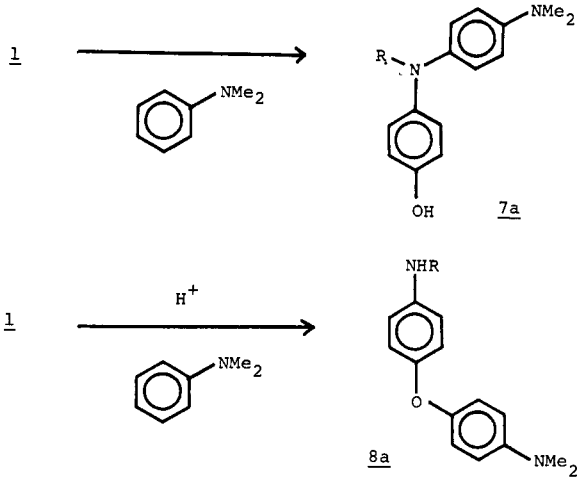
Chart III



the *oxygen* atom of the quinone imine. Another product identified was 4-hydroxymethanesulfonylanilide (**4a**), the formation of which could be explained as due to an oxidoreduction between **1a** and **3a**. The reduction of **1a** to **4a** was effected by the reaction of **1a** with isolated **3a**. The presence of excess phenol and high dilution increased the yield of **3a** and decreased the formation of **4a**. The presence of an acid, trifluoroacetic acid (TFA, 2 equiv to **1a**), increased the reaction rate: the reaction (**1** → **3**) is acid catalyzed. The formation of **3a** was not affected by air, light, benzoyl peroxide, azobis(isobutyronitrile), diphenyl(trinitrophenyl)hydrazyl, *m*-dinitrobenzene, or 1,1-diphenylethylene.

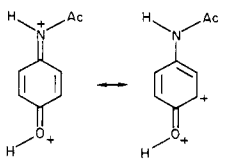
Reaction under strongly acidic conditions (5 equiv of trifluoromethanesulfonic acid) gave a diphenyl derivative **5a**.[6] Addition of triethylamine to the reaction also abolished the formation of the diphenyl ether **3a** and gave another diphenyl ether, **6a** (Chart II).[7]

The reaction of **1a** with excess *N*,*N*-dimethylaniline in methylene chloride in the presence of a catalytic amount of acid gave 4-(dimethylamino)-*N*-(4-hydroxyphenyl)methanesulfonylanilide (**7a**) in 50–60% yield. However, addition of excess protonic acid partially changed the reaction site from the nitrogen atom to the oxygen atom. Thus, a diphenyl ether (**8a**) was formed in 20–30% yield in the presence of TFA (5–10 equiv to dimethylaniline), though accompanied with **7a** (30–35%) (Chart III). This confirmed that the reaction on the oxygen atom requires the presence of a proton.

The reaction of **1a** with aniline proceeded similarly, but the yield of the corresponding products was low (15%) because of their instability under the reaction conditions. *N*-Acetyl- and *N*-(*p*-nitrobenzoyl)-*p*-benzoquinone imines (**1b** and **1c**) reacted similarly with phenol in methylene chloride, leading to formation of diphenyl ethers **3b** and **3c**, respectively. In these cases too, acid is required for the reaction at the oxygen atom.

The reaction on the oxygen atom can be explained as involving the *N*-protonated *N*-acyl-*p*-benzoquinone imine,[8] a kind of phenoxenium ion (**2**), which reacts with nucleophilic phenol or anilines.[9] Carbonyl polarization against atomic electronegativity is made possible by the aromatization of the protonated species, and the cation is stabilized by the acylamino group. No reasonable pathway which leads to **3** or **8** by rearrangement of an intermediate product is conceivable. A homolytic or radical chain mechanism cannot be involved, since the reaction is not affected by radical scavengers nor initiators. A reaction on the oxygen and carbon atoms of the *p*-nitrophenoxenium ion with anisole has been reported,[10] while unsubstituted phenoxenium ion reacts with the phenyl ring but not the oxygen atom in the reaction with phenol.[11] The present phenoxenium ion **2** must be more stable than the above species; this is consistent with the preferred attack at the para position of phenol.[12] It does not react with anisole on the oxygen atom in the presence of 2 equiv of TFA.[12] Concerning the attack on the carbonyl oxygen, the Perkow reaction can be cited as a related reaction, though its mechanism is not clear.[13] Few reactions of nucleophiles on positively charged heteroatoms, especially on oxygen and nitrogen, are known.[14] In view of the data presented above, we believe that the stabilized phenoxenium ion is an interesting chemical species, like the unsubstituted phenoxenium ion previously reported.[11] We are continuing to investigate various aspects of positively charged heteroatoms.

