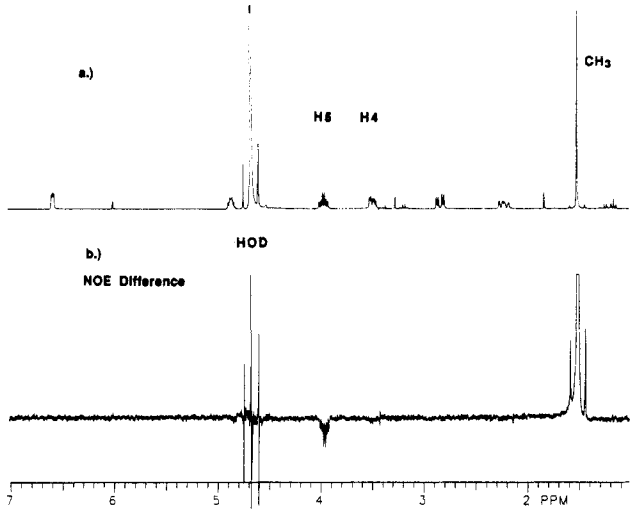

Figure 2. (a) ^{1}H NMR spectrum of EPSP ketal in D_2O at pD 9.0. (b) NOE difference spectrum resulting from irradiation of the methyl signal at 1.68 ppm showing the excitation of the H-5 protons selectively. Spectra were taken on a Varian XL 400 instrument.

the reaction mixture is allowed to stand with excess **3**, the ketal becomes the only detectable shikimate species separable from the mixture without denaturing EPSPS. Maximum production of **5** occurs while **4** is maintained by the enzyme. EPSPS catalytically converts **1** to **5** at $k = 0.2$/h (pH = 6.3, 25 °C), a rate much slower than the reverse reaction.[4] Figure 1 shows a ^{31}P NMR spectrum of an enzymatic synthesis of **5** with the equilibrium mixture containing S3P (2.49 ppm), EPSP (2.31 ppm), EPSP ketal (1.16 ppm), P_i (0.81 ppm), and PEP (-1.65 ppm).

The EPSP ketal is easily isolated from the reaction mixture in Figure 1 by anion-exchange chromatography.[5] A number of corroborative experiments confirm the structure of **5**. Labeling with [U-^{14}C]S3P and [1-^{14}C]PEP indicates that all 10 carbon atoms must be present. Degradation of **5** in dilute acid produces **2** and pyruvate. The permethylated derivative of [2′-^{13}C]-**5** displays a molecular ion at $m/z = 382$ compared to methylated **1** at $m/z = 381$ by CI mass spectrometry.[6] The key structural features of **5** are readily observed by ^{1}H and ^{13}C NMR.[7] The ^{13}C-2′ carbon is quaternary by APT sequence, appears as a quartet in the ^{1}H-coupled ^{13}C spectrum, and is readily seen in the ^{13}C NMR spectrum of the internal equilibrium mixture at 110.6 ppm.[3,12] The ^{1}H spectrum (Figure 2a) contains the C-3′ methyl signal coupled (d, $J = 4.7$ Hz) to the C-2′ carbon (99% ^{13}C). The stereochemistry at the C-2′ position is *R* by 1-D NOE with transfer occurring between the C-3′ (CH_3) signal at 1.68 ppm and the H-5 proton (Figure 2b). The EPSP ketal is stereochemically pure on the basis of this NOE result and the absence of a diastereomeric methyl ^{1}H NMR signal at 1 Hz line width.

