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.

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

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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

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Table I. Solvolysis and Oxygen-18 Scrambling Data for Some Secondary Alkyl Benzenesulfonates

alkyl group[a]	solvent	other solute[b]	temp, °C	$10^5 k_t$[c]	$10^5 k_{eq}$[d]	minimum fraction of internal return[e]
2-adamantyl	CF_3COOH	CF_3COONa	25.0	147 ± 2	182 ± 6	0.71
2-adamantyl	CH_3COOH	CH_3COONa	80.0	2.16 ± 0.03	5.7 ± 0.3	0.84
2-adamantyl	80% EtOH		80.0	6.60 ± 0.01	7.4 ± 0.4	0.69
2-propyl	CF_3COOH	CF_3COONa	25.0	3.61 ± 0.15	0.79 ± 0.02	0.30
cyclopentyl	CF_3COOH	CF_3COONa	25.0	383 ± 3	84.8 ± 8	0.31
3,3-dimethyl-2-butyl	CF_3COOH	CF_3COONa	25.0	733	*f*	*f*

[a] The alkyl benzenesulfonate was ca. 0.03 M in kinetic experiments and ca. 0.05 M in oxygen scrambling experiments. Specifically labeled substrates (18–28% ^{18}O in the sulfonyl oxygens) were prepared by using ^{18}O-labeled benzenesulfonyl chloride. [b] Always 0.1 M, when present. [c] k_t, solvolysis rate constant, was determined titrimetrically in CH_3COOH and in 80% EtOH solvents and spectrophotometrically in CF_3COOH (P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *J. Am. Chem. Soc.* 1965, *87*, 5169). [d] k_{eq} tabulated is an average of k_{eq} evaluated from the sulfone and the alcohol GC/MS data for two or more experiments. For 2-propyl benzenesulfonate, the alcohol was not analyzed. Standard deviations are shown. [e] $2k_{eq}/(2k_{eq} + k_t)$. [f] No scrambling observable in recovered ester.

with $HgCl_2$ with subsequent purification of the CO_2 by GLC;[8] (6) mass spectrometric analysis of the CO_2.

We have developed a much simpler procedure,[10] one which takes advantage of the convenience and power of GC/MS equipment such as now available in many laboratories and reports not only the oxygen-18 content of the alkoxyl moiety of the recovered benzenesulfonate ester but also, as earlier procedures had failed to do, the oxygen-18 content of the sulfonyl moiety. Briefly, after cleavage of recovered ester with 2 equiv of sodium in ammonia (stage 3), we replace the ammonia solvent by acetonitrile, methylate with CH_3I to convert benzenesulfinate ion to methyl phenyl sulfone (but without much methylation of the alkoxide ion), dissolve the organic constituents of the resulting mixture in diethyl ether, dry and concentrate the ether solution, and subject it to GC/MS analysis.[11,12]

Starting with esters labeled with 18–28% of oxygen-18 in the sulfonyl moiety, we have obtained consistent measures of the scrambling rate constant from the phenylsulfonyl and the alcohol data.[13]

Using this technique, we have determined the minimum fraction of internal return during the solvolysis of four *sec*-alkyl benzenesulfonates, representing the four systems that have figured most prominently in recent investigations. Salient data are summarized in Table I. Rate constants for the titrimetric rate of solvolysis (k_t) and for scrambling (k_{eq}) were reckoned by means of standard kinetic expressions.[14] On the basis that scrambling occurs via internal return, a minimum estimate of the fraction of intimate ion pairs that undergo internal return is provided by $2k_{eq}/(2k_{eq} + k_t)$.[13] For solvolyses in trifluoroacetic acid, scrambling is extensive with 2-adamantyl benzenesulfonate, considerable with isopropyl and cyclopentyl benzenesulfonates, and undetectable with 3,3-dimethyl-2-butanyl (pinacolyl) benzenesulfonate. Our observation of the extent of scrambling for the isopropyl ester in CF_3COOH is nearly the same as that of Diaz, Lazdins, and Winstein[8] for 2-octyl *p*-bromobenzenesulfonate in the same solvent.[15] For solvolysis of 2-adamantyl benzenesulfonate, the incidence of scrambling is high in three solvents: CF_3COOH, acetic acid, and 80% ethanol/20% water.

Accepting that 2-adamantyl benzenesulfonate solvolyzes by an ionization mechanism,[16] one must attribute the observed scrambling to internal return from intimate ion pairs.[17] Doubts have been expressed as to whether the ion pairs that undergo ^{18}O scrambling are the same as those that undergo solvolysis.[16] This is a skeptic's question that can be asked with regard to any postulated reaction intermediate for which there is chemical evidence for more than one mode of reaction. To answer the skeptic, one must first explain what "the same" means. If, within its lifetime, the intermediate can explore a number of different conformations, conditions of solvation, etc., it is effectively "the same" even though the particular conformation or state of solvation that engages in one mode of reaction is different from that involved in another.[18] In the case of immediate interest, separation of the intimately paired cation and anion involves moving apart large molecular entities, such as the benzenesulfonate ion and the 2-adamantyl cation, and is therefore slow compared to a minor conformational change or the flickering of hydrogen-bonding interactions with solvent molecules. The intimate ion pair is therefore "the same".

