Addition of 1,4-$CH_3OC_6H_4NC$ to **2A** in $CDCl_3$ gave immediate displacement of water to form **2C** (^{1}H NMR, δ 0.94 (t, J = 6.0 Hz 3 H) 3.79 (s, 3 H, OCH_3), and subsequent growth of a singlet resonance at 1.41 ppm with concomitant decay of the triplet at 0.94 ppm. This reaction mixture had IR absorption bands at 2189 (NC) and 1600 cm^{-1} (CO). The isonitrile in **4C** could not be replaced by anions, and instead several such complexes were isolated as crystalline materials [Anal. for $[Ir(PPh_3)_2(CH_3CO)Cl(CH_3C_6H_4NC)_2]BF_4$ ($C_{54}H_{47}N_2OClIrP_2BF_4$) C, H, N; IR (cm^{-1}, Nujol) 2211, 2181 (NC), 1610 (CO), 1051–1087 (BF). Anal. for $[Ir(PPh_3)_2(CH_3CO)Cl(PhCH_2NC)_2]BF_4$ ($C_{54}H_{47}N_2OClIrP_2BF_4$) C, H, N; IR (cm^{-1}, Nujol) 2254, 2223, (NC), 1606, 1054–1090 (BF). Anal. for $[Ir(PPh_3)_2(CH_3CO)Cl(ClC_6H_4NC)_2]BF_4$ ($C_{52}H_{41}OBCl_3F_4IrP_2$) C, H, N; IR (cm^{-1}, Nujol) 2178, 2208 (NC), 1608 (CO), 1030–1090 (BF)].

The methyl migration reaction promoted by the addition of isonitrile was found to be first order in **2C** and independent of isonitrile concentration.[10] The rates of migration with 1,4-substituted benzene isonitriles are not highly dependent on electronic factors; however, the migration rates were slower with benzyl isonitrile and 2,6-diisopropylbenzene isonitrile.

Addition of benzonitrile to **2A** in $CDCl_3$ leads to displacement of water and formation of **2D** (NMR δ 1.11 (t, 5.5 Hz)) and very slow transformation to migrated products **3D** and **4D**. σ donor ligands which were added to **1** which did not lead to migration of the methyl ligand from Ir to CO gave complexes **2** with ν(CO) shifted from 2038 cm^{-1} to the following frequencies (cm^{-1}): Et_3P, 2049; Ph_3PO, 2041; py, 2044; $(CH_3)_2S$, 2047; CH_3CN, 2055; Ph_3As and Ph_3P, 2040; and *p*-anisidine, 2055. Neutral derivatives of **2** where L is an anionic ligand which have been previously reported by Strope and Shriver[11] similarly do not undergo the methyl migration reaction. For example, treatment of the neutral complex **2E** (where L is the chloride anion) in benzene with 20 psi CO for 20 h did not give a methyl migrated product. Weaker π acceptor ligands such as $P(OPh)_3$, $P(OMe)_3$, or dimethyl acetylenedicarboxylate were found not to promote the methyl migration.

The promotion of methyl migration by the π acceptor CO and isonitrile ligands, but not by σ donor ligands, observed in this study is in accord with the calculations of activation energies for methyl migration by Berke and Hoffmann.[6] Complexes **2B** and **2C** with CO and isonitrile ligands trans to the migrating methyl ligand had CO stretching frequencies in the 2068–2077 cm^{-1} region, whereas complexes with σ donor ligands trans to the methyl ligand had CO frequencies in the 2038–2060-cm^{-1} region. In addition to exerting a trans labilization on the migrating methyl ligand, the π acceptor ligands also increase the susceptibility of the CO ligand to nucleophilic attack.[12] Interestingly, organophosphines which promote migration in the 16-electron Pt(II) system[13] do not appear to promote methyl migration in the 18-electron Ir(III) system.

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Supplementary Material Available: Experimental details and analyses (2 pages). Ordering information is given on any current masthead page.

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[10] The rates of migration were determined by measuring the decrease in absorbances of the CO stretching bands of the isonitrile complexes **2C** at 2074 cm^{-1} in dichloromethane at 25 °C. The rate constants ($\times 10^3$ s) observed for the 1,4-X benzene isonitrile complexes were for X = F, 8.6; X = Cl, 7.8; X = H, 8.8; X = CH_3, 8.5; X = CH_3O, 8.3; for $PhCH_2NC$, 3.5; and for 2,6-diisopropylbenzene isonitrile, 2.2.

