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Heterogeneous hydrogen and deuterium transfer in the excited state of 2-methylbenzophenone in ether–pentane–alcohol glasses at 77 K

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Abstract

The phosphorescence decays of benzophenone, 2-methylbenzophenone (OMBP), 3-methylbenzophenone, 4-methylbenzophenone PMBP), and deuterated analogues of the *ortho* and *para* derivatives have been observed at 77 K in ether–pentane–alcohol glasses. The decays were fitted to gaussian distributions of exponentials. An isotope effect on the decay is observed in the OMBP case, but not for PMBP. All decays, except those of the two OMBP derivatives, were well fitted to single-moded distributions of 5–6 ms with standard deviations of about 1 ms. The somewhat faster and markedly less homogeneous decay of the OMBP derivatives is attributed to internal hydrogen abstraction whose rate is dependent on the conformation of the molecule and is competitive with radiative and other non-radiative decay pathways. Supporting this hypothesis is the observation of a fluorescence attributed to the appearance of the appropriate *ortho*-quinodimethane enol.

Keywords: Heterogeneous hydrogen transfer; Heterogeneous deuterium transfer; Excited state; 2-Methylbenzophenone

1. Introduction

Numerous studies on the Norrish type-II reaction of ketones based on product analysis, quenching experiments and absolute rate measurements have been carried out in solution and organized or rigid systems at ordinary temperatures [1]. Reported activation parameters ($E_a = 2$–4 kcal mol^{-1}; $\log A = 9$–11) [2–5] suggest the possibility that activated intramolecular hydrogen atom transfer at cryogenic temperatures might be competitive with radiative and other non-radiative decay pathways of n–π^* triplets (10^2–10^4 s^{-1}). Indeed, the photoenolization of certain *ortho*-methylaryl ketones has been shown to occur in polar (ether–pentane–alcohol (EPA)) glasses at 77 K to give the corresponding photoenols [6,7]. However, recent reports by Al-Soufi et al. [8] and Gritsen et al. [6] implicate the importance of hydrogen atom tunneling below about 125 K and in the singlet manifold respectively. Recent work in our own laboratories strongly suggests that quantum-mechanical tunneling is the dominant triplet deactivation mechanism for 1,4-dimethylanthrone derivatives below about 30 K [9,10].

The methylanthrone study concerned a case of a rigid, nearly ideal hydrogen abstraction geometry. In order to probe the geometrical requirements of hydrogen abstraction, it would be ideally desirable to study a series of ketones, each of which was rigid, but with successively poorer geometries, and work toward this goal is ongoing in one of our laboratories [11]. Here we report a study of the phosphorescence of a flexible molecule, 2-methylbenzophenone (OMBP), and its derivatives, a case in which the matrix holds many different conformations at once.

Under favorable circumstances, it is possible to rely on the observation of phosphorescence for a very simple strategy for the study of photochemical hydrogen abstraction. With this in mind, and with the goal of exploring a methodology for a kinetic study of solid-state reactions, in which transient absorption experiments are inherently much more difficult than for solution work, we address here the significance of hydrogen atom abstraction at cryogenic temperatures in the case of OMBP. It represents the more general case, in which a distribution of conformations with varying "qualities" is expected and observed.

To the extent that ^{3}OMBP has similar radiative and radiationless decay rates (other than H abstraction) as triplet benzophenone (^{3}BP), comparison of phosphorescence yields and decay traces of the ketones should reflect the importance of the prospective hydrogen abstraction reaction of the former. To help to confirm our assignments, we have considered conformational heterogeneity by inclusion of 3-methylbenzophenone (MMBP) and 4-methylbenzophenone (PMBP)

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and isotope effects by including 2-(d_3-methyl)-benzophenone (d_3-OMBP) and d_7-4-methylbenzophenone (d_7-PMBP). These compounds also serve as controls for any small electronic effects due to methylation of the aromatic ring.

2. Experimental details

2.1. Materials

BP, OMBP, MMBP and PMBP were obtained commercially (Aldrich) and purified by repeated recrystallization or by chromatography on silica, as appropriate, until impurities were not observed by capillary gas chromatography. d_3-OMBP was obtained by repeated photolysis of OMBP in a mixture of acetonitrile:D_2O (9:1) followed by purification by chromatography. Proton nuclear magnetic resonance was used to determine the extent of deuteration. d_7-PMBP was prepared by Friedel-Crafts condensation of d_8-toluene (Aldrich) and benzoyl chloride (Aldrich) and similarly purified.

