Internal and External Heavy-atom Effects on the Photolysis of 1-Benzyloxy-2-pyridone

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The emission efficiencies of the title compound (BP) are subject to pronounced internal and external heavy-atom effects while the efficiency of its photoreaction is insensitive to these heavy-atom perturbations. This result is explained in terms of the mechanism in which the N–O bond cleavage in a BP molecule takes place from higher vibrational states of the first excited singlet state in competition with vibrational relaxation to the fluorescent state. Further supporting evidence for this mechanism is obtained from temperature effects on the fluorescence and reaction efficiencies of BP.

Both the introduction of heavy atoms into the molecule of interest and the presence of heavy-atom solvents increases spin–orbit coupling and thereby leads to an increase in the rates of radiative ($S_0 \leftarrow T_1$) and non-radiative ($T_1 \rightsquigarrow S_1$, $S_0 \rightsquigarrow T_1$) processes.[1] The increased efficiency of intersystem crossing ($T_1 \rightsquigarrow S_1$) should be reflected in the fluorescence quenching of the parent molecule. Several attempts to observe heavy-atom effects on photochemical processes have suggested that photochemical reactions from π,π^* excited states are subject to remarkable heavy-atom effects,[2] whereas n,π^* excited states are relatively insensitive to heavy-atom substitution.[3] Our previous study on the photolysis of 1-benzyloxy-2-pyridone (BP) revealed that the reaction proceeds preferentially through the excited singlet state to give benzaldehyde and 2-pyridone as the main products along with a small amount of benzyl alcohol.[4] The first excited singlet states of 2-pyridone and 1-methyl-2-pyridone, the structure of which is similar to that of BP, have been shown to possess π,π^* character.[5] By analogy with these two molecules, the first excited singlet state of BP is also suggested to be mainly π,π^* in character. Thus it is expected that the photolysis of BP as well as its fluorescence should be sensitive to heavy-atom perturbation.

In order to clarify the mechanism of BP photolysis in more detail, we have investigated internal and external heavy-atom effects on the reaction and emission efficiencies of this molecule, and, in addition, the effects of temperature on these efficiencies. In this paper we present results which demonstrate that the N–O bond cleavage in a BP molecule takes place, not from the fluorescent state, but from higher vibrational states of the first excited singlet state.

Results and Discussion

Internal and External Heavy-atom Effects.—A bromine atom was introduced at the 5-position of the pyridone skeleton in a BP molecule in order that a significant heavy-atom effect be exerted. In Figure 1 are shown the u.v. absorption spectra of BP and 1-benzyloxy-5-bromo-2-pyridone (BBP) in cyclohexane at room temperature. While BP shows the first π,π^* absorption band at 305 nm (molar absorption coefficient, ε = 5 300 dm^3 mol^{-1} cm^{-1}), that for BBP is observed at 319 nm (ε = 4 300 dm^3 mol^{-1} cm^{-1}). Both of these two bands undergo a hypsochromic (blue) shift to some extent (*ca.* 400 cm^{-1}) in acetonitrile and methanol. Excitation of BBP into excited states with 313-nm light causes the N–O bond cleavage to afford benzaldehyde and 5-bromo-2-pyridone as the main products (Scheme 1) in any oxygen-free solvent employed. As shown in Figure 2, the phosphorescence of BBP (the first singlet excitation energy, E_{S_1} = 80; the first triplet excitation energy, E_{T_1} = 62 kcal mol^{-1})† was quenched efficiently by 2,5-dimethylhexa-2,4-diene (E_{S_1} = 103; E_{T_1} = 59 kcal mol^{-1}),[6] whereas this triplet quencher does not affect the reaction. This finding provides supporting evidence for photolysis taking place preferentially from the singlet state; this is consistent with the results from the BP photolysis.

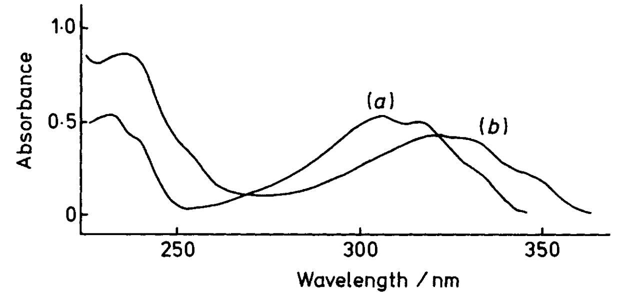
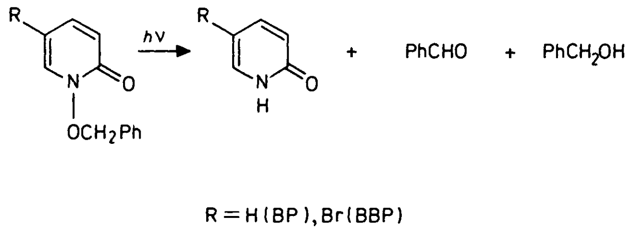


Figure 1. U.v. absorption spectra of BP (*a*) and BBP (*b*) in cyclohexane at room temperature. [BP] = [BBP] = 10^{-4} mol dm^{-3}.