The addition of **5** back to EPSPS with or without P_i does not result in conversion to **1** or **2**. A mixture of EPSPS (55 μM), [^{14}C]S3P (32 μM), and PEP (0.5 mM) formed and maintained **5** for 10 months at 4 °C. This nonreversibility suggests that EPSPS is not actually catalyzing the formation of **5** directly, since with time the equilibrium should favor the products with the least energy, S3P and pyruvate.[2a] Formation of **5** is stopped in the presence of glyphosate [*N*-(phosphonomethyl)glycine], which sequesters enzyme with S3P in the herbicidal dead-end complex.[8] Incubation of **1** (50 mM) at pD 4.8 does not produce **5** after 16 days at 25 °C; however, **2** (21%) is observed from hydrolysis.[3,12] Incubation of [^{14}C]S3P (8 μM) with pyruvate (1.7 mM) with or without EPSPS (7 μM) at pH 7.0 for 18 days at 4 °C also does not produce **5**. Therefore, EPSP ketal formation is not an artifact of these incubations.

EPSPS has a cysteine reactive to DTNB at position 408 that is protected from modification by **2** and glyphosate or **1**,[9] but **5** (2 mM) with or without P_i (100 mM) does not protect Cys-408 from modification by DTNB (60 μM). This suggests that productive association of **5** does not occur with the EPSPS active site. Taken together, all of these results preclude **5** from being an intermediate along the catalytic pathway and clearly demonstrate the need for corroborative information when enzyme intermediates are spectroscopically characterized.[12]

EPSPS catalyzes a direct addition-elimination reaction through **4**, which has been isolated and fully characterized.[10] The internal equilibrium conditions maximize the concentration of **4**, facilitating optimum production of **5**. It is tempting to propose that **4** produces **5** from an S_N2 displacement of P_i by the shikimate 4-OH in the active site. However, direct formation at the active site seems unlikely from the protection and reversibility studies discussed above. Nevertheless, EPSPS catalytic activity is required, suggesting that **5** forms in solution from an enzymatically produced species. If the prolonged stabilization of enzyme-bound **4** permits its occasional release, then the solution degradation of **4** must account for the stereospecific formation of **5**. The stereochemistry of **4** and its relationship to **5** is not clear[11] and is the subject of a detailed investigation.[12]

(10) Anderson, K. S.; Sikorski, J. A.; Benesi, A. J.; Johnson, K. A. *J. Am. Chem. Soc.* **1988**, *110*, 6577-6579.

(11) (a) Alberg, D. A.; Bartlett, P. A. *J. Am. Chem. Soc.* **1989**, *111*, 2337-2338. (b) Bartlett, P. A.; McLaren, K. L.; Alberg, D. G.; Fassler, A.; Nyfeler, R.; Lauhon, C. T.; Grissom, C. B. *Prospects for Amino Acid Biosynthesis Inhibitors in Crop Protection and Pharmaceutical Chemistry*; Copping, L. G., Dalziel, J., Dodge, A. D., Eds.; British Crop Protection Council Mono. No. 42; The Lavenham Press Ltd.: Lavenham, Suffolk, U.K., 1989; pp 155-170.

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Stereochemical Course of the Key Ring-Forming Reactions in Clavulanic Acid Biosynthesis

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Clavaminate synthase (CS) is an Fe(II)/α-ketoglutarate (α-KG)-dependent oxygenase central to the clavulanic acid (**4**) biosynthetic pathway. It carries out a four-electron oxidative cyclization of proclavaminic acid (**1**) to clavaminic acid (**2**) with concomitant formation of 2 mol of CO_2 and succinic acid[1,2] (Scheme I). An ^{18}O-labeling experiment has established that the 3-OH in **1** gives rise to the oxazolidine oxygen in **2** without detectable loss or exchange of heavy isotope, signaling a significant departure from conventional α-KG-dependent dioxygenase behavior.[3] In this paper, the stereochemical course of this oxidative cyclization at C-4′ of proclavaminic acid (**1**) is determined and a correlation is completed to an earlier configurational analysis.[4] The stereochemical course of each clavulanic acid ring-forming reaction can now be defined and suggests possible mechanisms of β-lactam formation distinct from those proposed for nocardicin (**6**)[5] and penicillin.[6]

Access to the stereospecifically 4′-deuteriated proclavaminates **1a** and **1b** was achieved through (4*R*)-(phenylthio)azetidinone

(1) Elson, S. W.; Baggaley, K. H.; Gillett, J.; Holland, S.; Nicholson, N. H.; Sime, J. T.; Woroniecki, S. R. *J. Chem. Soc., Chem. Commun.* **1987**, 1736-1738.

