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Physical and chemical quenching rates and their influence on stereoselective photooxygenation of oxazolidinone-functionalized enecarbamates†‡

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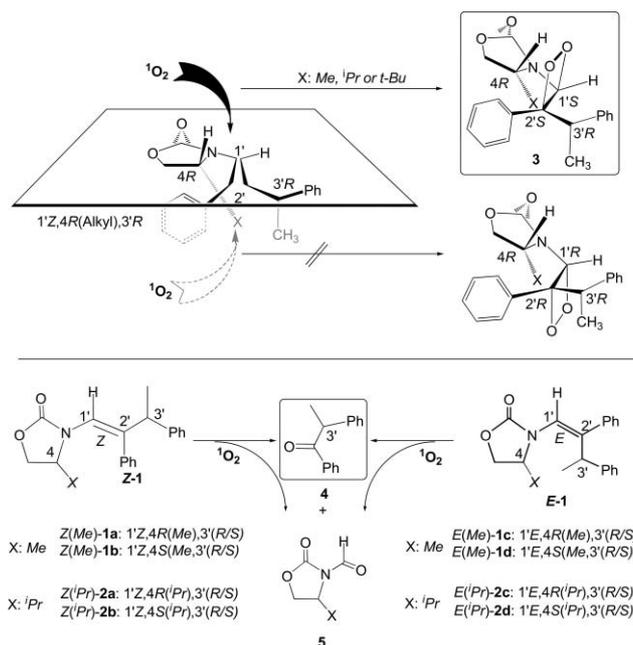
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Physical and chemical quenching rate constants were measured for the reaction of singlet oxygen with oxazolidinone-functionalized enecarbamates to investigate the role of vibrational deactivation in product stereoselectivity.

Stereocontrol in photoreactions is problematic for photochemists, chiefly owing to the short lifetimes of reactive species and intermediates.^{1,2,3} In an attempt to influence stereoselection, photochemists have employed a variety of confined media with varying degree of success.^{3–7} In spite of some elegant methodologies that are employed to carry out asymmetric phototransformations,^{3–7} excited-state stereocontrol in solution presents new opportunities and challenges to chemists.

Previous investigations in our laboratories have focused on the reaction of the enecarbamates **1–2** with singlet oxygen (¹O₂) to form the dioxetane **3**. The dioxetane subsequently decomposes to the ketone **4** (methyldeoxybenzoin, MDB) and the chiral aldehyde **5** (Scheme 1). In studying the stereoselectivity in the dioxetane product **3** we employed optically pure enecarbamates. The enantioselectivity in the MDB product **4** was obtained after utilizing an epimeric mixture (50/50 *R/S*-isomers at the C-3' position) of the starting enecarbamate.

In exploring this system, several remarkable features came to light with respect to the approach of ¹O₂ on to the enecarbamates **1**: (a) ¹O₂ reacts with the *Z*-enecarbamates (*Z*-**1**) to produce the dioxetane product **3** with diastereoselectivity values >95% (Scheme 1, top).^{8–10} That is, >98% of the approaching ¹O₂ reacted with one face of the π bond to form one dioxetane product and <2% reacted with the other face to form the other dioxetane product; (b) selectivity in both dioxetane product **3**, and in the MDB product **4** is independent of the size of the C-4 alkyl group (Me, ⁱPr or ^tBu) of the enecarbamates;^{11,12} (c) the *R/S* configuration of the MDB product **4** is dependent on the C-4 *R/S* configuration of the enecarbamates;¹¹ (d) for the *Z*-enecarbamates, the selectivity in the dioxetane product **3**, is independent of the C-3'



Scheme 1 Photooxidative cleavage of *Z/E* enecarbamates **1–2** with singlet oxygen (¹O₂).

