisi,[16] which consists of measuring the fluorescence intensity at two different points along the diagonal in the cell. The original cell holder was replaced by a homemade "cell-shift" compartment that permits the operator to move the cell manually along its diagonal. The two positions of the cell-holder were adjusted to l_1 = 1.82 mm and l_2 = 8.12 mm. Then, the corrected fluorescence intensity is given by the equation

$$F = F_1\left(\frac{F_1}{F_2}\right)^{l_1/(l_2 - l_1)}$$

where F_1 and F_2 are the fluorescence intensities measured with the cell in position 1 and 2, respectively.

Correction for the Intrinsic Fluorescence of the Amine. The intrinsic fluorescence intensity of histamine at λ_{ex} = 320 nm was of the same order as that of the benzoxazolic derivative at the concentration used. For every point, it was necessary to measure F_0 = fluorescence of 2-(4-chlorophenyl)benzoxazole alone, F = fluorescence of the mixture after addition of the amine, and F_H = fluorescence of histamine alone at the same concentration (read on the standard plot $F_\mathrm{H} = f([\mathrm{H}])$). The ratio $F_0/(F - F_\mathrm{H})$ was calculated to make it possible to study the variation of the fluorescence intensity of the benzoxazole derivative vs. the concentration of histamine.

Photoreduction of 2-(4-Chlorophenyl)benzoxazole in the Presence of Amines. The photochemical procedures have been described in detail previously. Methanol or cyclohexane (in the case of piperidine) solutions of 2-(4-chlorophenyl)benzoxazole (2 mL, 2.6×10^{-3} M) were added to solutions of amines (2 mL, from 10^{-1} to 10^{-2} M). The test tubes containing the mixture were degassed by three freeze-pump-thaw cycles with liquid nitrogen and sealed in vacuo. Irradiations were conducted in a Rayonnet reactor equipped with 16 mercury lamps with a maximum output at 300 nm. The chamber temperature was approximately 30 °C. Equal illumination of samples being photolyzed simultaneously was assured by use of a merry-go-round apparatus. The light intensity was calculated with benzophenone/benzhydrol actinometry.

Analytical Procedures. HPLC chromatography was performed with a 120 FL chromatograph equipped with a HP Model 3390 A electronic integrator and a variable-wavelength UV detector set at 254 nm. An analytical μ-Bondapack C_{18} column was used. A 0.7 mL/min. flow rate was maintained for the methanol-water (85:15) eluent.

Reduction Potential of 2-(4-Chlorophenyl)benzoxazole in Acetonitrile. Polarography was carried out with a Metrohm Model E 505 polarograph equipped with a polarography stand. Half-peak reduction potential was obtained with platinum foil as counter electrode vs. a reference calomel electrode, the working electrode being the dropping mercury electrode. The supporting electrolyte was tetrabutylammonium perchlorate (0.2 M). Solutions of 2-(4-chlorophenyl)benzoxazole (from 10^{-3} to 10^{-2} M) were poured into the cell and degassed by flushing the solution with a stream of nitrogen. The cell was kept under an inert atmosphere during the measurements.

Lifetime of the Singlet of 2-(4-Chlorophenyl)benzoxazole in Acetonitrile. Lifetime measurements were performed on a multifrequency phase-modulation fluorometer. The light source was an HeCd laser from Liconix Inc., equipped with UV optics for 325 nm. Continuously variable modulation frequencies were used from 80 to 180 MHz.

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Registry No. **1**, 280-57-9; **2**, 7087-68-5; **3**, 102-82-9; **4**, 102-69-2; **5**, 121-44-8; **6**, 120-94-5; **7**, 766-09-6; **8**, 110-68-9; **9**, 109-89-7; histamine, 51-45-6; 2-(4-chlorophenyl)benzoxazole, 1141-35-1.