(2) This enzyme has been purified to homogeneity: Salowe, S. P.; Marsh, E. N.; Townsend, C. A., unpublished.

(3) Krol, W. J.; Basak, A.; Salowe, S. P.; Townsend, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 7625-7627.

(4) Townsend, C. A.; Mao, S.-s. *J. Chem. Soc., Chem. Commun.* **1987**, 86-89.

(5) Townsend, C. A.; Wilson, B. A. *J. Am. Chem. Soc.* **1988**, *110*, 3320-3321. Townsend, C. A.; Brown, A. M.; Nguyen, L. T. *Ibid.* **1983**, *105*, 919-927. Townsend, C. A.; Brown, A. M. *Ibid.* **1982**, *104*, 1748-1750.

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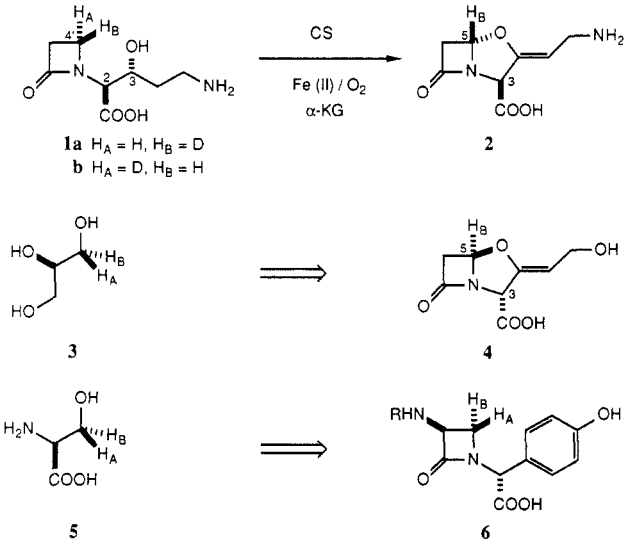
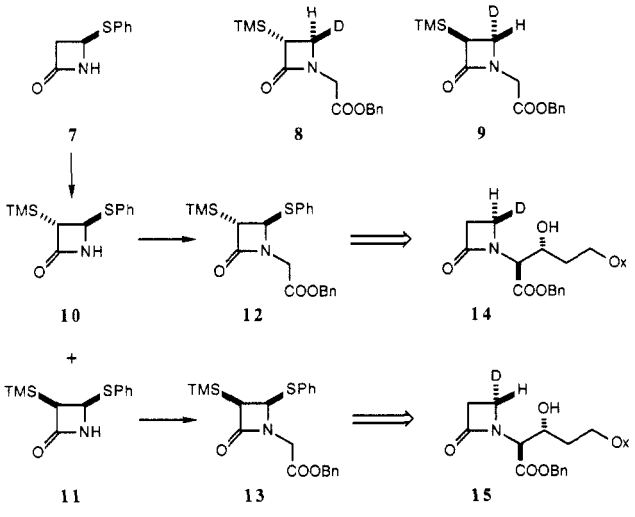
0002-7863/90/1512-1654$02.50/0