Ethanol and ethyl ether were freshly distilled from CaH_2 immediately before use. 2-Methylbutane (Aldrich) was spectro grade and used as received. Solvent blanks were free from absorption in the relevant regions and free from emission.

2.2. Spectroscopy

Most spectra and all lifetimes were obtained with an Edinburgh FL900 spectrometer. Some spectra were obtained with a SPEX-Fluorolog spectrometer equipped with an R 928 PMT and a 1943D phosphorimeter. Excitation was generally at 260 nm. Samples were optically dilute (optical density, less than 0.1) at the excitation wavelength, bubbled with Ar to remove O_2, and quick frozen by immersion in liquid nitrogen.

2.3. Fits

Lifetimes were fitted to gaussian distributions of exponentials [12–15] using software provided by Edinburgh Instruments. In essence, rather than fixing a number of exponentials, the fitting routine returns one or more gaussian "bands", each with a central lifetime and width. Decays that are reasonably well fitted by two (or more) closely spaced exponentials with comparable contributions are usually well fitted by a single-moded distribution fit whose width is comparable with the difference between the two exponential lifetimes. The values of X^2 are not necessarily better with the distribution fit, since the comparison is being made to polyexponentials, which are also notoriously flexible. As the molecules reported here are frozen in glasses in a wide variety of conformations and environments, the distribution fits make more physical sense than a fixed, two-exponential or three-exponential fit. As a calibration for the significance of the reported widths, in our experience when a decay that is well-fitted by a single exponential (e.g. fluorescence decay of anthracene in solution) is subjected to distribution analysis, it returns a single-moded distribution with a central lifetime nearly identical with the single-exponential value and a width usually 10% or less of the lifetime.

3. Results and discussion

The phosphorescence spectra of BP, MMBP, PMBP and d_7-PMBP in EPA at 77 K are virtually identical. The spectra of OMBP and d_3-OMBP are virtually identical with each other but somewhat blue-shifted (about 4 nm) and broadened relative to that of BP (Fig. 1). In pure hydrocarbon solvents, the observed spectra were dependent on excitation wavelength and somewhat time dependent, as has been observed with other ketones [16–18]. In the present case, spectra obtained in EPA (ether:pentane:alcohol, 5:5:2) glass were found to be essentially insensitive to excitation wavelength and were time independent. Therefore studies were conducted with EPA to simplify analysis.

Under conditions of conformational freedom, OMBP is known to undergo quantitative intersystem crossing and to possess a triplet lifetime determined by an intramolecular hydrogen atom transfer [19–22]. Fast reaction has been shown to occur only from *syn* conformers of ^{3}OMBP (Fig. 2). Based on the well-known behavior of several unreactive aryl ketones at 77 K, unusual spectral and/or kinetic heterogeneity (i.e. non-exponential decay) in the case of ^{3}OMBP should be an indication of a competing hydrogen abstraction whose rate is dependent on conformation and/or site effects in the glass. MMBP and PMBP serve as controls for conformational and electronic effects induced by the methyl group.

The relative phosphorescence intensities of BP, OMBP and d_3-OMBP, measured in triplicate with optically matched glasses, are shown in Table 1. The phosphorescence intensities of OMBP and d_3-OMBP are smaller than those of BP with relative values of 0.59 ± 0.02 and 0.67 ± 0.05 respectively. The decrease in intensity for OMBP, relative to BP, and the isotope effect on intensity are suggestive that internal

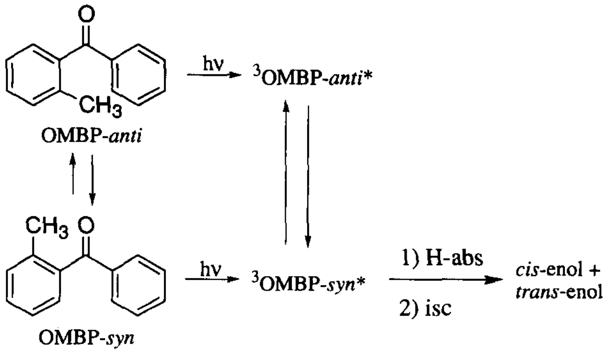

Fig. 1. A two-conformer model in the photoenolization of OMBP.