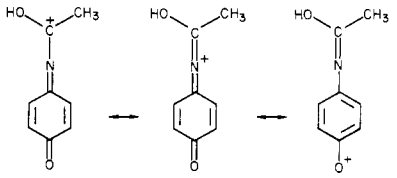
(6) This reaction may involve formation of an O,N-diprotonated species:



A similar species, the protonated species of *p*-nitrosophenol, has been proposed by: Olah, G. A.; Donovan D. J. *J. Org. Chem.* **1978**, *43*, 1743. Trifluoromethanesulfonic acid can double protonate *N*-phenylhydroxylamines to give iminium–benzenium dications (Okamoto, T.; Shudo, K.; Ohta, T. *J. Am. Chem. Soc.* **1975**, *97*, 7184). A similar reaction catalyzed by $AlCl_3$ has been reported by: Adams, R.; Eiler, K. R. *J. Am. Chem. Soc.* **1951**, *73*, 1149.

(7) This is a usual nucleophilic reaction of quinone imines.[1]

(8) O-Protonation of the acyl oxygen atom is equally possible and gives a phenoxenium ion such as **2'b**



2'b

(9) Concerted (**1** → **3**) and stepwise (**1** → **5**) pathways suggested by a referee are better defined by general and specific acid catalyses, respectively. However, two separate pathways from a single reactant to different products by general and specific acid catalyses are unlikely, because in a general acid catalysis the best catalyst is the strongest acid, the lyonium ion, which is also the catalyst in a specific acid catalysis. In addition the reaction **1** → **3** seems to be specific acid catalyzed, since it does not occur in PhOH/PhO^-. Consequently, we interpreted the formation of **5** as involving a doubly protonated species.[6]

(10) Abramovitch, R. A.; Inbasekaran, M.; Kato, S. *J. Am. Chem. Soc.* **1973**, *95*, 5428.

(11) Endo, Y.; Shudo, K.; Okamoto, T. *J. Am. Chem. Soc.* **1977**, *99*, 7721. *p*-Nitrophenoxenium ion prepared from *p*-NO_2PhONHTs with benzene gave only 2-hydroxy-5-nitrobiphenyl (unpublished result).

(12) Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1965**, *1*, 36. Klopman, G. "Chemical Reactivity and Reaction Path"; Wiley: New York, 1974; p 81. More stable electrophiles attack more para positions. For example, benzenediazonium ion reacts with phenol at its para position and does not have enough reactivity to react with anisole.

(13) Lichetenthaler, F. W. *Chem. Rev.* **1961**, *61*, 607. Borowitz, I. J.; Anschel, M.; Firstenberg, S. *J. Org. Chem.* **1967**, *32*, 1723. Allen, J. F. *J. Am. Chem. Soc.* **1957**, *79*, 3071.

(14) Gassman, P. G. *J. Am. Chem. Soc.* **1980**, *102*, 1214.

Direct Determination of the Temperature Dependence of the Reactions of a Singlet Carbene. Intersystem Crossing and the Cyclopropanation of Olefins by Fluorenylidene in Acetonitrile Solution

Joseph J. Zupancic and Gary B. Schuster*,†

Department of Chemistry, Roger Adams Laboratory University of Illinois, Urbana, Illinois 61801

Received September 15, 1980

We recently reported the first direct spectroscopic observation of a singlet carbene in fluid solution at room temperature.[1]

† Fellow of the Alfred P. Sloan Foundation 1977–1979; Dreyfus Teacher-Scholar, 1979–84.