R/S configuration of the enecarbamates;^{10,11,13} (e) the *E*-isomer shows a solvent and temperature dependence of stereoselectivity in the MDB product **4**, in contrast to the corresponding *Z*-isomer.^{11,14,15}

These results raised key questions about the role of the C-4 position and its ability to direct the approach of ¹O₂—a small enophile that is blocked to the same extent by substituents of varying size.^{11,12} Consequently, in view of these results, we hypothesized that factors apart from steric ones were playing a crucial role in the observed selectivity.^{11,13,14}

To rationalize our observations we envisioned two distinct quenching processes during the photooxidation of enecarbamates **1–2** by ¹O₂: the formation of dioxetane **3** (chemical quenching), and/or deactivation of ¹O₂ to ³O₂, the triplet ground state (physical quenching). The rate constant for the reaction leading to dioxetane **3** is called the chemical quenching rate constant (*k*_{cq}) and the rate constant for deactivation (leading to ³O₂) is called physical quenching rate constant (*k*_{pq}). The sum of both rate constants is *k*_q, the rate constant for total quenching (eqn (1)).

$$k_q = k_{cq} + k_{pq} \quad (1)$$

¹O₂ is known to be deactivated from its singlet excited state to its triplet ground state when it encounters C–H bonds.¹⁶ For

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this reason, the lifetime of $^1\text{O}_2$ is longer in deuterated solvents than in proteated solvents. This physical quenching phenomenon is referred to as vibrational deactivation of $^1\text{O}_2$ since the coupling of the C–H vibration with the electronic excited state of molecular oxygen leads to relaxation of the singlet excited state. To better understand the role of vibrational deactivation in the observed high stereoselectivities, we performed a systematic study of the rate constants for both chemical (k_{cq}) and physical (k_{pq}) quenching. Because **1** and **2** are electron deficient alkenes, these quenching rate constants are expected to be relatively low and therefore challenging to measure accurately. In addition, sorting out the role of physical and chemical quenching adds another level of experimental difficulty. In spite of the difficulty of extracting accurate relative rate constants for the chemical portion of the quenching, we felt that a careful study of the total quenching would be important for exploring structure–reactivity relationships.

The chemical quenching rate constants (k_{cq}) were measured using competitive kinetics. *trans*-4-Octene was utilized as a standard ($k_{\text{cq}} = 4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$).^{17,18} The relative ratios of the standard and enecarbamate peaks were monitored by $^1\text{H-NMR}$ spectroscopy upon reaction with $^1\text{O}_2$.¹² After determining k_{cq} for **1a** (3'*R* and 3'*S*), these values were used as additional standards for subsequent measurements.¹²

Total quenching rate constants (k_{q}) of $^1\text{O}_2$ by enecarbamates were determined by using a chemiluminescence method, in which $^1\text{O}_2$ was generated by thermal decomposition of 1,4-dimethylnaphthalene-1,4-endoperoxide.¹⁹ Chemiluminescence (phosphorescence of $^1\text{O}_2$) at 1270 nm was monitored to determine Stern–Volmer quenching constants by varying the quencher (enecarbamates **1** or **2**) concentration. To convert the Stern–Volmer quenching rate constants (K_{SV}) into the total quenching rate constants (k_{q}), the known total rate constant of *trans*-4-octene ($k_{\text{q}} = 1.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$)^{17,18} was used as standard to calculate τ_0 , the $^1\text{O}_2$ lifetime under our experimental conditions (eqn (2)).¹² After determining k_{q} and k_{cq} for the enecarbamates experimentally, k_{pq} was derived from these two values using eqn (1).

$$K_{\text{SV}} = k_{\text{q}} \tau_0 \quad (2)$$

As we had employed a 50/50 epimeric mixture of enecarbamates at C-3' position, the relative rates of photooxygenation, known as

Table 1 Conversion and stereoselectivity in the MDB product **4** upon photooxidative cleavage of enecarbamates with $^1\text{O}_2$ in CDCl_3 at 15°C^a

Substrate	Configuration		s^a [enhanced MDB enantiomer]
	C-4	C-3'	
<i>Z</i> (<i>Me</i>)- 1a	<i>R</i>	<i>R/S</i>	1.2 [<i>R</i>]
<i>Z</i> (<i>Me</i>)- 1b	<i>S</i>	<i>R/S</i>	1.5 [<i>S</i>]
<i>E</i> (<i>Me</i>)- 1c	<i>R</i>	<i>R/S</i>	9.2 [<i>R</i>]
<i>E</i> (<i>Me</i>)- 1d	<i>S</i>	<i>R/S</i>	10 [<i>S</i>]
<i>Z</i> (<i>iPr</i>)- 2a	<i>R</i>	<i>R/S</i>	2.2 [<i>R</i>]
<i>Z</i> (<i>iPr</i>)- 2b	<i>S</i>	<i>R/S</i>	1.4 [<i>S</i>]
<i>E</i> (<i>iPr</i>)- 2c	<i>R</i>	<i>R/S</i>	5.0 [<i>R</i>]
<i>E</i> (<i>iPr</i>)- 2d	<i>S</i>	<i>R/S</i>	3.4 [<i>S</i>]