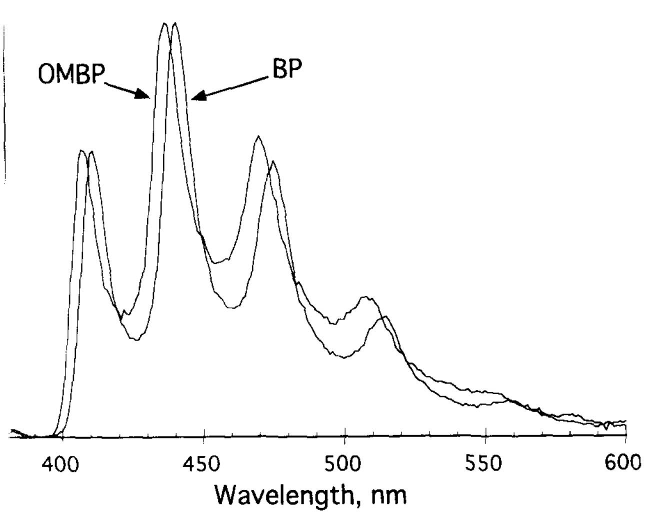

Fig. 2. Phosphorescence spectra of BP and OMBP in EPA at 77 K.

Table 1
Phosphorescence data

Compound	Relative intensity	Average τ [a] (ms)	Contribution [b] (%)
BP	1.00	5.4 ± 0.8	
d_3-OMBP	0.67 ± 0.05	3.5 ± 1.0	99
		0.8 ± 0.1	1
OMBP	0.59 ± 0.02	2.8 ± 0.8	97.5
		0.5 ± 0.1	2
		0.06 ± 0.01	0.5
MMBP		5.9 ± 1.0	
PMBP		6.0 ± 1.0	
d_7-PMBP		5.9 ± 1.0	

[a] Center of gaussian distribution and width of distribution.

[b] Approximate contribution of each gaussian band calculated from the amplitude and lifetime of center value.

hydrogen abstraction by OMBP is probably a competitive pathway for deactivation of ^{3}OMBP. However, further insight and stronger evidence were obtained by examination of the actual decays of these and related compounds.

Conformational distributions of flexible molecules and site effects in EPA glasses at 77 K almost invariably lead to non-exponentiality of phosphorescence decays, although these deviations often go unreported [23]. In some cases of rigid molecules (e.g. anthrone), rigorously exponential decays are observed at 77 K but, even then, site effects can cause kinetic inhomogeneity at near liquid-He temperatures [10]. The decay observed for the more flexible benzophenone at 77 K in EPA is not as well fitted by a single exponential, and those of the other compounds were very poorly fitted by single exponentials. Because of this inherent kinetic heterogeneity, a gaussian distribution of exponentials was used to fit the current data [12–14,24]. Much of the rest of our analysis is designed to show that additional kinetic heterogeneity observed for OMBP is due to conformationally dependent hydrogen abstraction, and not site effects or unusual conformational effects on radiative rates.

As seen in Table 1, the overall triplet lifetimes of OMBP and d_3-OMBP are somewhat shorter than that of BP. Examination of MMBP and PMBP decays suggests that the additional decay pathway for OMBP is largely reaction and not simple internal conversion. Methyl substitution and loss of symmetry per se were shown to be relatively insignificant to the decays, as BP, MMBP and PMBP were satisfactorily fitted to distributions with very similar averages and widths (Table 1), the methyl-substituted benzophenones being about 10% longer lived. In contrast, both OMBP and d_3-OMBP yielded decays that could not be satisfactorily fitted to single-mode distributions, having shorter-lived components and proportionately broader bands. This result can be anticipated in the obvious curvature of the OMBP and d_3-OMBP data (Fig. 3). The physical significance of the values of the reported shorter components is probably minimal in that there is no real basis for assuming gaussian distributions for them. However, we attribute the shorter components to molecules which are frozen in particularly favorable conformations for hydrogen abstraction.