0002-7863/81/1503-944$01.25/0

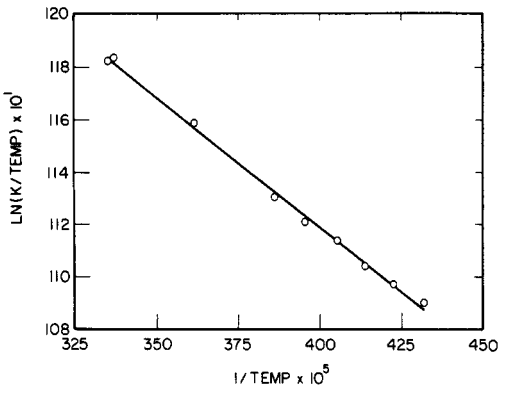
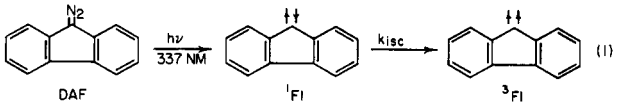


Figure 1. Eyring plot for intersystem crossing of ^{1}Fl to ^{3}Fl in acetonitrile solvent. Determined by monitoring the rise of the absorption of ^{3}Fl following laser flash photolysis.

Irradiation of diazofluorene (DAF) at 337 nm with a nitrogen laser in acetonitrile gives sequentially singlet (^{1}Fl) and triplet (^{3}Fl) fluorenylidene (eq 1). The ability to detect ^{1}Fl and monitor its



rate of reaction allows a detailed analysis of the properties of this extremely reactive intermediate. Herein we report the results of our investigation of the temperature dependence of ^{1}Fl intersystem crossing and its reaction with olefins to form cyclopropanes. The rate of the latter of these processes is determined primarily by the activation entropy.

Irradiation of a 6×10^{-4} M acetonitrile solution of DAF generates a short-lived transient product which has been identified as ^{1}Fl by spectroscopic, kinetic, and chemical means.[1] In the absence of a trapping reagent the ^{1}Fl intersystem crosses to ^{3}Fl with high efficiency. The rate constant for formation of ^{3}Fl from ^{1}Fl (k_{isc}) can be readily determined by monitoring the rate of appearance of the characteristic absorption of ^{3}Fl at 400 nm following the excitation pulse. Alternatively, k_{isc} can be measured by monitoring the decrease in the absorption of ^{1}Fl at 470 nm. The two procedures give the same result within the experimental error.[2]

The temperature dependence of k_{isc} reveals considerable detail about the mechanism for the conversion of ^{1}Fl to ^{3}Fl. We determined the value of k_{isc} over a 65 °C temperature range (from 23 to −42 °C) in acetonitrile solution. Over this range the value of k_{isc} decreased by a factor of about 3. Figure 1 shows an Eyring activation energy plot for the conversion of ^{1}Fl to ^{3}Fl. Over the temperature range studied, the Eyring plot is linear, giving $\Delta H^{\ddagger} = 1.99 \pm 0.05$ kcal/mol and $\Delta S^{\ddagger} = -17.0 \pm 2.0$ eu.

The activation parameters for intersystem crossing of ^{1}Fl reveal an unusual unimolecular reaction. The activation enthalpy is quite modest, but the activation entropy is large and negative. These findings can be easily interpreted in terms of the potential-energy surfaces depicted schematically in Figure 2. The ground spin state of fluorenylidene has been shown by EPR spectroscopy to be the triplet.[3,4] INDO calculations, which may overestimate the magnitude of this quantity, indicate that the energy difference between the singlet and triplet states for fluorenylidene is 21 kcal/mol.[5] Our findings show that an activation barrier of ca. 2 kcal/mol must be overcome to convert ^{1}Fl to ^{3}Fl. This barrier

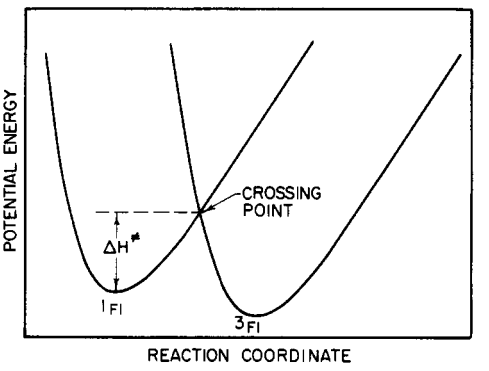


Figure 2. Reaction coordinate for intersystem crossing of ^{1}Fl. The most likely structural change accompanying intersystem crossing is an opening of the bond angle for the divalent carbon.