Scheme 1.

We first discuss internal heavy-atom effects on the fluorescence (Φ_f) and phosphorescence (Φ_p) efficiencies of BP based on the data collected in the Table. Clearly the heavy-atom effect exerted by the bromine substituent on the pyridone skeleton is manifested by a marked reduction in the BP

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† The first singlet excitation energy was estimated from the u.v. absorption and fluorescence spectra measured at room temperature. The phosphorescence spectrum, the 0–0 band of which appears at *ca.* 460 nm as a shoulder at 77 K, enabled us to estimate the first triplet excitation energy.

Table. Internal heavy-atom effects on the fluorescence, phosphorescence, and photolysis of BP.

Solvent (temperature)	$\Phi_f(BP)/\Phi_f(BBP)^a$ (23 ± 1 °C)	$\Phi_p(BP)/\Phi_p(BBP)^a$ (77 K)	$\Phi_{-BBP}(\Phi_{-BP})^b$ (25 ± 3 °C)	Φ_{-BP}/Φ_{-BBP}
Cyclohexane	10		0.28 ± 0.01(0.27 ± 0.03)	1.0
Methylcyclohexane		0.2		
Benzene			0.25 ± 0.01 (0.24 ± 0.02)	1.0
Acetonitrile			0.22 ± 0.01 (0.22 ± 0.03)	1.0
Methanol	20		0.43 ± 0.02 (0.29 ± 0.01)	0.7
Methanol–ethanol (1:1 v/v)		0.5		

[a] The absorbance of BP and BBP at the excitation wavelength (313 nm) are both 0.1 in any solvent. [b] [BP] = [BBP] = 10^{-4} mol dm^{-3}.

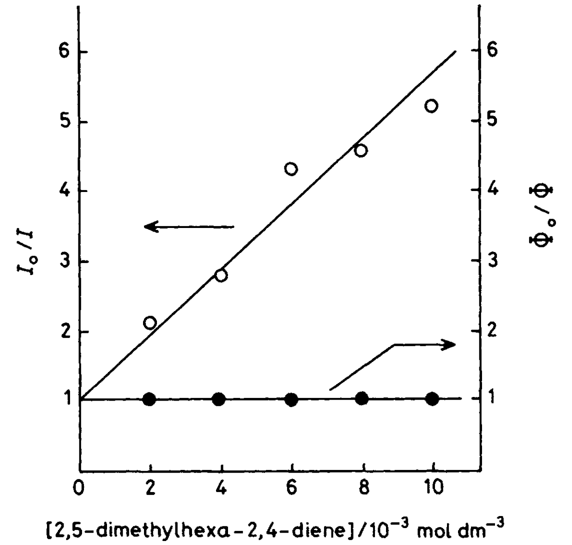

Figure 2. Stern–Volmer plots for phosphorescence (○) and photolysis (●) quenching of BBP (10^{-4} mol dm^{-3}) by 2,5-dimethylhexa-2,4-diene at 313nm. Solvent (temperature), ○, methylcyclohexane (77 K); ●, cyclohexane (24 ± 1 °C).

fluorescence efficiency accompanied by an increase in the phosphorescence efficiency. These observations indicate that the first excited singlet (S_1) state (fluorescent state) of BP is subject to pronounced internal heavy-atom effects. Thus we expect that the photolysis of BP is also subject to heavy-atom effects, the magnitude of which should be comparable to that of the effects on the fluorescence efficiency if the reaction occurs from the fluorescent state in competition with intersystem crossing to the excited triplet state. The quantum yields for the disappearance of BBP (Φ_{-BBP}) irradiated at 313 nm were determined at low conversions (10–20%) under nitrogen by using a potassium trioxalatoferrate(III) actinometer[7] and are collected in the Table, which also lists data for the BP photolysis (Φ_{-BP}).