The decrease in phosphorescence intensities of the *ortho*-methyl-substituted compounds and the effect of deuterium substitution on the decays are indicative of a competing process that contributes to the depletion of the triplet state. While both hydrogen abstraction and radiationless decay are suitable candidates, we observe virtually identical decays for PMBP and d_7-PMBP, and it has been known for some time that aryl group deuteration causes no effect on the lifetime of d_{10}-benzophenone in EPA at 77 K [25,26]. These observations allow us to rule out a significant kinetic isotope effect on radiative decay or radiationless internal conversion. Rather, the extra kinetic inhomogeneity in OMBP and d_3-OMBP is assigned to internal hydrogen abstraction, whose rate depends on the conformation of the molecules as they are frozen in the glass. In support of this assignment, we were able to detect the fluorescence of the photoenol which was

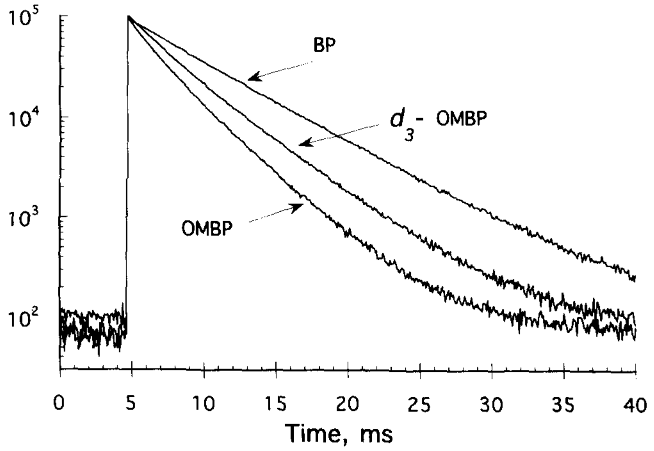

Fig. 3. The first 40 ms of the phosphorescence decays of BP, OMBP and d_3-OMBP.

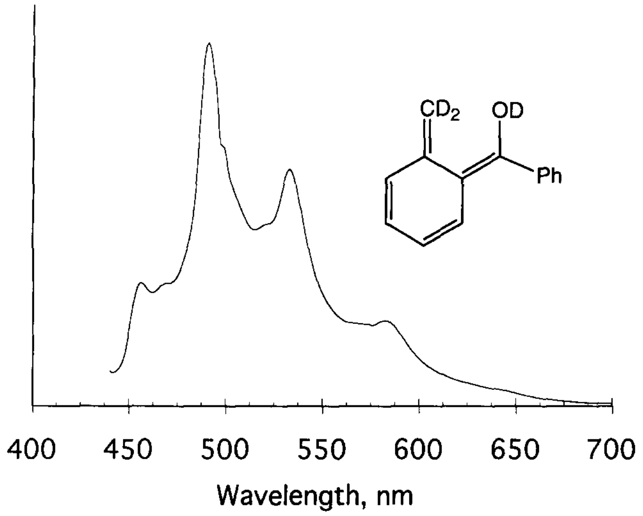

Fig. 4. Fluorescence spectrum of d_3-methylbenzophenone enol in EPA at 77 K (λ_{ex} = 430 nm). Photoenol was accumulated by irradiation of the sample with a high intensity source prior to fluorescence detection.

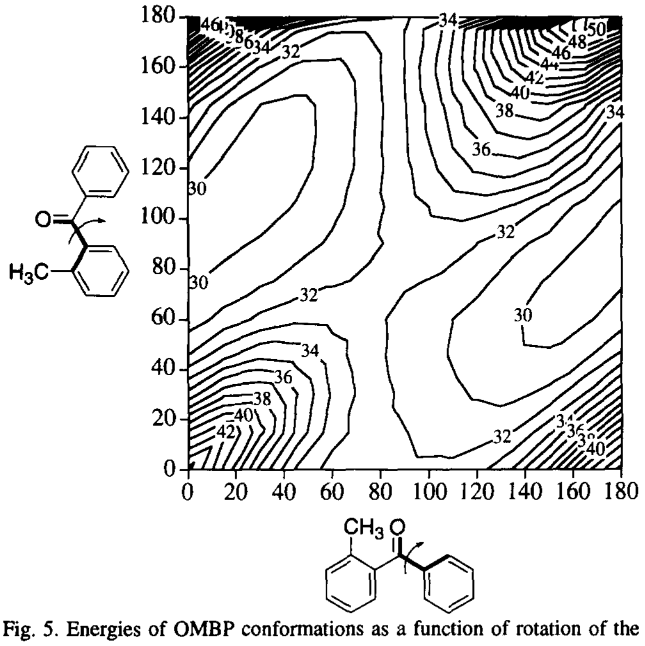

Fig. 5. Energies of OMBP conformations as a function of rotation of the phenyl rings relative to the CO.