Scheme I



Scheme II



(7, mp 68–69 °C, $[\alpha]_D$ = 137°; lit.[7] mp 58–60 °C, $[\alpha]_D$ = 105°). To exploit the sensitivity of trialkyltin hydride reductions to steric effects,[8] **7** was N-silylated and then treated with LDA and TMSCl to give a 2:1 mixture[9] of **10** and **11**, respectively, after mildly acidic workup (Scheme II). The trans- and cis-disubstituted β-lactams **10** and **11** were easily separated by silica gel chromatography (hexanes/EtOAc)[10] and reacted with benzyl bromoacetate to give correspondingly **12** and **13**. Reaction of **12** with 2 equiv of nBu_3SnD (cat. AIBN, PhH, reflux, 6 h, 70%) gave the 4′*R*-deuteriated β-lactam **8**, while analogous reaction of the cis isomer **13** proceeded considerably more slowly (4 equiv of nBu_3SnD, 24 h, 50%) to give the *enantiomeric* 4′*S*-deuteriated azetidinone **9**. Mass spectral measurements revealed deuterium contents in **8** and **9** to be 97–98% d_1,[12] and careful ^1H NMR analyses established that in both instances deuterium was oriented trans to the TMS group to an extent 17 ± 1:1 ($^3J_{trans}$ = 2.7 Hz). Stereospecific introduction of label having been securely established, the TMS group was removed and the syntheses of the racemic N,O-protected (Ox = 4,5-diphenyl-4-oxazolin-2-one)[13] proclavaminates **14** and **15** were completed as previously described.[3] The success of this route and the potential broader applicability of intermediates as **12** and **13** derives from the facilitation by the trialkylsilyl group of reactions in which the thiophenyl is replaced in either a radical or cationic regime with substituents whose entry is simultaneously governed by the steric bulk of the silyl group.

(4′*R*)- and (4′*S*)-D,L-[4′-^{2}H]proclavaminic acid, **1a** and **1b**, respectively, were incubated[3] with CS[2] to give samples of clavaminic acid, which were purified, derivatized,[3] and examined for their deuterium content at C-5 by ^1H NMR spectroscopy and CIMS. The β-deuteriated substrate **1a** was incubated to 65–70% conversion to afford a sample of clavaminate where the vast majority of the label was retained, 94 ± 1% d_1 (MS). In the ^1H NMR spectrum, only a trace of hydrogen was detectable in the integral of H-5 (δ 5.70), and the multiplicity of the resonances for the H-6 hydrogens reduced to a simple AB quartet. The α-deuteriated substrate **1b** reacted significantly more slowly than its diastereomer **1a**. The clavaminate produced was isolated at approximately 50% conversion and contained 12 ± 1% (MS) deuterium at C-5 as revealed in the intensity of the resonance at δ 5.70 (H-5) and the appearance of a small upfield-shifted signal (ca. 0.005 ppm) at the base of the resonances for H-6α (δ 3.08) owing to this minor vicinal deuterium substitution.[14] Assuming that the enzymic cyclization is stereospecific and there exists no discrimination against labeled substrates at partial extents of reaction, i.e., no *V*/*K* isotope effect,[15] the expected levels of deuterium in clavaminate may be computed in these reactions to be 91–92% and 5–6%, respectively.[16] It can be seen that the intervention of a *V*/*K* isotope effect would raise the level of deuterium in the product of *both* experiments. Nevertheless, while the data are insufficient to quantitatively address this issue, it can be seen that, even in the absence of such discrimination, the stereoselectivity of the oxidative cyclization is (conservatively) greater than 90%.

In conclusion, proclavaminates stereospecifically deuteriated at C-4′ have been prepared and incubated with purified CS. The 4′(*S*)-hydrogen was specifically lost (H_A in **1**, Scheme I), accompanied by a significant kinetic isotope effect on the overall reaction rate, and the 4′(*R*)-hydrogen was correspondingly retained (H_B in **1**). Therefore, CS, while unconventional in its utilization of molecular oxygen during catalysis,[3] introduces a substrate oxygen intramolecularly at C-4′ with retention of configuration as expected for hydroxylation.[17] H_B in clavaminic acid (**2**, Scheme I) survives the subsequent configurational inversion at C-5 that occurs in the formation of clavulanic acid (**4**).[18] It has been shown previously that H_B in **4** correlates to the *pro*-1(*R*)-hydrogen of glycerol (H_B in **3**),[4] whose absolute configuration remains unchanged through the intermediates of glycolysis to glyceric acid, the primary metabolic precursor of the clavulanate β-lactam

(7) Shibasaki, M.; Nishida, A.; Ikegami, S. *J. Chem. Soc., Chem. Commun.* **1982**, 1324–1325. See also: Hiemstra, H.; Wynberg, H. *J. Am. Chem. Soc.* **1981**, *103*, 417–430.