[11] Strope, D.; Shriver, D. F. *J. Am. Chem. Soc.* **1973**, *95*, 2652.

[12] Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335.

[13] Anderson, G. K.; Cross, R. J. *Acc. Chem. Res.* **1984**, *17*, 67.

UV-Laser Photochemistry: Diffusion-Controlled Trapping of Cyclic 1,3-Diradicals by Molecular Oxygen. Conformational Effects on Triplet Lifetimes

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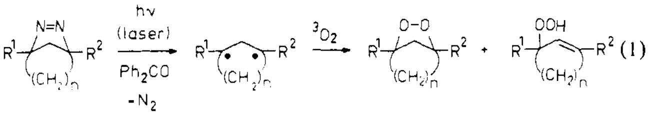
Oxygen trapping of triplet diradicals, generated via benzophenone-sensitized laser photolyses of azoalkane precursors has provided an effective tool for estimating lifetimes of such transient species, especially with localized radical centers such as the cycloalka-1,3-diyls **1** (eq 1).[2] In view of the lack of chromophores in the near UV–vis region, such diradicals are "invisible" in the more usually employed time-resolved laser flash spectroscopic detection.[3] Consequently, the oxygen-trapping method constitutes a complementary and useful extension, which permits probing such subtle features as conformational effects[4] in intersystem crossing processes.



1

1a ($R^1 = R^2 = H$; $n = 2$) **1b** ($R^1 = R^2 = Me$; $n = 2$)
1c ($R^1 = R^2 = H$; $n = 3$) **1d** ($R^1 = H$; $R^2 = Me$; $n = 3$)
1e ($R^1 = R^2 = Me$; $n = 3$)

For assessing the absolute triplet lifetimes in the oxygen-trapping method (competition kinetics), a critical parameter is the rate constant k_t for oxygen trapping (eq 2). Diffusion control

$$1/X_P = 1/[1 - X_H] = 1/T_f + 1/(k_t \cdot \tau_T \cdot [O_2]) \qquad (2)$$

X_P = mole fraction of peroxide (trapped product)

X_H = mole fraction of hydrocarbon (untrapped product)

$T_f = k_t/(k_t + k_c)$, the trapping factor

k_t = rate constant for oxygen trapping

k_c = rate constant for oxygen-catalyzed intersystem crossing

$\tau_T = 1/k_{ISC}$, the triplet lifetime

k_{ISC} = rate constant for intersystem crossing

was assumed[2] to estimate k_t for the cyclopenta-1,3-diyl (**1a**), as shown in (eq 3),[2] where the $^4/_9$ factor is the spin-statistical correction.[5] On one hand, free radicals react with $^3O_2$ at diffusion rates[6] and on the other hand the rate data available from time-

$$k(O_2) = k_t + k_c = (^4/_9) \cdot k_{diff} \qquad (3)$$

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[1] (a) Doctoral Fellow (1985–1987), Fonds der Chemischen Industrie. (b) Undergraduate Research Participant (spring 1986).

[2] (a) Adam, W.; Hannemann, K.; Wilson, R. M. *J. Am. Chem. Soc.* **1986**, *108*, 929. (b) Adam, W.; Hannemann, K.; Wilson, R. M. *Angew. Chem.* **1985**, *97*, 1072.

[3] (a) Scaiano, J. C. *Acc. Chem. Res.* **1982**, *15*, 252. (b) Caldwell, R. A. *Pure Appl. Chem.* **1984**, *56*, 1167. (c) Wirz, J. *Pure Appl. Chem.* **1984**, *56*, 1289.

[4] Salem, L.; Rowland, C. *Angew. Chem.* **1972**, *84*, 86.

[5] For the reaction of two triplets only the singlet and the three triplet encounter complexes lead to products, whereas the five quintets are dissociative.