Interestingly, a negligible difference is observed between Φ_{-BP} and Φ_{-BBP}, except in methanol ($\Phi_{-BP}/\Phi_{-BBP} = 0.7$). The fact that an alcoholic solvent molecule forms a hydrogen bond to the carbonyl oxygen atom of 1-methyl-2-pyridone[8] suggests that this type of hydrogen bond may affect the photoreactivity of BP and BBP to different extents. The finding that substitution of bromine atom for hydrogen has little effect on reaction efficiency reveals that the photoproducts obtained do not originate from the fluorescent state (the lowest vibrational state of the S_1 state). It is likely that the photolysis of BP occurs from higher vibrational states of the S_1 state. However, the bathochromic (red) shift of the first absorption band is observed upon a bromine substituent being introduced into the BP molecule as shown in Figure 1, which implies that electronic configuration of the BP S_1 state should also be perturbed by the presence of this heavy atom. This fact casts some ambiguity on our interpretation of the internal heavy-atom effects.

To explore this possibility we attempted to observe external heavy-atom effects on the emission and reaction efficiencies of BP in polar and non-polar solvents to which dibromomethane (DM) had been added. The addition of DM was shown to alter neither the u.v. absorption spectrum of BP nor the product distribution derived from the photolysis. An examination of Figure 3 reveals that the fluorescence intensity of BP decreases with increased concentration of added DM both in cyclohexane and in methanol, whereas the quantum yields for the reaction (Φ_{-BP}) are not affected by added DM in these two solvents. In addition, this decrease in the fluorescence intensity is accompanied by an increase in the phosphorescence intensity [I_p([DM] = 10^{-2} mol dm^{-3})/I_p([DM] = 0 mol dm^{-3}) = 4 in methylcyclohexane and 3 in methanol–ethanol [(1:1 v/v) at 77 K], demonstrating that the effects of added DM on the BP emission are a result of external heavy-atom effects on spin–orbit coupling. These observations, therefore, provide further supporting evidence for the mechanism proposed on the basis of the internal heavy-atom effects (Scheme 2).

$$^1BP \xrightarrow{h\nu} {}^1BP^{*\ddagger}$$

$$^1BP^{*\ddagger} \longrightarrow {}^1BP^*$$

$$^1BP^{*\ddagger} \longrightarrow \text{Photoproducts}$$

$$^1BP^* \longrightarrow {}^3BP^*$$

$$^1BP^* \longrightarrow {}^1BP$$

* Electronic excitation. ‡ Vibrational excitation.

Scheme 2.

Previously Koz'menko and Kuz'min obtained similar results in the quenching experiment for the photoisomerization of 9-(t-butyl)anthracene. They found that aniline and *N*,*N*-dimethylaniline quench the fluorescence of this molecule but do not affect the isomerization reaction at all. Based on these results they proposed a mechanism in which the isomerization reaction proceeds through a non-relaxed Franck–Condon state but not through the fluorescent state.[9] Turro *et al.* suggested that photoreactions such as bond dissociation could presumably take place from higher vibrational states of a given excited electronic state in competition with vibrational relaxation.[10] A typical example for such a reaction has been found by Becker *et al.*[11] From a detailed analysis of the wavelength dependence of the fluorescence quantum yields of 3,3-dimethyl-3*H*-benzo[*f*]chromene at 77 K they showed that the C–O bond cleavage in this molecule proceeds through higher vibrational states of the S_1 state. Thus it is not unreasonable to interpret our results concerning internal and external heavy-atom effects in terms of Scheme 2 in which the N–O bond cleavage occurs from

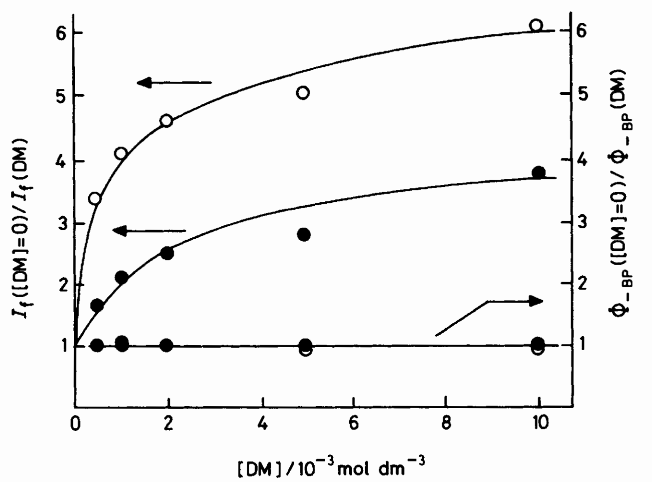

Figure 3. Effects of DM on the fluorescence (I_f at 23 ± 1 °C) and photolysis ($\Phi_{-\mathrm{BP}}$ at 25 ± 2 °C) of BP (10^{-4} mol dm^{-3}) in cyclohexane (●) and methanol (○). Excitation wavelength = 313 nm.

