The Photolysis of 1-Benzyloxy-2-pyridone and its Methyl Derivatives. Correlation with ^1H NMR-derived Ground-state Conformation

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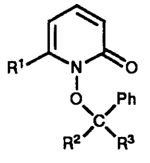
In addition to methyl substituent effects on the reactivities of the vibrationally unrelaxed excited singlet state of 1-benzyloxy-2-pyridone (1), deuterium isotope effects on the reaction efficiencies of (1) and its methyl derivatives are discussed on the basis of their major ground-state conformations, as analysed by ^1H NMR spectroscopy. It is suggested that intramolecular hydrogen abstraction of the benzylic hydrogen by the amido carbonyl oxygen in (1) competes with N–O bond cleavage in polar solvents. Effects exerted by both a methyl group and a non-polar solvent are manifested by the predominant N–O bond cleavage in the vibrationally 'hot' excited singlet state.

A molecule, excited to higher vibrational levels of the first excited singlet (S_1) state, rapidly transfers its excess vibrational energy to the medium to reach the lowest vibrational level of the S_1 state (fluorescent state). Thus, the usual photochemical processes in condensed phases generally occur from this vibrationally relaxed S_1 state in competition with radiative and non-radiative decay processes. There are, however, several studies concerning reactions from a vibrationally unrelaxed electronic excited state.[1–12] Such reactions have been proposed to rationalize the wavelength dependence of emission or reaction quantum yields in condensed phases at room or low temperature.[8–11]

Previously we have reported an intriguing photolysis of 1-benzyloxy-2-pyridone (1) which takes place from the vibrationally 'hot' S_1 state, based on internal and external heavy-atom effects on the emission and reaction efficiencies of this molecule.[13] A methyl substituent introduced into the pyridone ring or the benzylic position is expected to affect the reactivity of the parent molecule. For this purpose we have prepared 1-(α-methylbenzyloxy)-2-pyridone (2) and 1-benzyloxy-6-methyl-2-pyridone (3).



(1) $R^1 = R^2 = R^3 = H$
(2) $R^1 = R^2 = H, R^3 = Me$
(3) $R^1 = Me, R^2 = R^3 = H$
($^2H_2$)-(1) $R^1 = H, R^2 = R^3 = {}^2H$
($^2H_1$)-(2) $R^1 = H, R^2 = {}^2H, R^3 = Me$
($^2H_2$)-(3) $R^1 = Me, R^2 = R^3 = {}^2H$

Conversely, the Franck–Condon principle suggests that (1), in the vibrationally unrelaxed excited singlet state, may adopt the ground-state conformation, which has been analysed by means of ^1H NMR spectroscopy. In addition, deuterium isotope effects on the reactivities of (1)–(3) are discussed on the basis of their major conformations.

Results and Discussion

External Heavy-atom and Temperature Effects.—As in the case of (1), the photolysis of (2) with 313 nm light under nitrogen gives 2-pyridone and acetophenone as main products while (3) forms mainly 6-methyl-2-pyridone and benzaldehyde on photolysis under the same conditions. In both photolyses a small amount of alcohol (α-methylbenzyl alcohol or benzyl alcohol) is also obtained. The phosphorescence intensity of (2) (10^{-4} mol dm^{-3}; the first singlet excitation energy, $E_{S_1} = 81$; the first triplet excitation energy, $E_{T_1} = 64$ kcal mol^{-1})* and of (3) (10^{-4} mol dm^{-3}; $E_{S_1} = 82$; $E_{T_1} = 63$ kcal mol^{-1}) was reduced to one-half or one-third its initial intensity in the presence of 2,5-dimethylhexa-2,4-diene (10^{-2} mol dm^{-3}; $E_{S_1} = 103$; $E_{T_1} = 59$ kcal mol^{-1})[14] in methylcyclohexane or in the presence of hexa-2,4-dien-1-ol (10^{-2} mol dm^{-3}; $E_{S_1} > 82$; $E_{T_1} = 60$ kcal mol^{-1})[14] in methanol–ethanol (1:1 v/v) at 77 K. However, these triplet quenchers do not affect the quantum yields for the disappearance of both (2) (φ_{-2}) and (3) (φ_{-3}) irradiated at 313 nm under nitrogen at room temperature. These results indicate that the photolysis of (2) and (3) and that of (1) proceeds preferentially through the excited singlet state.

