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Absolute Rates of Heterocyclic Singlet Biradical Reactions Determined by Nanosecond Time-Resolved Absorption Spectroscopy. Dimerizations and Cycloadditions to Alkenes and to Dioxygen[1]

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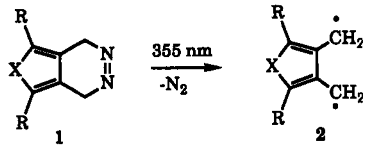
Singlet biradicals of the 3,4-dimethyleneheterocycle series, where the heterocycle is furan, thiophene, or *N*-substituted pyrrole, with chromophores in the UV–vis region (560–640 nm), are generated by nanosecond laser flash photolysis of diazene precursors in fluid solution. The rate constants for disappearance of these transients are determined by time-resolved absorption spectroscopy using the long-wavelength band. The rate constants for dimerization are near the encounter-controlled rate. Rates of trapping by alkenes are well described by a frontier orbital model. Oxygen trapping rate constants range between 10^7 and 10^9 M^{-1} s^{-1}. The ratios of rate constants for trapping of 3,4-dimethylene-*N*-(*p*-toluenesulfonyl)pyrrole by pairs of alkenes in preparative competition experiments are in good agreement with those determined by the flash photolytic method. This confirms assignments of the 3,4-dimethyleneheterocycle structure to the chromophore of the biradical transients.

Objectives and Experimental Design

Knowledge of the kinetics and mechanisms of the cycloadditions of biradicals can elucidate the electronic structure and spin of these elusive species. Some prior kinetic work has been done on π-conjugated singlet biradicals, but little is known of the effect of systematic structural alteration. For example, previous studies[3–6] have described the generation of the singlets 3,4-dimethylenefuran (**2a**)and 3,4-dimethylenethiophenes (**2b** and **2c**) from the diazene precursors **1a–c**. In the cycloadditions of a given biradical, the relative and absolute diylophilic reactivities of a series of alkenes correlate well with the Diels–Alder dienophilic reactivities of the same alkenes toward cyclopentadiene. The latter in turn are related to the LUMO energy[7] of the dienophile.



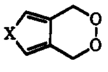
	R	X
a:	H	O
b:	H	S
c:	CH_3	S
d:	H	NCH_3
e:	H	NCOt-Bu
f:	H	$NSO_2C_7H_7$

One objective of the present paper is to test whether the complementary behavior can be observed when the alkene is held constant and the HOMO energy of the diyl is systematically varied. Substitution of the imino functional hydrogen of 3,4-dimethylenepyrroles (**2d–f**) offers the means to adjust the HOMO energy by synthetic alteration of the molecular structure.[8]

A second objective is to test whether the extremely fast rate of dimerization found[9] for the hydrocarbon biradical 1,2,4,5-tetramethylenebenzene (TMB) is a common property of singlet biradicals. A third is to clarify the dynamics of formally spin-forbidden processes through a study of reactions of triplet O_2 with singlet biradicals, and a fourth is to compare the profile of relative reactivity of alkene trapping agents toward the biradicals as measured by two independent methods. Agreement of the relative reactivities of the alkene trapping agents determined by preparative competition experiments and by quenching of the chromophore generated in nanosecond flash photolysis would be strong evidence that the transient species in the two experiments are identical.

Characterization and Preparative Reactivity of the Biradicals

The diazene precursors (**1d–f**) of the 3,4-dimethylenepyrrole series of biradicals were synthesized by methods described elsewhere.[8b,c] Independent preparative scale experiments showed that the thermally or photochemically generated biradicals **2d–f**, like their furan and thiophene counterparts **2a–c**, could be trapped by dioxygen or alkenes in fluid media or in thawed matrices to give cycloadducts with the fused structures **3** and **4**, respectively. The alkene adducts were formed by stereospecific syn addition.[8a]



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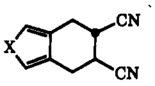

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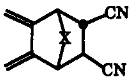

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The diazene precursors **1a–f** upon irradiation (λ ≥ 350 nm) in glassy 2-methyltetrahydrofuran matrices at 77 K gave visibly colored preparations with UV–vis spectra showing long wavelength absorption maxima in the range 560–665 nm, $\epsilon \sim 5000$ M^{-1} cm^{-1}, ascribed to the corresponding biradicals **2a–f**. The spectra and color disappeared when the matrix was softened by warming. All of the preparations were ESR-silent, which supports the evidence from trapping and other studies[3–6,8a] that these are singlet species.