Table I. Lifetimes (τ_T) of Triplet Diradicals **1a–e**[a]

diradical	solvent	slope^{-1} $k_t\ \tau_T{}^b$ (M^{-1})	viscosity π^c [cp]	diffusion rate constants $10^{-10}\cdot k(O_2)$ [m^{-1} s^{-1}] eq 4	eq 5[d]	triplet lifetimes[e] τ_T [ns] eq 4	eq 5
1a	n-C_7H_{16}	1700 ± 200	0.47	0.53	1.8	320 ± 40	93 ± 11
1a	C_6H_6	1860 ± 300	0.80	0.31	1.6	600 ± 100	115 ± 20
1a	n-$C_{12}H_{26}$	840 ± 60	1.94	0.13	*f*	620 ± 50	
1a	n-$C_{14}H_{30}$	780 ± 40	3.05	0.08	*f*	920 ± 50	
1a	$(CH_3)_2CHOH$	840 ± 200	3.78	0.07	0.85	1100 ± 300	93 ± 28
1b	n-C_7H_{16}	710 ± 100	0.47	0.53	1.8	140 ± 20	42 ± 7
1c	n-$C_{12}H_{26}$	70 ± 10	1.94	0.13	*f*	56 ± 18	
1d	n-$C_{12}H_{26}$	58 ± 5	1.94	0.13	*f*	52 ± 21	
1e	n-$C_{12}H_{26}$	53 ± 10	1.94	0.13	*f*	40 ± 20	

[a] Determined by benzophenone-sensitized photolysis (Coherent argon ion laser, Innova 18, 363.8-nm line (0.2 W)) under oxygen pressure (1–10 atm) at 8 °C by using eq 2 (cf. ref 2a for experimental details). [b] The trapping factor (T_f) was unity in the error limit for all systems, thus the rate constant for oxygen-catalyzed intersystem crossing (k_c) was negligible compared to trapping (k_1). Quoted error limits are standard errors. [c] Weast, R. C.; Astle, H. J. *Handbook of Chemistry and Physics*, 60th ed.; CRC Press: Boca Raton FL, 1980; p F-52f. Riddig, J. A.; Bunger, W. B. *Organic Solvents*; John Wiley and Sons: New York, 1970: p 29f. [d] The diffusion constants (D) and radii (r) of the 1,3-diradical **1a** in n-heptane, benzene, and isopropyl alcohol were approximated as those of anthracene, cf. ref 8 and 9 and Bowen et al. (Bowen, E. J.; Metcalf, W. S. *Proc. Roy. Soc. A, London* **1951**, *206*, 437). [e] These error limits reflect reproducibility, but the systematic error can be much larger. [f] Data not available.

resolved laser flash spectroscopy[7] justifies this assumption also for diradicals. However, an attempt to verify diffusion control for the cyclopenta-1,3-diyl (**1a**) in a variety of solvents (Table I; entries 1–5, seventh column) using the Smoluchowski–Einstein–Stokes relationship (eq 4) failed.

$$k_{\text{diff}} = 2\cdot 10^5\cdot T/\eta \qquad (4)$$

As expected[8] at the molecular level, the macroscopic property viscosity does not adequately account for the diffusional behavior of small, symmetrical molecules like oxygen. According to eq 4, in the more viscous solvents oxygen diffuses slower than in actual fact and consequently the lifetimes are too long.

An analogous problem was encountered in the quenching of anthracene (A) fluoescence by $^3O_2$.[9] Nevertheless, the use of the original Smoluchowski relationship (eq 5) gave good agreement

$$k_{\text{diff}} = 4\pi N_L\cdot 10^{-3}[D(O_2) + D(A)][r(O_2) + r(A)] \qquad (5)$$

N_L = Avogadro number

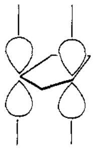
D = diffusion constant

r = diffusion radius

between experiment and theory. Indeed, by making the rough approximation that the D and r values of the cyclopenta-1,3-diyl (**1a**) are approximately those of anthracene, for the few solvents (n-heptane, benzene, and isopropyl alcohol) for which data are available, the τ_T values fall in the range 100 ± 30 ns (Table I; entries 1, 2, and 5, last column). Not only are these values substantially lower (ca. four- to sixfold) than previously published[2] but also more significantly within the experimental error they are constant over an almost eightfold variation in viscosity. Clearly, diffusion control upholds for the trapping of triplet diradicals by molecular oxygen, provided the molecular diffusion constants (eq 5) and not the macroscopic viscosities (eq 4) are employed in estimating $k(O_2)$.