We examined the effects of added dibromomethane (DM) on the emission and reaction of (2) and (3) in order to confirm that the N–O bond cleavage in these two molecules takes place from higher vibrational levels of the first excited singlet state ('hot' S_1 state). As seen from the data collected in Table 1, the fluorescence intensity (I_f) of (2) and (3) decreases with increased concentration of added DM both in cyclohexane and in methanol, whereas the quantum yields for the reaction (φ_{-2} and φ_{-3}) are not affected by added DM in these two solvents. The phosphorescence intensity of (2) and (3) (10^{-4} mol dm^{-3}) in the presence of DM (10^{-2} mol dm^{-3}) is increased by a factor of 3–10 in methylcyclohexane and methanol–ethanol (1:1 v/v) at 77 K. These findings demonstrate that the fluorescent state of these molecules is subject to pronounced external heavy-atom effects and hence are consistent with the mechanism in which the N–O bond cleavage occurs from the 'hot' S_1 state as in the case of (1). Further supporting evidence for the 'hot' S_1 mechanism is obtained from a comparison of temperature effects on the fluorescence intensity and reaction efficiency of (2) and (3) with those of (1) (Table 2). The fluorescence intensity of (2) and (3) decreased with increased temperature to almost the same extent as that of (1), while all the quantum yields (φ_{-1}, φ_{-2}, and φ_{-3}) increased slightly in the temperature range investigated. Thus we can conclude that the photolysis of (2) and (3) also proceeds through the vibrationally unrelaxed S_1 state.

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* 1 cal = 4.184 J.

Table 1. Effects of added dibromomethane (DM) on the fluorescence (I_f at 24 ± 1 °C) and reaction (φ at 25 ± 2 °C) of **(2)** and **(3)** under nitrogen.[a]

Solvent		[DM]/10^{-3} mol dm^{-3}					
		0	0.5	1.0	2.0	5.0	10.0
Cyclohexane	I_f(**2**)[b]	1.0	0.77	0.67	0.59	0.48	0.29
	φ_{-2}[b]	1.0	1.0	0.90	1.0	1.1	0.90
Methanol	I_f(**2**)[b]	1.0	0.83	0.67	0.50	0.38	0.33
	φ_{-2}[b]	1.0	0.90	0.90	1.0	0.90	0.90
Cyclohexane	I_f(**3**)[b]	1.0	0.49	0.36	0.31	0.29	0.28
	φ_{-3}[b]	1.0	1.0	1.0	1.0	1.0	1.0
Methanol	I_f(**3**)[b]	1.0	0.63	0.53	0.45	0.32	0.25
	φ_{-3}[b]	1.0	0.90	0.90	0.90	1.0	1.0

[a] Excitation wavelength = 313 nm; [**(2)**] = [**(3)**] = 10^{-4} mol dm^{-3}. [b] Relative values.

Table 2. Temperature effects on the fluorescence (I_f) and quantum yield of reaction (φ) of **(1)**–**(3)** under nitrogen in methylcyclohexane.[a]

	T/°C					
	10	20	30	40	50	60
I_f(**1**)[b,c]	1.0	0.60	0.34	0.25	0.16	
φ_{-1}[b,c]		1.0		1.07		1.19
I_f(**2**)[b,d]	1.0	0.59	0.34	0.23	0.16	
φ_{-2}[b,d]		1.0		1.26		1.44
I_f(**3**)[b,d]	1.0	0.45	0.33	0.25	0.17	
φ_{-3}[b,d]		1.0		1.14		1.31

[a] Excitation wavelength = 313 nm; [**(1)**] = [**(2)**] = [**(3)**] = 10^{-4} mol dm^{-3}. [b] Relative values. [c] Results from previous work (see reference 13). [d] Present work.

Table 3. Substituent effects on the quantum yield of reaction (φ) of **(1)** under nitrogen at 25 ± 3 °C.