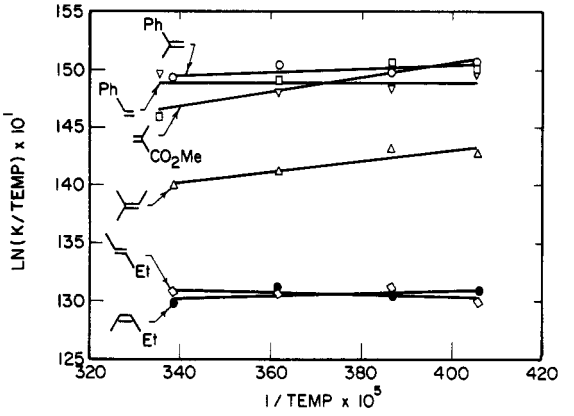
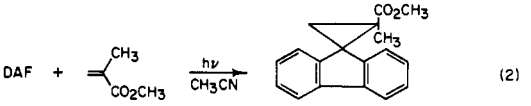


Figure 3. Eyring plots for the reaction ^{1}Fl with a variety of olefins in acetonitrile solution.

is represented in Figure 2 as the distance to the crossing point of the ^{1}Fl and ^{3}Fl potential-energy surfaces, and its magnitude is probably related to the geometry and energy differences between ^{1}Fl and ^{3}Fl. The relatively large negative value of $\Delta S^{\ddagger}$ indicates that the frequency factor for intersystem crossing is small. This is almost certainly a result of the relatively weak interaction between the ^{1}Fl and ^{3}Fl surfaces at the crossing point due to the multiplicity difference of the states. Presumably it is the rather small spin–orbit coupling interaction that mixes the states at the crossing point.[6]

Reaction of ^{1}Fl with olefins gives cyclopropanes as the exclusive or major product.[7] Thus, for example, irradiation of DAF at 337 nm with the laser in acetonitrile containing methyl methacrylate (MMA) gives the expected cyclopropane (eq 2).



The rate constant for reaction of MMA with ^{1}Fl (k_s) can be calculated from eq 3 where ϕ_t and ϕ_t^0 are the yields of ^{3}Fl, obtained

$$[(\phi_t^0/\phi_t) - 1] = k_s/k_{isc}[\text{MMA}] \quad (3)$$

by measuring the transient absorbance at 400 nm 200 ns after the excitation pulse, in the presence and absence of MMA, respectively. With knowledge of the temperature dependence of k_{isc}, the effect of temperature on k_s is readily available from application of eq 3 at various temperatures. The data for the

(1) J. J. Zupancic and G. B. Schuster, *J. Am. Chem. Soc.*, **102**, 5958 (1980).
(2) This observation indicates that the singlet carbene is the primary percursor to triplet carbene and the efficiency of intersystem crossing is high.
(3) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *J. Am. Chem. Soc.*, **84**, 4990 (1962).
(4) R. W. Brandon, G. L. Closs, C. E. Davoust, C. A. Hutchinson, Jr., B. E. Kohler, and R. Silbey, *J. Chem. Phys.*, **43**, 2006 (1965).
(5) J. Metcalfe and E. A. Halevi, *J. Chem. Soc., Perkin Trans. 2*, 634 (1977).
(6) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972); E. A. Helevi and C. Trindle, *Isr. J. Chem.*, **16**, 283 (1977). Also, it is problematic whether this rate retardation is better ascribed to the activation entropy or the transmission coefficient of the Eyring formalism.
(7) W. von E. Doering and M. Jones, Jr., *Tetrahedron Lett.*, 791 (1963); M. Jones, Jr., and K. R. Rettig, *J. Am. Chem. Soc.*, **87**, 4013, 4015 (1965); N. Shimizu and S. Nishida, *J. Chem. Soc., Chem. Commun.*, 389 (1972); N. Shimizu and S. Nishida, *J. Am. Chem. Soc.*,**96**, 6451 (1974).