(8) Seyferth, D.; Yamazaki, H.; Alleston, D. L. *J. Org. Chem.* **1963**, *28*, 703–706. Kuivila, H. G. *Synthesis* **1970**, 499–509. For examples in the β-lactam series, see: Whitesitt, C. A.; Herron, D. K. *Tetrahedron Lett.* **1978**, 1737–1740. Aimetti, J. A.; Hamanaka, E. S.; Johnson, D. A.; Kellogg, M. S. *Ibid.* **1979**, 4631–4634. Manhas, M. S.; Khajavi, M. S.; Bari, S. S.; Bose, A. K. *Ibid.* **1983**, 2323–2326.

(9) Slow addition of trimethylsilyl chloride at low temperatures gave **10** and **11** in a ca. 5:1 ratio. For a related case, see: Kano, S.; Ebata, T.; Funaki, K.; Shibuya, S. *Synthesis* **1978**, 746–747.

(10) **10**: mp 59–60 °C, $[\alpha]_D$ = 95.3° (*c* = 1.5, $CHCl_3$); lit.[11] mp 58–60 °C, $[\alpha]_D$ = 857.4° ($CHCl_3$); this rotation is anomalously high as reported. **11**: mp 71–73 °C, $[\alpha]_D$ = 120.7° (*c* = 2.15, $CHCl_3$).

(11) Fritz, H.; Sutter, P.; Weis, C. D. *J. Org. Chem.* **1986**, *51*, 558–561.

(12) Deuterium contents were measured in the protected proclavaminates **14** and **15**.

(13) Sheehan, J. C.; Guziec, F. S. *J. Am. Chem. Soc.* **1972**, *94*, 6561–6562. Sheehan, J. C.; Guziec, F. S. *J. Org. Chem.* **1973**, *38*, 3034–3040.

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(15) Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; Wiley-Interscience: New York, 1980; pp 95–128.

(16) The expected deuterium levels in clavaminate were readily obtained by multiplying the observed stereospecificity of the nBu_3SnD reduction, 94:6 to 95:5, by the actual deuterium content of the proclavaminates, 97–98%.

(17) Review: Hanson, K. R.; Rose, I. A. *Acc. Chem. Res.* **1975**, *8*, 1–10. α-Ketoglutarate-dependent dioxygenases: Fujita, Y.; Gottlieb, A.; Peterkofsky, B.; Udenfriend, S.; Witkop, B. *J. Am. Chem. Soc.* **1964**, *86*, 4709–4716. Townsend, C. A.; Barrabee, E. B. *J. Chem. Soc., Chem. Commun.* **1984**, 1586–1588. Townsend, C. A. *J. Nat. Prod.* **1985**, *48*, 708–724. Englard, S.; Blanchard, J. S.; Midelfort, C. F. *Biochemistry* **1985**, *24*, 1110–1116. Stubbe, J. *J. Biol. Chem.* **1985**, *260*, 9972–9975.

(18) Townsend, C. A.; Krol, W. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1234–1236.

carbons.[19] Therefore, in the creation of the monocyclic β-lactam ring of proclavaminate, the N-C-4′ bond is formed with net retention of configuration, in keeping with either 0 or an even number of inversions at the carbon that becomes C-4′. In contrast, monocyclic β-lactam formation in nocardicin A (**6**, Scheme I) from L-serine (**5**) occurs with inversion of configuration.[5] Although no intermediates between glycerate and proclavaminate have been unequivocally established,[20] the results of the present experiments suggest several possible mechanisms for β-lactam formation more complex than the simple S_N2 process apparent in nocardicin biosynthesis[5] and distinct from the oxidative cyclization involved in isopenicillin N formation.[6]

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Registry No. 1a, 124603-44-7; **1b**, 124603-45-8; **2**, 112296-12-5; **4**, 58001-44-8; **7**, 85270-00-4; **8**, 124603-41-4; **9**, 124649-51-0; **10**, 100188-51-0; **11**, 124649-49-6; **12**, 124603-40-3; **13**, 124649-50-9; **14**, 124603-42-5; **15**, 124603-43-6; CS, 111693-82-4; benzyl bromoacetate, 5437-45-6.