^a Data taken from previously published reports: ref. 11, 15, 20.

the stereoselectivity factor (s factor),²¹ could be derived from the observed enantiomeric excess (ee) values in **4** based on eqn (3). The stereoselectivity factor (s), is a quantitative measure (corrected for the extent of conversion) of the relative reaction rates for the two stereoisomers in question (eqn (3)). In the present case, the s factor may be computed for the two-epimeric enecarbamates [C-3'(*R*) and C-3'(*S*) epimers] from the substrate conversion and the MDB enantiomeric excess by using eqn (3).²² In the present case, k_1 is the reactive rate constant leading to formation of the predominant MDB isomer and k_2 the reactive rate constant leading to formation of the subordinate isomer. A large s value translates to high enantiomeric excess in the MDB product but corrected for conversion. From Table 1, it is evident that the s factor and consequently ee of the MDB products is higher in the *E*-enecarbamates than in the *Z*-enecarbamates. By exploring the chemical and total quenching rates independently, it would be of relevance to the relative rates of the individual epimers, as it would shed light into the factors that control the photooxygenation process.

$$s = \frac{k_1}{k_2} = \frac{\ln[1 - C(1 + ee)]}{\ln[1 - C(1 - ee)]} \quad (3)$$

The experimentally measured rate constants are presented in Table 2. The $k_{\text{pq}}/k_{\text{cq}}$ values are experimentally the same for all the entries in the table regardless of alkene geometry

Table 2 Chemical quenching rate constant (k_{cq}), physical quenching rate (k_{pq}) and total quenching rate constant (k_{q}) for photooxygenation of enecarbamates

Substrate ^a	Configuration		Quenching rate constants ^b /M ⁻¹ s ⁻¹				s_{cq}^f
	C-4	C-3'	$k_{\text{cq}} (\times 10^{-3})^c$	$k_{\text{q}} (\times 10^{-3})^d$	$k_{\text{pq}} (\times 10^{-3})$	$k_{\text{pq}}/k_{\text{cq}}$	
<i>Z</i> (<i>Me</i>)- 1a	<i>R</i>	<i>R</i>	2.4	43 ^e	41	17	1.3
<i>Z</i> (<i>Me</i>)- 1a	<i>R</i>	<i>S</i>	1.8	44 ^e	42	23	
<i>Z</i> (<i>iPr</i>)- 2a	<i>R</i>	<i>R</i>	1.7	26	24	16	1.2
<i>Z</i> (<i>iPr</i>)- 2a	<i>R</i>	<i>S</i>	1.3	24	22	17	
<i>Z</i> (<i>iPr</i>)- 2b	<i>S</i>	<i>S</i>	1.6	27	25	16	1.8
<i>E</i> (<i>iPr</i>)- 2c	<i>R</i>	<i>R</i>	1.6	23 ^e	21	13	
<i>E</i> (<i>iPr</i>)- 2c	<i>R</i>	<i>S</i>	0.9	20	19	21	

^a Concentration of the substrates is given in ESI. [†] ^b Experimental error within 25–35%; average of 2 or more runs. ^c Data from ref. 11, determined by competitive kinetics using *trans*-4-octene as standard; in CDCl_3 at $20 \pm 1^\circ\text{C}$. ^d CDCl_3 , $22 \pm 1^\circ\text{C}$; for experimental details see ESI. [†] ^e Values obtained from optical antipode. ^f s_{cq} is the ratio of the chemical quenching rates of the C-3' epimers.

Table 3 Stereoselectivity factors obtained upon photo-oxygenation of proteated and C-4 deuterated *E(Me)-1d* in CDCl₃

Substrate	Temperature/°C	<i>s</i> [enhanced MDB enantiomer]
<i>E(Me)-1d</i>	15	10 [S] ^a
	-15	39 [S] ^a
	-40	71 [S] ^a
<i>E(Me)-1d(D₃)</i>	15	11 [S]
	-15	25 [S]
	-40	41 [S]

^a Data taken from previously published report: ref. 11.