Table I. Activation Parameters for the Reaction of Olefins with Singlet Fluorenylidene

olefin[a]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	reaction[b]
	0.16 ± 0.4	−17.6 ± 1.5	cyclopropanation
	−0.31 ± 0.2	−18.6 ± 0.8	cyclopropanation
	−1.2 ± 0.5	−22.3 ± 1.6	cyclopropanation
	−0.94 ± 0.3	−22.5 ± 1.01	cyclopropanation
	0.19 ± 0.21	−20.1 ± 0.80	cyclopropanation and CH insertion[c]
	−0.20 ± 0.25	−22.2 ± 0.94	cyclopropanation and CH insertion[d]

[a] In acetonitrile solution, 6×10^{-4} M DAF, olefin concentration varies from 0 to 9.1×10^{-1} M. [b] Products were determined from analysis of samples that had been subjected to multiple pulses from the nitrogen laser under the conditions of the spectroscopic investigation. Analysis by ^{1}H NMR and mass spectrometry as well as by comparison with authentic samples was used to identify the major products. [c] The ratio of cyclopropane to allylic CH insertion product is ca. 3:1 as determined from the ^{1}H NMR spectra. [d] The allylic CH insertion product is formed in only trace quantities.

reaction of ^{1}Fl with MMA and with other olefins over a temperature range from 22 to −26 °C are presented as Eyring plots in Figure 3, and the derived activation parameters are summarized in Table I.

The activation enthalpies for reaction of ^{1}Fl with a series of olefins examined are very small. In fact, for the most part these values are statistically indistinguishable from zero. Thus there is practically no enthalpy barrier for these reactions. The activation entropies, on the other hand, are large and negative.

There have been previous attempts to estimate the activation parameters for the solution-phase cyclopropanation of olefins by carbenes using competitive trapping techniques.[8] Our results provide the first direct measure of these quantities. These findings are consistent with previous experimental[8] and computational[9] results which conclude that the reaction to form cyclopropane proceeds by an initial nonlinear approach of the carbene to the olefin. The theoretical calculations indicate that this path should have no activation energy. Indeed, that is the result of our study. We find that the activation entropy for the cyclopropanation is the dominant factor in the activation free energy, and, therefore, it controls the rate of the reaction. The values we have measured for $\Delta S^{\ddagger}$ are similar to those of other bimolecular reactions having negligible $\Delta H^{\ddagger}$.[10] The observation that $\Delta S^{\ddagger}$ varies only slightly with the structure of the olefin is consistent with the notion that the transition state is early for this reaction, a conclusion similar to that reached by Skell and Cholod.[8] Our findings offer a contrast to the reactions of phenylchlorocarbene with olefins.[11] The halogen-substituted carbene has a singlet ground state and is somewhat less reactive and considerably more selective than ^{1}Fl. The different properties of these carbenes may be traced to a considerable stabilization of singlet phenylchlorocarbene by donation of nonbonding electrons of the chlorine to the vacant carbene orbital. Finally, the absence of an activation enthalpy for the cyclopropanation reactions and the modest enthalpy barrier observed for intersystem crossing indicate that the fraction of reaction originating from the singlet state of ^{1}Fl increases as the temperature decreases. This conclusion may indicate a profitable stratagem for increasing the amount of singlet reactions of carbenes that have triplet ground states.

In sum, we have obtained the first direct measurements of the activation parameters for intersystem crossing and cyclopropanation of olefins by a singlet carbene in fluid solution. The experimental values are consistent with modern theory describing intercombinational processes and are consistent with the very exothermic nature of the reaction of ^{1}Fl with olefins.

Acknowledgment. This work was supported in part by the National Science Foundation and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Mr. James Wehmer for his valuable assistance in setting up and using the laser apparatus.