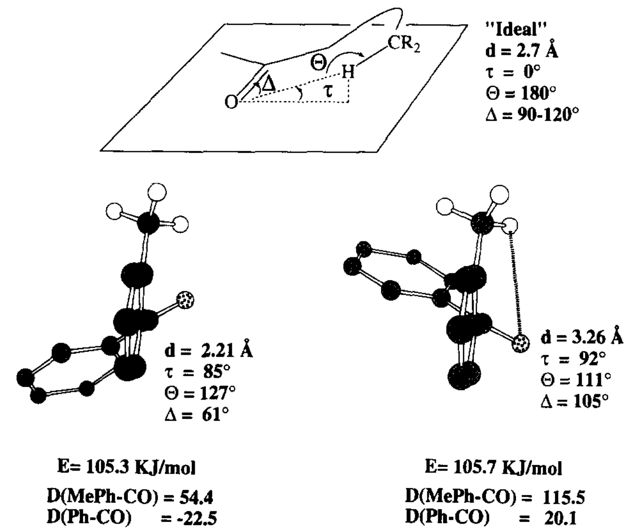

Fig. 6. Calculated geometries of two low energy conformers and their relationship to ideal hydrogen abstraction geometry. The distance between O and the abstracted H is *d*. The angle Δ is that determined by the carbonyl carbon, the carbonyl oxygen, and the hydrogen being abstracted. The angle *Θ* is defined by the carbonyl oxygen, the hydrogen being abstracted, and the carbon to which it is attached. The angle *τ* is that defined by the O–H vector, relative to the carbonyl nodal plane.

assigned by analogy to other *o*-quinodimethanes (Fig. 4) [27,28].

A distribution of rate constants for internal hydrogen abstraction by ^{3}OMBP is a necessary result of the conformational heterogeneity which undoubtedly exists in the frozen glassy samples. Our data do not allow for the deconvolution of the conformational distribution and the variation in rate constant with conformation. In principle, extraction of one distribution given the other might be possible. An MMP2 conformational map[1] (Fig. 5) of isolated OMBP is in qualitative agreement with results recently reported from an MM2(85) conformational map of benzophenone and with X-ray diffraction data from 38 derivatives analyzed by Rappoport et al. [29]. The lowest energies are found for "propeller" conformations with the two aryl rings rotated relative to the carbonyl function. A Monte Carlo search with the MM3 force field from MacroModel [30] yields two close minima (ΔE = 0.4 kJ mol^{-1} (Fig. 6)). One of these, with a O=C–Ph(Me) dihedral angle of 115.4°, presents a conformation that is particularly far from an ideal *syn*-coplanar arrangement that brings hydrogen atoms from the methyl group into close proximity with the carbonyl *n*-orbital (i.e. O=C–Ph(Me) dihedral angle, about 0°) [31–34]. The other low energy conformer has an O=C–Ph(Me) dihedral of 54.4°. Thus the major components in the decays of OMBP and d_3–OMBP are dominated by conformations in which hydrogen abstraction is not a rapid process but are shortened and (proportionately) broadened, relative to the other ketones, by conformations in which the geometry is suitable, if non-ideal. The short components are attributable to populations with more nearly ideal geometry and their small contribution is consistent with the relatively small decline in phosphorescence quantum yield. We stress that conformational diversity without a competing reaction in the glass is not sufficient to account for the observed decays, as shown by the behavior of the other ketones and by the observed isotope effects.

We have found that geometrically locked 1,4-dimethylanthrone and its deuterated isotopomer undergo hydrogen atom transfer at ultralow temperatures (e.g. 17 K), demonstrating the importance of activated and tunneling mechanisms, particularly for systems locked in nearly ideal geometry. At 77 K, almost no phosphorescence is observed from even the deuterated dimethylanthrone [9,10]. We

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[1] The dihedral driver facility of PC-Model was used with 15° steps between 0 and 180° for the two Ar–(CO)–Ar bonds to obtain energies for 142 conformations.

consider the anthrone systems to be analogous to OMBP, but only for that very small fraction of OMBP molecules that are frozen in near ideal conformations. The reactivity of the other conformers clearly fall off dramatically. While a strict analysis of the kinetic isotope effect in heterogeneous samples is not an easy task, the phosphorescence results discussed here are consistent with variable rate hydrogen atom abstraction by ^{3}OMBP in EPA which belies the simple two-conformer model of Fig. 1. The results reported here suggest the utility of phosphorescence measurements for the indirect study of hydrogen abstraction and other reactive processes of phosphorescent triplets. This technique should prove particularly valuable in the analysis of solid-state samples where radiative decay and reaction may concur over a large temperature range [35].

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