To explore the effects of methyl substitution at the radical sites and the ring size, the 1,3-diradicals **1b–e** were generated from the respective azoalkanes (eq 1) and oxygen-trapping determined quantitatively.[10] The triplet lifetimes of these diradicals are also given in Table I. For experimental reasons (gas chromatographic analysis of the hydrocarbon products), instead of n-heptane, it was necessary to use n-dodecane as solvent for the cyclohexa-1,3-diyls **1c–e**. Unfortunately, no diffusion constants were available in n-dodecane, so that the oxygen-trapping rate constants $k(O_2)$ had to be estimated from eq 4 with use of viscosities (Table I; entries 7–9, seventh column). Making the reasonable correction that the τ_T values based on viscosity are about three- to fivefold too large, the true lifetimes of the cyclohexa-1,3-diyls **1c–e** lie in the 10–20 ns range (Table I; entries 7–9, last column).

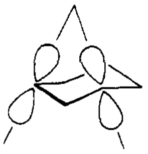
Clearly, methyl substitution at the radical sites causes a minor reduction in the triplet lifetimes (Table I; entries 1 vs 6; last column); however, the ring size effect is substantial. For example, for the parent diradicals the lifetime of the cyclopenta-1,3-diyl (**1a**) is about 10-fold longer than for the cyclohexa-1,3-diyl (**1c**), cf. Table I (entries 2 and 7, seventh column). Recalling the fact[2] that the bicyclo[2.2.1]hepta-2,7-diyl (**2**) can not be trapped with $^3O_2$ (i.e., its lifetime must be under diffusion limit or $\tau_T \leq 0.1$ ns), conformational effects are presumably responsible for the large variation in the τ_T values (1000-fold) of the triplet diradicals **1a**, **1c**, and **2**.



1a

θ ~ 0°

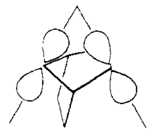
τ_T ~ 70–130 ns



1c

θ ~ 45°

τ_T ~ 10–20 ns



2

θ ~ 60°

τ_T < 0.1 ns

According to the Salem rule,[4] optimal spin-orbit coupling, i.e., fast intersystem crossing and consequently short triplet lifetimes, should prevail when the two interacting radical orbitals are oriented at each other with a 90° interorbital angle. The total angular momentum is then conserved, since the change in the spin angular momentum is exactly offset by the change in orbital momentum during the intersystem crossing process.

Molecular mechanics calculations[11] suggest that in the lowest energy conformations the interorbital angles are ca. 0°, 45°, and 60° for the 1,3-diradicals **1a**, **1e**, and **2**, respectively. Thus, for the planar cyclopenta-1,3-diyl (**1a**) (planarity confirmed by ESR[12]) intersystem crossing by spin-orbital coupling should be most difficult, and hence it should have a relatively long triplet lifetime. In contrast, the rigid puckered bicyclo[2.2.1]hepta-2,7-diyl (**2**) should be the most short-lived species of the three. The flexible twist-boat conformation of the cyclohexa-1,3-diyl (**1c**) possesses intermediate lifetime. Other than such conformational effects, it is difficult to rationalize the lifetimes of these rather similar 1,3-diradicals.

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(6) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

(7) (a) Barton, D. H. R.; Charpiot, B.; Ingold, K. U.; Johnston, L. J.; Motherwell, W. B.; Scaiano, J. C.; Stanforth, S. *J. Am. Chem. Soc.* **1985**, *107*, 3607. (b) Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* **1977**, *48*, 354. (c) Kobashi, H.; Ikawa, H.; Kondo, R.; Morita, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3013. (d) Kobashi, H.; Kondo, R.; Ikawa, H.; Morita, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1197. (e) Takamuku, S.; Schnabel, W. *Chem. Phys. Lett.* **1980**, *69*, 399. (f) Naito, I. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2851.

(8) Osborne, A. D.; Porter, G. *Proc. Roy. Soc. A, London* **1965**, *284*, 9.

(9) Ware, W. R. *J. Phys. Chem.* **1962**, *66*, 455.