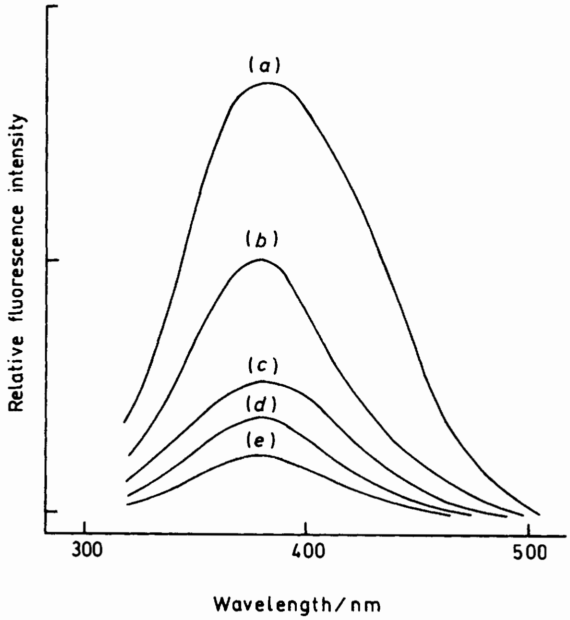

Figure 4. Temperature effects on the fluorescence of BP (10^{-4} mol dm^{-3}) in methylcyclohexane. Excitation wavelength = 313 nm. Temperature: (*a*) 10; (*b*) 20; (*c*) 30; (*d*) 40; (*e*) 50 °C.

higher vibrational states of the S_1 state ($^1BP^{*\ddagger}$) but not from the fluorescent state ($^1BP^*$).

Temperature† *Effects*.—The dependence of reaction or emission efficiency on temperature has often been investigated in order to verify reaction or emission from a higher excited electronic state or a vibrationally hot S_1 state.[10] We examined temperature effects on the fluorescence intensity (I_f) and quantum yield for the photolysis ($\Phi_{-\mathrm{BP}}$) of BP in the range 10–60 °C in order to gain additional evidence for the proposed mechanism (Scheme 2). A significant decrease in the BP fluorescence intensity with increased temperature was observed while the emission maximum and band shape remained unaltered (Figure 4). The observed change in fluorescence intensity was found to be reversible in this temperature range. In addition to a negligible dependence of the u.v. absorption spectrum on temperature, BP decomposed to a very small extent during the fluorescence measurements. These observations suggest that there is some activated non-radiative decay process competing with radiative decay (fluorescence).

If the reaction takes place from the fluorescent state in competition with radiative and non-radiative decay processes, then $\Phi_{-\mathrm{BP}}$ is expected to decrease to an extent comparable to that for a decrease in the fluorescence intensity because the process for N–O bond cleavage in an excited BP molecule is thought to require a very small activation energy which implies that the photochemical process has an almost temperature-independent rate constant. The values of $\Phi_{-\mathrm{BP}}$, after irradiation at 313 nm, were determined to be 0.27 ± 0.01, 0.29 ± 0.01, and 0.32 ± 0.01 in methylcyclohexane at 20, 40, and 60 °C, respectively. The finding that the quantum yield increases slightly with increased temperature is not consistent with our expectation and hence constitutes additional support to the assumption that the fluorescence and photolysis are not competitive processes occurring from the same vibronic state.

Because the N–O bond in a BP molecule undergoes homolytic cleavage in the excited singlet state,[4] it is likely that the N–O stretching vibrational modes of the S_1 state promote the reaction more efficiently compared with other vibrational modes as in the case of 3,3-dimethyl-3*H*-benzo[*f*]chromene.[11] However, the poorly defined vibrational structure of the first absorption band [250–350 nm, curve (*a*) in Figure 1] made it difficult to assign each vibrational mode in this absorption band.