Kinetic Measurements

For the determination of dimerization rate constants, fluid methylene chloride solutions of the diazene precursors **1a–f**[10] were deoxygenated in 7 × 7 mm static cells (initial optical densities ~0.5 at 355 nm), kept at 220–230 K to minimize thermal decomposition and subjected to 355-nm nanosecond light pulses from a YAG laser. Initial transient concentrations typically were near 10^{-5} M. Transient spectra with maxima corresponding to

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TABLE I: Absolute Rate Constants[a] of Reactions of Biradicals

biradical	$2k_t \times 10^{-10}$	$k_{O_2} \times 10^{-8}$	$k_{FN} \times 10^{-9}$
2a	3.3[b]	7.58	0.317[b]
2b	0.93[b]	0.0894	0.0111[b]
2c	3.7	0.529	*c*
2d	*c*	0.0339	1.44
2e	6.6	8.26	0.129
2f	2.8	1.31	0.0318

[a] All measurements in this paper were made in methylene chloride solvent at 220–230 K. Rate constants in units of $M^{-1} s^{-1}$. Estimated errors in the values of $2k_t$ are 50% except for **2e**, where the error can be as much as a factor of 2. [b] Reference 5; solvent CH_3CN at 295 K. [c] Not measured.

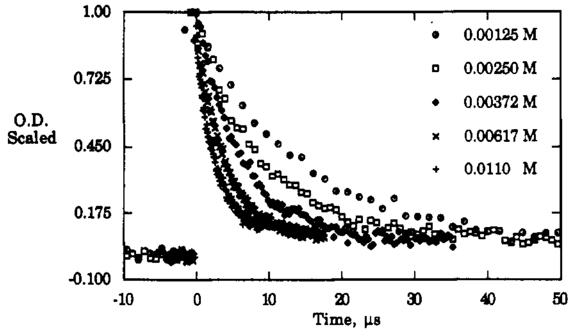


Figure 1. Quenching kinetics for the reaction of *N*-(*p*-toluenesulfonyl)-3,4-dimethylenepyrrole biradical **2f** with varying concentrations of fumaronitrile monitored by relative optical density (OD) at 600 nm.

those observed in the matrices were obtained from delay traces at various wavelengths. The decay of each transient was monitored at or near the wavelength maximum with a photomultiplier–transient digitizer system.[11] The decay kinetics in each case fit a second-order equation and gave rise to the dimerization rate constants ($2k_t$) shown in Table I. We estimate that the error in the dimerization rate constants is about 50% and is primarily attributable to the uncertainty of about 20% in the extinction coefficients. In the particular case of the 3,4-dimethylene-*N*-pivaloylpyrrole biradical **2e**, the error, estimated to be about a factor of 2, is caused by a temporary instrumental instability during that set of runs.

Samples of the precursors **1a–f** in methylene chloride containing an alkene or oxygen in large excess (pseudo-first-order conditions) were subjected to light pulses, and the transient absorptions were monitored in the same way. The rate constants were determined by fitting observed decay curves of the type shown in Figure 1 and were strictly linear ($r > 0.99$) in the trapping agent concentration. Measurements of reactivities of biradicals toward O_2 and/or fumaronitrile gave the results collected in Table I.

In one case, the reactivity of the transient toluenesulfonyl derivative **2f** was measured toward four alkenes: acrylonitrile, diethyl fumarate, fumaronitrile, and maleic anhydride. These data are collected in Table II, which for comparison also gives rates (measured earlier[5]) of trapping of the furan and thiophene biradicals **2a** and **2b** with the same alkenes.