(10) All new compounds were fully characterized (elemental analyses, spectral data, etc.).

(11) An MMPMI program was used, kindly provided by K. E. Gilbert and J. J. Gajewski, Serena Software, Bloomington, IN.

(12) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688.

We consider these lifetime data as experimental verification of Salem's orbital orientation rule.[4] It should be possible to devise long-lived, localized triplet diradicals by incorporating the radical sites into planar and rigid molecular skeletons.

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UV-Laser Photochemistry of the Azoalkane 1-Phenyl-2,3-diazabicyclo[2.2.2]oct-2-ene: Detection and Lifetime Determination of the Triplet Diradical 1-Phenyl-1,4-cyclohexadiyl by Time-Resolved UV Spectroscopy (Flash Photolysis) and by Trapping with Molecular Oxygen

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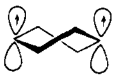
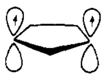
The short lifetime (τ_T) of the triplet diradical 1,4-cyclohexadiyl (**1**) compared to the relatively long-lived 1,3-cyclopentadiyl (**2**)

1a

τ_T~0.1 ns



1b



2

τ_T~100 ns

was previously[2] rationalized in terms of Salem's orbital orientation rule.[3] It was argued that in its boat conformation the 1,4-cyclohexadiyl (**1a**) suffers fast intersystem crossing through favorable orientation of the orbital lobes for spin-orbit coupling, resulting in a short lifetime and thus inefficient trapping by $^3O_2$. In analogy to the planar 1,3-cyclopentadiyl (**2**), the twist-boat conformation of the 1,4-cyclohexadiyl (**1b**) should be a relatively long-lived triplet diradical, since the parallel radical lobes constitute an unfavorable arrangement for intersystem crossing. Indeed, theoretical work[4] on the tetramethylene fragment predicts a triplet ground state, provided the radical lobes are aligned parallel, i.e., analogous to the twist-boat conformation of the 1,4-cyclohexadiyl (**1b**). Presently we provide experimental evidence that phenyl stabilization promotes conformational relaxation to the favored twist-boat triplet ground state, resulting in the long-lived 1-phenyl-1,4-cyclohexadiyl (**3b**). The generation of the 1,4-diradical **3** via photolysis (Coherent Supergraphite CR 18 argon ion laser) and product formation (with and without oxygen trapping) is summarized in Scheme I, together with the rate constants used to derive eq 1.[2a]

Direct laser photolysis of azoalkane **4**[5] in benzene at 364 nm gave diene **5**, presumably via the singlet diradical **S-3**. Control experiments showed that prolonged photolysis gave about 5% of the unknown bicyclo[2.2.0]hexane **6** as secondary product.[6] Under benzophenone sensitization (333 nm) small amounts of the bicyclo[2.1.1]hexane **7** were formed.[7] In the presence of molecular oxygen (10 atm), the benzophenone-sensitized laser photolysis (333 nm) in $CFCl_3$ at −10 °C gave besides the hexadiene **5** the peroxides **8** (1.3%), **9** (4.6%), and **10** (5.7%), isolated by means of flash chromatography on silica gel at −25 °C.[6] An authentic sample of the cyclic peroxide **8** was prepared by photooxygenation of 1-phenyl-1,3-cyclohexadiene[8] and diimide reduction.[9]