Experimental

Materials.—1-Benzyloxy-2-pyridone (BP) was the same as in the previous study.[4] 1-Benzyloxy-5-bromo-2-pyridone (BBP) was prepared by treatment of 5-bromo-2-ethoxypyridine 1-oxide with benzyl chloride according to the method of Paquette.[12] The crude BBP was purified by column chromatography over silica gel (70–230 mesh, Merck) using $CHCl_3$ as the eluant followed by repeated recrystallization from hexane–EtOAc to give colourless needles, m.p. 65.5–67.0 °C (Found: C, 51.5; H, 3.5; N, 4.95. $C_{12}H_{10}BrNO_2$ requires C, 51.45; H, 3.60; N, 5.00%); δ_H(200 MHz; $CDCl_3$) 7.40 (5 H, s), 7.30 (1 H, dd, *J* 7.8, 2.7 Hz), 7.27 (1 H, d, *J* 3.0 Hz), 6.61 (1 H, dd, *J* 7.8, 3.0 Hz), and 5.27 (2 H, s). 5-Bromo-2-pyridone was synthesized by the method of Tee and Parenti,[13] then recrystallized from benzene, m.p. 178–180 °C (lit.,[14] 175–177 °C). The structure of this compound was also established by i.r. and n.m.r. spectroscopy. 2,5-Dimethylhexa-2,4-diene and dibromomethane were fractionally distilled and stored under nitrogen in a refrigerator.

Solvents.—Cyclohexane and benzene were of spectroscopic grade and were used as received. Methanol, ethanol, acetonitrile, and methylcyclohexane were purified according to standard methods.[15] All solvents used for measuring emission spectra showed no significant impurity emission both at room temperature and at 77 K.

Measurements.—U.v. absorption and fluorescence spectra at room temperature were measured with a Shimadzu UV-210A spectrophotometer and a Shimdazu RF-500 spectrophoto-

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† In addition to temperature effects we attempted to observe wavelength effects on $\Phi_{-\mathrm{BP}}$. It was found that the photolysis of BP at 254 nm afforded the same products as those derived from the photolysis at 313 nm. However, careful examination of the wavelength effects reveals that the absorption of incident light by the photoproducts (mainly benzaldehyde and 2-pyridone) appreciably lowers the accuracy of the estimated quantum yields [$\Phi_{-\mathrm{BP}}$ (254 nm)] even at low conversions owing to much stronger absorption of the products (molar absorption coefficient at 254 nm, ε_{254} = 6 000 dm^3 mol^{-1} cm^{-1}) compared with that of the starting BP (ε_{254} = 500 dm^3 mol^{-1} cm^{-1}).

fluorimeter, respectively. Phosphorescence spectra were determined on a Shimadzu RF-500 spectrophotofluorimeter equipped with a cylindrical rotating sector at 77 K. Relative emission quantum yields were determined by measuring the emissions of solutions of BP and BBP, the absorbances of which at 313 nm are both 0.1 under the same conditions. The cut and weigh method was applied to these determinations.

Quantum yields for the reaction were determined according to the method of Hatchard and Parker[7] which employs a potassium trioxalatoferrate(III) actinometer solution. A 450 W high pressure Hg lamp was used as the light source from which light of wavelength 313 nm for irradiation was isolated by means of potassium chromate (0.002 mol dm^{-3}) in a 1% aqueous solution of potassium carbonate and Corning 7–54 filters. All the quantum yields obtained under nitrogen at low conversions (10–20%) are average values from more than three determinations. The only photoproduct to absorb at 313 nm was 2-pyridone and 5-bromo-2-pyridone the rate of disappearance of which was found to be much slower than that of the starting BP and BBP under our irradiation conditions. Thus secondary photoreactions of the primary photoproducts must be negligible at low conversions. The amount of BP and BBP consumed was determined spectroscopically from absorbance changes at wavelengths where the differences in the molar extinction coefficient between the starting material and 2-pyridones were the largest.

For the purpose of isolating the photoproducts, a solution of BP or BBP (10^{-2} mol dm^{-3}) in acetonitrile (250 ml), placed in a Pyrex vessel, was irradiated for 30 min under nitrogen with a Pyrex-filtered light from a 400 W high pressure Hg lamp. After the solvent had been removed by evaporation, the resulting residue was chromatographed on silica gel (70–230 mesh, Merck) eluting with benzene and then with chloroform to give benzaldehyde (70–80% yield) and 2-pyridones (66–70% yield) as main products. The formation of a small amount of benzyl alcohol (4–6% yield) was confirmed by g.l.c. analysis of the photolysate. It was shown that the photolysis of BP or BBP (10^{-4} mol dm^{-3}) at 313 nm in any solvent employed affords benzaldehyde and 2-pyridones (2-pyridone or 5-bromo-2-pyridone) in more than 90% yield by comparison of the u.v. absorption with those of authentic benzaldehyde and 2-pyridones.

The reaction temperature was controlled by circulating water of a given temperature through a jacketed reaction vessel. The temperature of a solution for measuring the fluorescence was controlled similarly.

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