(19) Townsend, C. A.; Ho, M.-f. *J. Am. Chem. Soc.* **1985**, *107*, 1066-1068.

(20) On the basis of whole-cell incorporation experiments, 3-hydroxypropionate has been claimed to be a specific precursor of the β-lactam segment of clavulanic acid (Gutman, A. L.; Ribon, V.; Boltanski, A. *J. Chem. Soc., Chem. Commun.* **1985**, 1627-1629). Despite very considerable effort using three fermentation media, we have been unable to duplicate the findings of this report. Low, nonspecific incorporations of radiolabel into clavulanic acid were obtained comparable to cysteine or β-alanine (Mao, S.-s.; Townsend, C. A., unpublished).

Structural Effects on the Yields of Singlet Molecular Oxygen ($^1\Delta_gO_2$) from Alkylperoxyl Radical Recombination

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Howard and Ingold,[1] following a suggestion of Russell, first reported singlet molecular oxygen from peroxyl terminations in 1968 (eq 1):

$$2R_1R_2CHOO^\bullet \rightarrow R_1R_2CO + R_1R_2CHOH + {}^3O_2 + {}^1O_2 \quad (1)$$

This reaction is important because it is a common termination step of the ubiquitous autoxidation process including many biological systems.[2] The reactions of the singlet oxygen formed must be taken into account in any comprehensive modeling scheme of these oxidation processes. Finally, we wondered whether reaction 1, possibly carried out under specialized conditions (e.g., combustion), might furnish singlet oxygen in synthetically useful yields.

(1) Howard, J. A.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 1056-1058.

(2) (a) Kanofsky, J. R. *J. Biol. Chem.* **1984**, *259*, 5596-5600. (b) Kanofsky, J. R. *J. Org. Chem.* **1986**, *51*, 3386-3388 and references therein.

Table I. Yields of $^1O_2$ from Radical-Initiated Autoxidation of Hydrocarbons[a]

substrate, MBHT[b]	T, °C	% $^1O_2$	substrate, MBHT[b]	T, °C	% $^1O_2$
PhMe, 0.050	79.8	6.0 ± 0.4	n-$C_{12}H_{26}$[d]	79.8	3.9 ± 0.3
PhEt	69.9	11.5 ± 1.2	n-Bu_2O	79.6	9.1 ± 0.6
PhEt, 0.020	79.6	14.0 ± 1.1	c-$C_5H_{10}CO$, 0.042	79.5	4.6 ± 0.5
$PhCMe_3$	79.8	3.4 ± 0.3	Me_2NCHO	77.2	0.0 ± 0.4
Ph_2CH_2	69.4	11.3 ± 0.6	$MeN(COC_3H_6)$[e]	79.5	0.0 ± 0.4
0.6 M fluorene	79.5	6.1 ± 0.3	$PhCH_2CN$, 0.050	80.0	0.0 ± 0.4
Ph_2CH_2, 0.020	79.2	11.6 ± 0.7	Me_3COOH[f]	79.8	0.0 ± 0.3
1-Me-naphthalene, 0.051	77.2	4.7 ± 0.3	TOOH[g]		7.8 ± 0.5
c-C_8H_{16},[c] 0.050	77.8	6.7 ± 0.4	CH_3CN[h]	65.2	0.5 ± 0.1
c-C_8H_{14}	78.5	6.4 ± 1.3			