Correlation of Reactivity of Alkenes with the 3,4-Dimethylene-*N*-(*p*-Toluenesulfonyl)pyrrole Biradical 2f against Their Reactivity with Biradicals 2a and 2b and against Their Diels–Alder Reactivity with Cyclopentadiene

The rate constants for quenching the absorption of biradical **2f** by the four alkenes shown in Table II are linearly correlated with those of the same alkenes quenching the furan biradical **2a** ($r = 0.98$) and the thiophene biradical **2b** ($r = 0.99$). A somewhat rougher correlation ($r = 0.97$) exists with the rate constants for Diels–Alder addition of cyclopentadiene to the same alkenes. A good correlation ($r > 0.99$) has been observed[3,4] between the reactivities of the thiophene biradical **2b** and cyclopentadiene.

TABLE II: Absolute Rates of Reaction ($\times 10^{-6}$ M s) of Biradicals with Alkenes

biradical	maleic anhydride	fumaronitrile	diethyl fumarate	acrylonitrile
2a[a]	1220	317	62.5	0.416
2b[a]	574	111	10.4	0.0238
2f[b]	728	31.8	7.20	0.0142

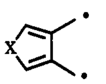
[a] Reference 5; solvent CH_3CN. [b] Present work; solvent CH_2Cl_2.

Correlation of Reactivity of Biradicals 2a–f with Fumaronitrile against the Reciprocal of the Frontier Orbital Energy Gap of the Reactants

The rate constants k_{FN} (Table I) for the capture of the series of biradicals **2a–f** by fumaronitrile are correlated ($r = 0.986$) by the approximate frontier orbital equation $\ln k_{FN} = \text{const}[1/(H_{2d} - L_{FN})] - [1/(H_x - L_{FN})]$, where H_{2d} and H_x are the PM3[13] energies of the HOMO of biradical **2d** and the HOMO of one of the other biradicals, respectively, and L_{FN} is the energy of the LUMO of fumaronitrile. This correlation of diyl reactivity, taken with the complementary correlation of diylophile reactivity described above, demonstrates that the relative rates of trapping of these singlet biradicals is satisfactorily modeled as a frontier orbital effect in both the diyl and diylophile components.

Absolute Rates of Dimerization of Singlet Biradicals

Previous studies[5,6,9] of the kinetics of dimerization of singlet biradicals in fluid solution showed that the rate constants were close to those predicted by a diffusion-controlled, spin-unrestricted process. In solvents methylene chloride at 230 K and acetonitrile at 260 K, the encounter-limited dimerization rate constants ($2k_{diff}$) calculated from the expression $k_{diff} = 8RT/(3000\eta)$ of the Debye–Stokes–Einstein model of the Smoluchowski theory[12] are about (1.5 and 2.26) $\times 10^{10}$ $M^{-1} s^{-1}$. The data in Table I show that the rates ($2k_t$) of the dimerizations all approach or even formally exceed the calculated values of the encounter limit. The dimerization rates in principle cannot exceed the encounter limit, but the calculated values of this limit are only approximate. One factor that is difficult to take into account is the variation of sizes and shapes of the biradicals. The truncated Spernol–Wirtz semiempirical procedure[12] sometimes can be used to refine the calculation of the diffusion rate, but in the present instances, the match of $2k_{diff}$ with $2k_t$ did not improve. Nevertheless, there can be little doubt that these reactions, which are among the fastest bimolecular processes in solution, are essentially diffusion-controlled. This result supports the previous assignments[3–6] of true biradical structures (**2**) rather than full-valence structures (*e.g.*, **6**) to the transient species that carry the chromophore.