Optically Active Amines. 33.[1] Circular Dichroism of Substituted Phenylcarbinols[2]

Luca P. Fontana and Howard E. Smith*

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

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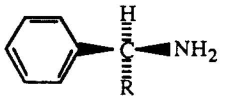
Examination of the isotropic electronic absorption and circular dichroism spectra of unsubstituted and ring-substituted phenylcarbinols indicates that the sign of the $^{1}L_{b}$ Cotton effects (CEs) at about 254–282 nm of the benzene chromophore of the unsubstituted phenylcarbinols is determined by vibronic borrowing from the $^{1}B_{b}$-allowed transition. On ring substitution by an atom or group with either a positive (Cl, CH_3O, CH_3) or a negative (CF_3, aza) spectroscopic moment, transition moments are induced in the benzene ring bonds adjacent to the attachment bond of the chiral group, resulting in enhanced coupling of the $^{1}L_{b}$ transition with the chiral group. The sign reversal from positive to negative for the $^{1}L_{b}$ CEs on para substitution of (*S*)-α-phenylethyl alcohol, (*R*)-phenylethylene glycol, (*R*)-mandelic acid, methyl (*R*)-mandelate, and (*S*)-β-hydroxy-β-phenylpropionic acid by an atom or group with a positive spectroscopic moment can be viewed as the overshadowing of the positive vibronic rotational strength by a negative induced contribution. On para substitution with an atom or group with a negative spectroscopic moment, bond moments of an opposite sense are induced, and the positive induced contribution to the rotational strength has the same sign as the vibrational contribution. As a result, both (*S*)-α-[*p*-(trifluoromethyl)phenyl]ethyl and (*S*)-α-(4-pyridyl)ethyl alcohol show a positive $^{1}L_{b}$ band origin CE. Meta substitution by a particular group will induce bond moments in an opposite sense from that induced by the same group in the para position. Thus, meta substitution by an atom or group with a positive and a negative spectroscopic moment of the analogues of (*S*)-α-phenylethyl alcohol results in positive and negative $^{1}L_{b}$ CEs, respectively. Ortho substitution again reverses the sense of the induced bond moments from that of the same meta substituent, and the sign of the $^{1}L_{b}$ CEs is reversed from that of the meta isomer.

Examination[3] of the isotropic electronic absorption (EA) and circular dichroism (CD) spectra of unsubstituted, para-substituted, and 3,5-disubstituted α-phenyl- and α-benzylethylamines and their hydrochlorides indicates that, for the unsubstituted compounds, the sign of the $^{1}L_{b}$ Cotton effects (CEs) at 254–282 nm of the benzene chromophore is determined by vibronic borrowing[4,5] from benzene transitions at shorter wavelength. Both (*S*)-α-phenylethylamine [(*S*)-**1a**] and its hydrochloride [(*S*)-**1a**·HCl] show positive CEs associated with transitions from the lowest energy vibrational mode in the ground state to totally symmetric vibrational modes in the first electronically excited state.[6,7] Other phenylalkylcarbinamines,[8,9] such as (*S*)-α-phenyl-*n*-propylamine[8,9] [(*S*)-**1b**] and (*S*)-α-phenylneopentylamine[8] [(*S*)-**1c**] and their hydrochlorides, also show positive $^{1}L_{b}$ CEs, the sign also being determined by vibronic borrowing from benzene transitions at shorter wavelength. On para substitution of (*S*)-**1a** and (*S*)-**1a**·HCl by an atom or group with either a positive (Cl, Br, CH_3, CH_3O) or a negative (CN, CF_3) spectroscopic moment,[10] the sign of the $^{1}L_{b}$ may be different from that of unsubstituted compound,[3,11] but the sign of the CEs can be correlated with the absolute configuration provided the spectroscopic moment of the additional substituent is taken into account.[3] Meta and ortho substitution by similar groups would also influence the sign of the $^{1}L_{b}$ CEs, but only the CD of the 3,5-dimethyl and 3,5-dichloro derivatives of (*S*)-**1a** and its hydrochloride have been reported.[3]



(*S*)-**1a**, R = CH_3

b, R = CH_3CH_2

c, R = $(CH_3)_3C$

Phenylalkylcarbinol analogues of (*S*)-**1a**, such as (*S*)-phenylethyl alcohol[12] [(*S*)-**2a**] and its derivatives for which

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0022-3263/87/1952-3386$01.50/0