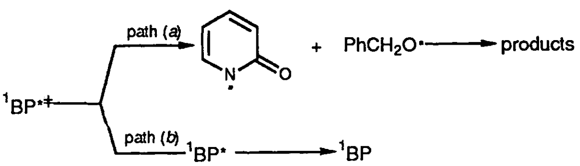
Solvent	φ_{-1}[a,b]	φ_{-2}[a,c]	φ_{-3}[a,c]
Cyclohexane	0.27 ± 0.03	0.25 ± 0.03	0.36 ± 0.02
Benzene	0.24 ± 0.02	0.25 ± 0.02	0.38 ± 0.03
Acetonitrile	0.22 ± 0.03	0.27 ± 0.03	0.48 ± 0.03
Methanol	0.29 ± 0.01	0.33 ± 0.04	0.34 ± 0.03

[a] Irradiation wavelength = 313 nm; [**(1)**] = [**(2)**] = [**(3)**] = 10^{-4} mol dm^{-3}. [b] Results from previous work (see reference 13). [c] Present work.

Effects of Methyl Substituents.—Simonaitis and Pitts have observed that methyl substitution in the α-position of γ-butyrolactone increases the quantum yield for the formation of the formate, whereas a methyl group in the γ-position does not greatly affect this quantum yield; the carbon–carbonyl carbon bond cleavage reaction possibly takes place from higher vibrational levels of an excited state.[11] Very recently it has been found that the introduction of a methyl group may promote vibrational relaxation of a vibrationally 'hot' molecule to suppress the reaction.[12]

As already mentioned no methyl group introduced into **(1)** affects the product distribution and the reactive state from which N–O bond cleavage occurs. In order to investigate the effects of a methyl group on the reactivity of the 'hot' S_1 state of **(1)**, the quantum yields (φ_{-2} and φ_{-3}) were determined in various solvents under the same conditions as those for **(1)**[15] and the data obtained are given in Table 3 which also lists data for the photolysis of **(1)** (φ_{-1}) for comparison. An examination of Table 3 reveals that substitution of a methyl group for hydrogen at the 6-position of the pyridone skeleton increases the reactivity of **(1)** in solvents other than methanol but that the methyl group at the benzylic position only alters the reactivity to a very small extent. On the other hand, there is not much difference in the reactivity of the 'hot' S_1 state in methanol which can form a hydrogen bond to the carbonyl oxygen atom of **(1)**–**(3)**.[16] This hydrogen-bond formation in the ground state is deemed to be responsible for the similar values of the quantum yields obtained in this polar protic solvent.

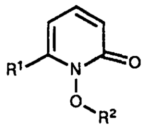
We have previously suggested that the N–O bond in **(1)** undergoes homolytic cleavage in the 'hot' S_1 state to give the amidyl and benzyloxyl radicals in competition with vibrational relaxation to the fluorescent state.[13,17] The increased quantum yield of **(3)** is then due to either an increase in the rate of the N–O bond cleavage [path (*a*)] or a decrease in the rate of vibrational relaxation [path (*b*)] or both (Scheme 1). On the contrary, the minor difference between the quantum yields of **(1)** and **(2)** is explained in terms of the theory that a methyl group at the benzylic position may not influence the relative rate of both processes or their rates.



Scheme 1. * Electronic excitation. ‡ Vibrational excitation.

Conformational Analysis.—The conformation of hydroxylamines has received considerable attention recently because the conformational interconversion of these molecules is associated with a substantial energy barrier, both to rotation about the N–O bond and to nitrogen inversion.[18] The possibility of the rate-determining nitrogen inversion can be excluded by using a model system in which the co-ordination geometry around the nitrogen atom is flattened by its incorporation into a ring and its conjugation to the carbonyl group adjacent to the nitrogen atom.[19,20]

^{1}H NMR studies have indicated that rotation about the N–O bond in cyclic hydroxamic acid derivatives, the structures of which are very similar to those of (1)–(3), possesses an energy barrier of 9–10 kcal mol^{-1}.[20] On the basis of the Franck–Condon principle and the fact that there is a substantial energy barrier to this rotation, the conformation in the vibrationally unrelaxed excited singlet state can be assumed to adopt the ground-state conformation, which has been analysed by ^{1}H NMR spectroscopy. For this purpose we have obtained ^{1}H NMR spectra of (1)–(3) along with those of 1-hydroxy-2-pyridone (4), 1-ethoxy-2-pyridone (5), 1-hydroxy-6-methyl-2-pyridone (6), *O*-benzylhydroxylamine (7), and α-methylbenzyl alcohol (8) as reference compounds.