[a] Solutions (5.0 mL) in Au-coated, water-jacketed cell; IR detected with North Coast Model E0817 instrument with phase-sensitive detection at 100 Hz. Average of three measurements relative to areas under decay curves of N02 under the same conditions. [b] Initial concentration of di-*tert*-butyl hyponitrite. Cage effect (f = escaped radical pairs) assumed 0.89, the value in $PhCMe_3$,[3] unless noted otherwise. [c] f = 0.85 determined experimentally from induction period as described.[3] [d] f = 0.84 estimated from relations derived by Kiefer and Traylor (Kiefer, H.; Traylor, T. G. *J. Am. Chem. Soc.* **1967**, *89*, 6667-6671) and published viscosity data (Stephen, K.; Incase, K. *Viscosity of Dense Fluids*; Plenum Press: New York, 1979). [e] *N*-Methylpyrrolidone. [f] Initially 0.25 M in $PhCMe_3$ solution. [g] Initially 0.10 M in $PhCMe_3$ solution. [h] Initiated with benzyl hyponitrite (0.060 M) with f = 0.65.[17]

In Table I we present yields of singlet oxygen from reaction 1, in which the peroxyl radicals were generated continuously from different oxygen-saturated solvents by free-radical initiation with hyponitrite esters[3] (eqs 2 and 3) or directly from the hydroperoxide and initiators.

$$RONNOR \rightarrow 2RO^\bullet + N_2 \quad (2)$$

$$RO^\bullet + R_1R_2CH_2 \rightarrow R_1R_2CH^\bullet \xrightarrow{O_2} R_1R_2CHOO^\bullet \quad (3)$$

The yields were determined from the areas under the curves of chemiluminescence emission at 1.27 μm vs time,[4] relative to similar areas from the thermal decomposition of 1,4-dihydro-1,4-dimethylnaphthalene 1,4-endoperoxide (NO2).[5]

For simple hydrocarbon substrates that are expected to terminate only by reaction 1, the yields of singlet oxygen are remarkably uniform. They range from 3.4 to 6.0% for primary and from 3.9 to 14.0% for secondary alkylperoxyl terminations. The values are in the same range as found by Kanofsky by oxidation in aqueous media[2] of several hydroperoxides with α-hydrogens. With additional functional groups present in the substrate, the yields either remain about the same (n-Bu_2O, cyclohexanone) or decrease (amides, nitriles).

We find a small but measurable quantity of $^1O_2$ from autoxidation of acetonitrile. This result is pertinent to some very interesting experiments reported recently by Sugimoto, Kanofsky, and Sawyer,[6] who detected 1.27-μm emission from the electrolytic reduction on Pt of O_2-saturated acetonitrile (but not from *N*,*N*-dimethylformamide, cf. Table I). The authors ascribed the result to singlet oxygen from termination of HOO• radicals bound to the electrode surface:

$$H^+ \xrightarrow{Pt/e^-} (Pt)H^\bullet \xrightarrow{O_2} (Pt)HOO^\bullet \rightarrow 0.5H_2O_2 + 0.5{}^1O_2 \quad (4)$$

(3) Lee, S. H.; Niu, Q.; Sheng, X. C.; Mendenhall, G. D. *Photochem. Photobiol.* **1989**, *50*, 249-256.

(4) Plots of starting initiator concentration (≤.08 M) vs initial detector response, or area under the decay curve of the luminescence, were linear for oxygen-saturated PhEt at 69 and at 78 °C.

(5) (a) Caminade, A. M.; ElKhatib, F.; Koenig, M.; Aubry, J. M. *Can. J. Chem.* **1985**, *63*, 3203-3209. (b) Turro, N. J.; Chow, M. F.; Rigaudy, J. *J. Am. Chem. Soc.* **1981**, *103*, 7218-7224.

(6) Sugimoto, H.; Kanofsky, J. R.; Sawyer, D. T. *J. Am. Chem. Soc.* **1988**, *110*, 8707-8708.

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