The benzyl chromophore should allow for a direct detection of the diradical **3** by UV spectroscopy.[10] This was achieved by kinetic and spectrographic nanosecond flash photolysis at ambient temperature using a XeF excimer laser (351 nm, 100 mJ, 25 ns).[11] No transient was observed after direct excitation of the azoalkane **4** ($5 \cdot 10^{-2}$ M, CH_3CN). In the presence of benzophenone and **4**, in concentrations ($5 \cdot 10^{-3}$ M and $2 \cdot 10^{-3}$–$1 \cdot 10^{-2}$ M, respectively) such that most of the 351-nm radiation was absorbed by the former, the first-order decay curves in the visible region indicated that triplet benzophenone (λ_{max} 530 nm) was quenched by **4** with a rate constant of ca. $6 \cdot 10^9$ M^{-1} s^{-1}. Transient absorption spectra, taken with a suitable delay such that essentially all the triplet benzophenone had decayed, showed an absorption band in the range of 300–330 nm which disappeared more slowly. Kinetic traces in that wavelength region were clearly biphasic and could be fitted quite well with a dual exponential rate law; the faster decay rate was within the limits of error equal to the single exponential decay rate determined in the visible region. The second transient is attributed to the triplet diradical **T-3**. Its decay rate grew linearly with increasing oxygen pressure, affording $k(O_2) = 1.6(\pm 0.1) \cdot 10^{10}$ M^{-1} s^{-1} and $2.2(\pm 0.2) \cdot 10^{10}$ M^{-1} s^{-1}, respectively, in C_6H_6 and CH_3CN. *We conclude that the rather long-lived diradical* ***T-3*** *(τ = 275 ± 15 and 248 ± 15 ns in C_6H_6 and CH_3CN, respectively) reacts with triplet oxygen at an essentially diffusion-controlled rate.*

To determine the triplet lifetime of the 1,4-diradical **T-3** by the quantitative oxygen-trapping technique, the benzophenone-sensitized photolysis was conducted in benzene at varying oxygen concentrations as previously described.[2a] According to the kinetic expression (eq 1), the slope ($6.2(\pm 1.0) \cdot 10^{-4}$ M^{-1}) and intercept (2.8 ± 0.1) were obtained from a $1/(1 - X_H)$ vs $1/[O_2]$ plot. The trapping factor was calculated to be $T_f = 0.36 \pm 0.01$ as the reciprocal intercept. Clearly, spin-catalyzed intersystem crossing (k_c) by $^3O_2$ dominates trapping (k_t) for this triplet diradical. The triplet lifetime was calculated from the slope, employing the $k(O_2)$ value from the flash photolysis results. The agreement in the triplet lifetimes in benzene from oxygen trapping (τ_T = 280 ± 40 ns) and flash photolysis (τ_T = 275 ± 15 ns) is most gratifying. This fact underscores the reliability of the oxygen-trapping method for estimating lifetimes of triplet diradical transients and validates the assumption of diffusion control in the oxygen trapping rate.[12]

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[1] (a) Kekulé Doctoral Fellow (1985–1987), Stiftung Volkswagenwerk. (b) Liebig Postdoctoral Fellow (1986–1988), Fonds der Chemischen Industrie.

[2] (a) Adam, W.; Hannemann, K.; Wilson, R. M. *J. Am. Chem. Soc.* **1986**, *108*, 929. (b) Adam, W.; Hannemann, K.; Wilson, R. M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1071.

[3] Salem, L.; Rowland, S. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

[4] Doubleday, C.; McIver, J.; Page, M. *J. Am. Chem. Soc.* **1985**, *107*, 7904.

[5] Engel, P. S.; Horsey, D. W.; Keys, D. E.; Nalepa, C. J.; Soltero, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 7108.

[6] All new compounds were fully characterized by elemental analyses and spectral data.

[7] Yamada, C.; Pahk, M. J.; Lin, R. S. *J. Chem. Soc., Chem. Commun.* **1970**, 882.

[8] Kaneko, C.; Sugimoto, A.; Tanaka, S. *Synthesis* **1974**, 876.

[9] (a) Adam, W.; Eggelte, H. J. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 713. (b) Coughlin, D. J.; Salomon, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 655.

[10] (a) Scaiano, J. C. *Acc. Chem. Res.* **1982**, *15*, 252. (b) Caldwell, R. A.; Sakuragi, H.; Majima, T. *J. Am. Chem. Soc.* **1984**, *106*, 2471. (c) Wirz, J. *Pure Appl. Chem.* **1984**, *56*, 1289.

[11] Leyva, E.; Platz, M. S.; Persy, G.; Wirz, J. *J. Am. Chem. Soc.* **1986**, *108*, 3788.

[12] (a) In special cases $k(O_2)$ can be as slow as $1 \cdot 10^9$ M^{-1} s^{-1}; cf. Hasler, E.; Gassmann, E.; Wirz, J. *Helv. Chim. Acta* **1985**, *68*, 777. (b) Adam, W.; Hössel, P.; Hümmer, W.; Platsch, H. *J. Am. Chem. Soc.*, preceding communication in this issue.