(4) $R^1 = R^2 = H$
(5) $R^1 = H, R^2 = Et$
(6) $R^1 = Me, R^2 = H$

$PhCH_2ONH_2$ **(7)**

$PhCH(Me)OH$ **(8)**

As shown in Table 4, on *O*-benzylation of (4) the signals arising from the pyridone ring protons are shifted upfield relative to those of (4), in the following order: 3-H ($\Delta\delta$ = 0.03) < 4-H (0.13) < 5-H (0.42) < 6-H (0.66). An examination of the spectrum of (5) establishes that this substantial upfield shift of the 5-H and 6-H signals must be due mainly to the presence of the benzene ring in (1), because all the pyridone ring proton signals are shifted to higher field by only 0.05–0.23 ($\Delta\delta$) on *O*-ethylation of (4). In contrast, an appreciable downfield shift ($\Delta\delta$ = 0.62) of the benzylic proton signal of (1), compared with that of (7), was observed whereas the phenyl protons of (1) resonate only very slightly downfield.

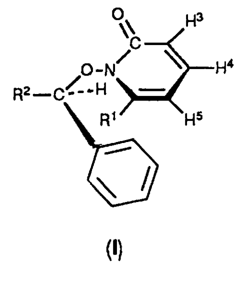
From an X-ray crystal-structure analysis of hydroxamic acids it has been found that the N–O–H plane approximately bisects the bond angle formed by the C(=O)–N–C bond.[21] This finding suggests that the N–O–C(H_2) plane in (1) will also be almost perpendicular to the planar pyridone ring when the compound is in solution. Thus an upfield shift of 5-H and (especially) 6-H signals and a downfield shift of the benzylic proton signal of (1) can be accounted for in terms of the conformation shown below, in which 6-H is placed above the shielding zone of the benzene ring and the benzylic protons are situated in the deshielding region of the amido carbonyl group. The conformations (I) and (II) are mirror images of each other for (1; R^1 = 6-H, R^2 = H) and (3; R^1 = 6-Me, R^2 = H) but not for (2; R^1 = 6-H, R^2 = Me).

Based on this conformation one can explain an upfield shift of the 6-Me signal [$\Delta\delta$ = 0.29, (6) as the reference] and a downfield shift of the benzylic proton signal [$\Delta\delta$ = 0.61, (7) as the reference] observed for (3) in addition to an upfield shift of the 6-H signal [$\Delta\delta$ = 0.86, (4) as the reference] in (2). On the other hand, the conformations of (2) corresponding to (I) and (II) are isomeric with each other. Although we cannot determine at present which conformation is the major contributor, the observation that both methyl and methine protons at the benzylic position of (2) are subject to the deshielding effects of the amido carbonyl group indicates that both conformations (I) and (II) exist in solution. The extent of any upfield or downfield shifts of the proton signals concerned does not differ much between (1) and its methyl derivatives, and this demonstrates that the introduction of a methyl group into (1) does not greatly alter the conformation of this molecule.

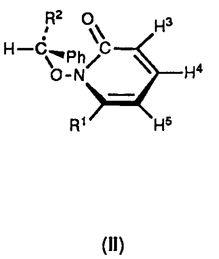
In order to obtain additional evidence to support the existence of the conformations described, variable-temperature ^{1}H NMR measurements on (1)–(3) were carried out in dichloro($^2H_2$)methane over the range of 24 to −80 °C. However, we were unable to find the coalescence temperature of any molecule, and so there was no definitive evidence for the exclusive existence of (I) and/or (II) in solution. Thus our results cannot rule out the possibility that small amounts of other conformations are present. From ^{1}H NMR spectral analysis of *N*-acylhydroxylamines at different temperatures, Riddell and Turner have indicated that the ^{1}H NMR spectra obtained at low temperature can be explained in terms of two conformations the interconversion of which occurs with rotation about the N–O bond.[19] In addition to our ^{1}H NMR results their finding suggests that conformations (I) and/or (II) exist in significant proportions in the ground state.