(8) P. S. Skell and M. S. Cholod, *J. Am. Chem. Soc.*, **91**, 7131 (1969).
(9) R. Hoffman, *J. Am. Chem. Soc.*, **90**, 1475 (1968).
(10) A. A. Gorman, G. Lovering, and M. A. J. Rodgers, *J. Am. Chem. Soc.*, **101**, 3050 (1979).
(11) N. J. Turro, J. A. Butcher, Jr., R. A. Moss, W. Guo, R. C. Munjal, and M. Fedorynski, *J. Am. Chem. Soc.*, submitted for publication. We thank Professor Turro for a preprint of this work.

Strong Dependence of the Incidence of Internal Return during Solvolysis of *sec*-Alkyl Benzenesulfonates on the Structure of the Alkyl Group[1]

Cristina Paradisi and J. F. Bunnett*

University of California
Santa Cruz, California 95064
Received October 1, 1980

In recent discussions, opinions have differed sharply as to the extent that intimate ion pairs undergo internal return[2] to substrate during solvolysis reactions. Shiner, Humski, and co-workers[3] invoke internal return as a major factor, for example, in solvolyses of cyclopentyl *p*-bromobenzenesulfonate. On the other hand, Bentley and Schleyer[4,5] have suggested that internal ion pair return "is not appreciable in solvolyses of simple secondary substrates", and in particular that it is not significant in solvolyses of 2-adamantyl *p*-toluenesulfonate in acetic acid and ethanol/water.

Determination of the extent and rate of oxygen-18 scrambling in suitable carboxylic and sulfonic esters is recognized to be "probably the single most powerful tool for the detection of ion pairs" and internal return in solvolysis reactions.[6] This criterion has been utilized extensively by Goering and co-workers,[7] especially for study of systems in which substrate racemization and other manifestations provide complementary evidence of the roles played by various solvolysis intermediates. However, it has been applied to solvolysis of simple secondary alkyl arenesulfonates only by Diaz, Lazdins, and Winstein.[8] No doubt the elaborate character of the oxygen-18 analysis procedures typically employed has been a barrier to its wider utilization.

A typical scrambling experiment with an arenesulfonate ester has comprised the following stages: (1) partial solvolysis of ester specifically labeled either in the alkoxy or sulfonyl oxygen positions; (2) recovery and purification of unsolvolyzed ester; (3) cleavage of the recovered ester by means of sodium or lithium in ammonia or sodium naphthalenide in tetrahydrofuran to generate alkoxide ion and ultimately the corresponding alcohol; (4) purification of the resulting alcohol or solid derivative thereof; (5) conversion of the alcohol or derivative thereof to CO_2 by heating it with carbon at 1120 °C or higher in a special pyrolysis train with ensuing I_2O_5 oxidation of the CO so produced,[7,9] or by oxidation

(1) Research supported in part by the National Science Foundation.
(2) Winstein, S.; Clippinger, E.; Fainberg, A. H.; Robinson, G. C. *J. Am. Chem. Soc.* **1954**, *76*, 2597.
(3) Seib, R. C.; Shiner, V. J., Jr.; Sendijarevic, V.; Humski, K. *J. Am. Chem. Soc.* **1978**, *100*, 8133. Shiner, V. J., Jr.; Nollen, D. A.; Humski, K. *J. Org. Chem.* **1979**, *44*, 2108.
(4) Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7658.
(5) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.
(6) Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. In "Ions and Ion Pairs in Organic Reactions"; Szwarc, M., Ed.; Wiley: New York, 1974; Vol. 2, p 279.
(7) Goering, H. L.; Levy, J. F. *J. Am. Chem. Soc.* **1964**, *86*, 120. Goering, H. L.; Thies, R. W. *Ibid.* **1968**, *90*, 2967, 2968; Goering, H. L.; Jones, B. E. *Ibid.* **1980**, *102*, 1628.
(8) Diaz, A. F.; Lazdins, I.; Winstein, S. *J. Am. Chem. Soc.* **1968**, *90*, 1904.
(9) Denney, D. B.; Goldstein, G. *J. Am. Chem. Soc.* **1957**, *79*, 4948.

0002-7863/81/1503-946$01.25/0