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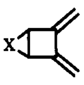

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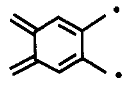

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Absolute Rates of Reaction of the Biradicals with Dioxygen

In numerous determinations of the rates of reaction of triplet biradicals[14–17] and triplet carbenes[18–20] with O_2, the rate constants cluster around the value 5×10^9 $M^{-1} s^{-1}$. This is close to the statistically modified[12] diffusion-limited encounter frequency, which takes into account the fact that only $^1/_9$–$^4/_9$ of the triplet–triplet encounters can lead directly to product. On the other hand, the few singlet carbenes for which measurements are available[21,22] show much slower rates of dioxygen trapping: $k_{O_2} = 2.24 \times 10^7$ $M^{-1} s^{-1}$ for (*p*-nitrophenyl)chlorocarbene and $<10^4$ $M^{-1} s^{-1}$ for phenylchlorocarbene. Recent determinations[23] of k_{O_2}

for the singlet non-Kekulé hydrocarbon 1,2,4,5-tetramethylenebenzene (**7**) gave slightly solvent-dependent values in the range (1.85–3.10) × 10^7 M^{-1} s^{-1}, which, like those for the singlet carbenes, again are far below the diffusion limited rate. Few, if any, other directly measured k_{O_2} values for singlet biradicals have been reported.

Table I shows the values of the dioxygen trapping rate constants for the series of singlet biradicals in the present work. The rate constants vary over the range 10^7–10^9 M^{-1} s^{-1}. In contrast to the fumaronitrile (FN) trapping data, which are well correlated with the biradical HOMO-FN LUMO energy separation (see above), the k_{O_2} values give only a scattered plot.

These findings suggest the need for caution in the assumption[24] of rates of reactions of singlet biradicals with dioxygen. It is clear that some singlet reactions with dioxygen can be quite fast. For example, the k_{O_2} value of 8.26 × 10^8 M^{-1} s^{-1} now observed for the singlet **2d** is within a factor of 6 of the statistically modified diffusion limit. This casts some doubt upon the generality of the proposal[24] that "the magnitude of the singlet–triplet splitting should be determinable by competition experiments with multiplicity-specific trapping agents."

Identity of the Carrier of the Chromophore and the Reactive Species Responsible for Adduct Formation

The biradical *N*-(*p*-toluenesulfonyl)-3,4-dimethylenepyrrole **2d** has recently been observed[8] in both the singlet and the triplet state in matrix-immobilized preparations. The singlet species appears as a blue, ESR-silent species which shows a band in the UV–vis spectrum at 600 nm, $\epsilon \sim 5100$ M^{-1} cm^{-1}. It is this same absorption band whose rate of disappearance forms the basis of the absolute rate constant measurements of the present work. In separate preparative experiments, we now have determined[25] relative rate constants for capture of a **2f** transient by pairwise competitions of alkene trapping agents. If the species responsible for the preparative chemistry is the same as the one that carries the UV–vis absorption spectrum, the competition ratios from the preparative experiments should match those derived from the absolute rate constants. From Table II, the ratio of rate constants calculated from the absolute rate data for the trapping reactions of biradical **2f** by the pair maleic anhydride:fumaronitrile is 22.9, as compared to the value of 17.8 determined in the preparative experiments. Similarly, the fumaronitrile:diethyl fumarate[26] ratios are 4.4 and 3.0, respectively. In both comparisons, the ratios match within experimental error. This supports the conclusion that the chromophore from diazene **1f** is the same species that is responsible for the preparative chemistry. Since the structures of the adducts from this species have been shown[8] to be **3**, **4**, and **5**, the structure 3,4-dimethylene-*N*-(*p*-toluenesulfonyl)pyrrole (**2f**) may be assigned confidently to the chromophore.

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References and Notes

(1) This paper is dedicated to the memory of Gerhard L. Closs.

(2) (a) Yale University. (b) Ottawa-Carleton Chemistry Institute.

(3) Greenberg, M. M.; Blackstock, S. C.; Berson, J. A. *Tetrahedron Lett.* **1987**, *28*, 4263.