Deuterium Isotope Effects.—Simple inspection of the major conformations (I) and/or (II) shows that the benzylic protons are located spatially near the carbonyl oxygen atom, so it would be expected that the hydrogen abstraction by this oxygen atom may compete with the N–O bond cleavage in the 'hot' S_1 state. If so, the replacement of the benzylic hydrogen by deuterium would slow down the rate of hydrogen abstraction, and so reduce the reaction efficiency.[22] Quantum yields for the disappearance of ($^2H_2$)-(1), ($^2H_1$)-(2), and ($^2H_2$)-(3) were determined under the same conditions as those for the corresponding undeuteriated compounds and the data obtained are collected in Table 5.

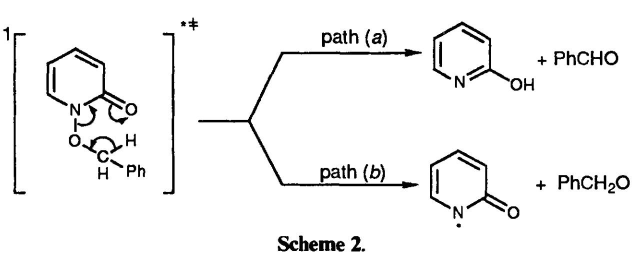
Negligible deuterium isotope effects on the quantum yields of any compound (φ_H/φ_D = 1.0) were observed in cyclohexane and benzene, suggesting that the N–O bond cleavage is the predominant reaction in these non-polar solvents. Interestingly there are small but perceivable isotope effects for the photolysis of (1) in acetonitrile (φ_H/φ_D = 1.6) and in methanol (φ_H/φ_D = 2.1). This finding implies that the hydrogen abstraction [path (*a*) Scheme 2], which is likely to proceed through a six-membered cyclic transition state, may compete with the N–O bond cleavage (path *b*) in the 'hot' S_1 state if no deuterium substitution affects the rates of both vibrational relaxation and the N–O bond cleavage in polar solvents. This assumption is



(I)



(II)



Scheme 2.

Table 4. ^{1}H NMR spectral data of (**1**)–(**8**) obtained in ($^2H_1$)chloroform at 24 °C.

	δ(ppm)								
Compound	3-H	4-H	5-H	6-H	6-Me	PhC*H*$_2$	PhC*H*Me	PhCH*Me*	Ph
(**4**)	6.71	7.39	6.34	7.78					
(**5**)	6.66	7.33	6.15	7.55					
(**1**)	6.68	7.26	5.92	7.12		5.28			7.37
(**7**)						4.66			7.34
(**6**)	6.56	7.26	6.16		2.48				
(**3**)	6.54	7.17	5.88		2.19	5.27			7.39
(**2**)	6.61	7.17	5.77	6.92			5.64	1.71	7.34
(**8**)							4.76	1.40	7.28

Table 5. Deuterium isotope effects on the quantum yields (φ_H/φ_D) for the disappearance of (**1**)–(**3**) under nitrogen at 25 ± 3 °C.[a]

Solvent	$\varphi_{-1(d_2)}$	φ_H/φ_D(**1**)[b]	$\varphi_{-2(d)}$	φ_H/φ_D(**2**)[c]	$\varphi_{-3(d_2)}$	φ_H/φ_D(**3**)[c]
Cyclohexane	0.26 ± 0.03	1.0	0.26 ± 0.03	1.0	0.38 ± 0.02	1.0
Benzene	0.24 ± 0.02	1.0	0.25 ± 0.02	1.0	0.39 ± 0.04	1.0
Acetonitrile	0.14 ± 0.01	1.6	0.35 ± 0.02	0.8	0.56 ± 0.03	0.9
Methanol	0.14 ± 0.03	2.1	0.37 ± 0.04	0.9	0.28 ± 0.02	1.2