(*E* vs. *Z*), the C-4 substituent or the C-4 and C-3' *R/S* configuration. The expected differences in physical quenching observed for the C-3' diastereomers are not evident. This, however, does not suggest the non-existence of vibrational quenching as one of the stereoselective mechanism in operation in the photooxygenation of the enecarbamates. The reactive rate constants are low, as expected, due to the electron deficient alkene double bonds²³ in enecarbamates. It must be noted that when calculations of rate constants are performed with k_q that are one order of magnitude larger than k_{cq} , then associated inaccuracy undermines possible conclusions.

As computed in Table 2, the ratio of chemical quenching rate constants s_{cq} (Table 2) is significantly higher for the *E* enecarbamates (s_{cq} of 1.8) compared to the corresponding *Z* enecarbamates (s_{cq} of 1.2). As the ratio of chemical quenching rate constants are not corrected for conversion they seem not to correlate with the *s* factor computed from *ee* values (Table 1). Nevertheless, we were encouraged to see the chemical quenching trend in line with the *s* factors computed from the *ee* values. We could not correlate physical quenching rates as it is not corrected for conversion. To overcome this, we took an indirect approach to verify the physical quenching process and to quantify the vibrational quenching contribution to stereoselective photooxidation of enecarbamates (in terms of the *ee* values in the product) by studying deuterated and the corresponding H enecarbamates (Table 3).

Deuteration of the vibrationally distinguishing groups allowed us to investigate vibrational quenching as a stereodifferentiation mechanism. The C-4 substituents of the *E(Me)-1d* enecarbamate (optically pure C-4 substituents and *R/S* epimer C-3' position) were deuterated and the *s* values at various temperatures were compared to the results for its proteated counterpart (Table 3). Upon inspection of Table 3, it is clear that deuterated and proteated enecarbamates gave different stereoselectivities under identical conditions. For example, at -40 °C, an *s* value of 41 favoring the *S*-MDB product was observed with the deuterated derivative, whereas an *s* value of 71 was observed with the corresponding H-derivative. The differences in stereodifferentiation decreased as the temperature was raised from -40 °C to 15 °C. At 15 °C, almost identical values were obtained for both the proteated (*s* = 10) and deuterated (*s* = 11) derivatives (Table 3). A rationale for the observation of a nearly doubled *s* values at -40 °C for proteated enecarbamates compared to deuterated enecarbamates is needed to quantify the selectivity. We believe that the difference in the selectivity between the two derivatives is a reflection of the ability of the proteated derivative to deactivate ¹O₂ selectively from one of the stereotopic faces of the epimeric enecarbamate (C-3' epimers) leading to noticeably

different stereoselectivities at a given temperature. As the rate constants (physical and chemical quenching rate constants) are dependent on the temperature, one would expect variation with the reaction temperature. Based on the *s* values, the difference in rate constants (physical and chemical) for a given pair of C-3' epimers is pronounced at lower temperatures leading to higher selectivities. At the present time, with our limited experimental data, we could only speculate about the origin of this difference. One possibility is the dynamic movement/restrictions involved leading to conformational changes in enecarbamates would be temperature dependent. If there is conformational bias towards a particular conformation of C-3' epimers, lowering the temperature could likely result in a conformation that interacts (chemically and/or physically) with ¹O₂ effectively from one C-3' epimer than the other. If sterics alone is involved in determining the extent of stereoselectivity, identical *s* values would be expected for both the proteated and the corresponding deuterated derivatives even at -40 °C. To rationalize the difference, factors apart from sterics would have to be involved in the stereodifferentiation process leading to the different stereoselectivities for the proteated and deuterated derivatives of *E(Me)-1d* enecarbamates. We attribute the additional stereoselectivity (nearly doubling of the *s* value in the case of *E(Me)-1d* at -40 °C; Table 3) obtained in the proteated enecarbamate to vibrational quenching of singlet oxygen by C-H bonds. This quenching is more pronounced at lower temperatures.

Thus our investigation has opened an opportunity to quantify the extent of physical quenching during the photooxygenation processes in terms of the enantiomeric excess in the photoproduct. Deuteration of enecarbamates offers a more accessible means of exploring this stereodifferentiating mechanism in the photooxygenation process. Efforts are underway in our laboratories to quantify the rate constants for the individual epimers of both the proteated and deuterated enecarbamates to obtain a more direct evidence of vibrational quenching.

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