(4) (a) Stone, K. J.; Greenberg, M. M.; Blackstock, S. C.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 3659. (b) Haider, K. W.; Clites, J. A.; Berson, J. A. *Tetrahedron Lett.* **1991**, *32*, 5305.

(5) Scaiano, J. C.; Wintgens, V.; Bedell, A.; Berson, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 4050.

(6) Scaiano, J. C.; Wintgens, V.; Haider, K.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 8732.

(7) (a) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779. (b) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley & Sons: New York, 1976; pp 23–29, and references cited therein.

(8) (a) Bush, L. C.; Heath, R. B.; Berson, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 9830. (b) Supplementary material to a. (c) The participation of W.-S. Chung and M. Walker in a phase of the synthetic work is gratefully acknowledged.

(9) Reynolds, J. H.; Berson, J. A.; Scaiano, J. C.; Berinstain, A. B. *J. Am. Chem. Soc.* **1992**, *114*, 5866.

(10) Although the *N*-(*p*-toluenesulfonyl)pyrrolo diazene **1f** was reasonably stable at room temperature, the others were not. The *N*-methylpyrrolo diazene **1d** was especially unstable and required manipulation below −40 °C.

(11) The nanosecond laser system has been described elsewhere: Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

(12) Saltiel, J.; Atwater, B. W. *Adv. Photochem.* **1988**, *14*, 1, and references cited therein.

(13) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209, 221.

(14) (a) Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res.* **1990**, *23*, 165. (b) Johnston, L. J.; Scaiano, J. C. *Chem. Rev.* **1989**, *89*, 521.

(15) Burnett, M. N.; Boothe, R.; Clarke, E.; Gisin, M.; Hassaneen, H. M.; Pagni, R. M.; Persy, G.; Smith, R. J.; Wirz, J. *J. Am. Chem. Soc.* **1988**, *110*, 2527.

(16) Naito, I. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2851.

(17) (a) Adam, W.; Hössel, P.; Hümmer, W.; Platsch, H.; Wilson, R. M. *J. Am. Chem. Soc.* **1987**, *109*, 7570. (b) Adam, W.; Grabowski, S.; Wilson, R. M.; Hannemann, K.; Wirz, J. *J. Am. Chem. Soc.* **1987**, *109*, 7572. (c) Adam, W.; Grabowski, S.; Platsch, H.; Hannemann, K.; Wirz, J.; Wilson, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 751.

(18) (a) Werstiuk, N. H.; Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 2391. (b) Casal, H. L.; Tanner, M.; Werstiuk, N. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 4616. (c) Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928. (d) Sugawara, T.; Iwamura, H.; Hayashi, H.; Sekiguchi, A.; Ando, W.; Liu, M. T. H. *Chem. Lett.* **1983**, 1261.

(19) Nazran, A. S.; Griller, D. *J. Am. Chem. Soc.* **1984**, *106*, 543.

(20) Sander, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344.

(21) Liu, M. T. H.; Bonneau, R.; Jefford, C. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1482.

(22) (a) Turro, N. J.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W.; Munjal, R.; Fedorynski, M. *J. Am. Chem. Soc.* **1980**, *102*, 7576. (b) Turro, N. J.; Lehr, G. F.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W. *J. Am. Chem. Soc.* **1982**, *104*, 1754.

(23) Reynolds, J. H.; Berson, J. A.; Kumashiro, K. K.; Duchamp, J. C.; Zilm, K. W.; Scaiano, J. C.; Berinstain, A. B.; Rubello, A.; Vogel, P. *J. Am. Chem. Soc.* **1993**, *115*, 8073.

(24) Roth, W. R.; Langer, R.; Ebbrecht, T.; Beitat, A.; Lennartz, H.-W. *Chem. Ber.* **1991**, *124*, 2751.

(25) The methodology of this type of experiment has been described.[3,4]

(26) High-performance liquid chromatographic analysis of the reaction mixtures required the use of dimethyl fumarate instead of diethyl fumarate in the competition experiment.