[a] Irradiation wavelength = 313 nm. [($^2H_2$)-(**1**)] = [($^2H_1$)-(**2**)] = [($^2H_2$)-(**3**)] = 10^{-4} mol dm^{-3}. The values of φ_H for the undeuteriated compounds are shown in Table 3. [b] Results from previous work (see reference 17). [c] Present work.

valid since the isotope effects on the values of φ_{-2} and φ_{-3} are not detected within the experimental error of 10–20% in the same polar solvents (φ_H/φ_D = 1.0 ± 0.2). Thus (**1**) and its methyl derivatives are inferred to adopt mainly a conformation which is slightly different from (**I**) and/or (**II**), depending on the nature of the solvent employed, although conformational analysis by ^{1}H NMR spectroscopy could not clarify this point. In addition, the introduction of a methyl group may change the major conformation of (**1**) so to reduce the likelihood that the benzylic hydrogen atoms are within abstracting distance of the carbonyl oxygen atom, owing to the steric bulkiness of this group. Because (**2**) possesses the chiral benzylic carbon atom, there are two forms for both conformations (**I**) and (**II**). Thus the hydrogen abstraction in (**2**) can occur from only one of the two forms, therefore the methyl group at the benzylic position reduces the reactivity for the hydrogen abstraction reaction of (**2**) compared with those of (**1**) and (**3**). This also may be responsible for the lack of deuterium isotope effects for (**2**).

Experimental

Materials.—1-Hydroxy-2-pyridone, 1-ethoxy-2-pyridone, 1-benzyloxy-2-pyridone, and 1-[(α-$^2H_2$)benzyloxy]-2-pyridone [($^2H_2$)-(**1**)] were prepared and purified according to the previously described procedures.[17] Similar methods were used to synthesize 1-hydroxy-6-methyl-2-pyridone (**6**), 1-(α-methylbenzyloxy)-2-pyridone (**2**), 1-benzyloxy-6-methyl-2-pyridone (**3**), 1-[α-methyl-α-($^2H_1$)benzyloxy]-2-pyridone [($^2H_2$)-(**2**)], and 1-[(α-$^2H_2$benzyloxy)]-6-methyl-2-pyridone [($^2H_2$)-(**3**)]. The content of deuterium in ($^2H_2$)-(**1**), ($^2H_1$)-(**2**), and ($^2H_2$)-(**3**) was determined to be 98 atom% by ^{1}H NMR spectroscopy. The physical properties of these compounds are the following. (**6**): m.p. 141–142 °C (from water) (lit.,[23] 141–142 °C); ν_{max} 2 430 (br, OH) and 1 640 cm^{-1} (CO); (**2**), m.p. 59–60 °C (from hexane–EtOAc); ν_{max} 1 660 cm^{-1} (CO); (Found: C, 72.4; H, 6.1; N, 6.6. $C_{13}H_{13}NO_2$ requires C, 72.56; H, 6.05; N, 6.51%); (**3**), m.p. 104.5–106 °C (from hexane–EtOAc); ν_{max} 1 670 cm^{-1} (CO); (Found: C, 72.8; H, 6.1; N, 6.5. $C_{13}H_{13}NO_2$ requires C, 72.56; H, 6.05; N, 6.51%). *O*-Benzylhydroxylamine and α-methylbenzyl alcohol were purified by distillation under reduced pressure. Purification of hexa-2,4-dien-1-ol was accomplished by distillation *in vacuo* followed by repeated fractional crystallization. Dibromomethane, 2,5-dimethylhexa-2,4-diene, cyclohexane, benzene, methanol, ethanol, acetonitrile, and methylcyclohexane were of the same purity as in the previous study.[13]

Measurements.—^{1}H NMR spectra were obtained on a JEOL FX-200 spectrometer in ($^2H_1$)chloroform at 24 °C. The chemical shifts were determined using tetramethylsilane as an internal standard. Other instrumentation and general methods including quantum yields, product analyses, and temperature effects have been described previously.[13]

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