Trifluoroacetic acid, acetic acid, and 80% ethanol differ hugely in nucleophilic reactivity. The fact that the rate of internal return exceeds the rate of formation of solvolysis products in all three of these solvents must be attributed in part to blocking of backside attack on the substrate or the intimate ion pair by the adamantane framework.[19] It suggests that coordination of the 2-adamantyl

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(12) The relative heights of the parent peak (with all atoms of their most abundant isotope) and the peak two mass units higher are measured. For the phenylsulfonyl cation (or redundantly for methyl phenyl sulfone radical cation), the ratio, *R*, of intensities of the (parent + 2) ions to the parent ions is slightly overcorrected for ^2H, ^{13}C, and ^{34}S contributions by subtraction of R^u (from the same peaks from sulfone of natural isotopic abundance) and finally adjusted by a small addition for the natural abundance of ^{18}O to give R_c. The fraction of ^{18}O among oxygen atoms is then $R_c/(R_c + 2)$. Similarly, letting *P* stand for the (parent + 2)/parent peak ratio for the alcohol radical cation, and correcting similarly, the fraction of ^{18}O atoms is $P_c/(P_c + 1)$.

(13) For a first-order rate process proceeding to a condition of equilibrium, the rate constant (k_{eq}) is the sum of forward and reverse components,[14] that is, of alkyl group shift from oxygen-16 to oxygen-18 sites (k_{to}) and of alkyl group shift from labeled to unlabeled oxygens (k_{ab}), in the ratio 2:1. Inasmuch as both directions involve alkyl shift from one oxygen to another, k_{eq} is a measure,[8] albeit an inadequate one, of the extent of alkyl group shift. A better measure is $(4/3)k_{eq}$; each shift from labeled to unlabeled oxygen is necessarily accompanied by an undetectable shift from one labeled oxygen site to another (k_{sh}), and $k_{sh} = k_{ab}$. Therefore total alkyl group shift rate is given by k_{eq} increased by one-third. This argument has been presented for the case in which the ester initially carries oxygen-18 at both sulfonyl sites. When it initially carries oxygent-18 at only one sulfonyl site, one must reverse the definitions of k_{to} and k_{ab}, but the argument and its conclusion are otherwise undisturbed. The foregoing is independent of shift mechanism. When shift occurs by an ionization–recombination mechanism, the sulfonate ion is at least as likely to recombine via the oxygen atom to which the alkyl group was attached before ionization as to either of the other two oxygens. Accordingly the rate of ionization–recombination must be at least 50% greater than the alkyl group shift rate; $^3/_2 \times (4/3)k_{eq}$ is $2k_{eq}$. Because it is most probable that the carbenium ion will reattach to the oxygen whence it separated,[8] that one being most favorably located, $2k_{eq}$ is a conservative minimum estimate of the ionization–recombination rate constant.

(14) Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism", 2nd ed.; Wiley: New York, 1961; p 186.

(15) $2k_{eq}/(2k_{eq} + k_t)$ is 0.33 for 2-octyl *p*-bromobenzenesulfonate[8] and 0.30 for isopropyl benzenesulfonate (Table I).

(16) Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1.

(17) For both 2-adamantyl and cyclopentyl benzenesulfonates, we have shown that external return is insignificant; when solvolysis is conducted in the presence of sodium *p*-toluenesulfonate (0.03–0.05 M) in CH_3COOH (with CH_3COONa) or CF_3COOH (with CF_3COONa) or 80% ethanol for the former substrate or in CF_3COOH (with CF_3COONa) for the latter, no detectable amount of *p*-toluenesulfonate ester is formed.

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cation with solvent, to form substitution product, is not the rate-limiting step.[20] The rate of bonding of the cation to solvent is indicated to be controlled in some other kind of process, such as separation of the intimate ion pair.[21]

These results call for reinterpretation of correlations with the solvent parameter, $Y_{2\text{-AdOTs}}$. As originally advocated,[4,5,16] they were predicated on the rate-limiting step in 2-adamantyl *p*-toluenesulfonate solvolysis being formation of the intimate ion pair.

As for pinacolyl benzenesulfonate, the backside of C-2 is considerably hindered;[22] accordingly S_N2 attack by the weakly nucleophilic CF_3COOH is extremely improbable, and even backside attack on the intimate ion pair is likely to be impeded. These are features shared by the 2-adamantyl system, and one might naively anticipate much internal return in the pinacolyl series. However, oxygen scrambling does not occur during solvolysis. This is compatible with either of two models recently advocated. In one, proposed on the basis of the nearly total incidence of carbon skeleton rearrangement and the high solvolytic reactivity of pinacolyl arenesulfonates in solvents of low nucleophilicity, rapid methyl shift occurs in the carbocation immediately after its formation.[23] The other, which accommodates the foregoing evidence as well as the substantial γ carbon-14 isotope effect reported by Ando and Morisaki,[24] is one of methyl shift concerted with ionization.

Our results greatly clarify the role of ion-pair return in solvolyses of *sec*-alkyl arenesulfonates. Judgments on controversial questions can now be made on the basis of straightforward fact with reduced reliance on indirect arguments and unverified hypotheses. The technique that we have employed should be attractive to other investigators.

(20) Some caution must be observed in interpreting the solvent dependence of the minimum fraction of internal return for the 2-adamantyl ester in Table I solely in terms of solvent nucleophilicity. The experiments in CF_3COOH were conducted at a much lower temperature (25 °C) than were those in acetic acid or 80% ethanol (80 °C). One does not know to what extent the fraction of internal return depends on temperature.

(21) In contrast, the extent of scrambling of 2-octyl *p*-bromobenzenesulfonate is sharply dependent on solvent nucleophilicity.[6] In this case the backside of C-2 is relatively accessible to solvent nulceophiles.

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Ring Strain in Bis(triethylphosphine)-3,3-Dimethylplatinacyclobutane Is Small[1]

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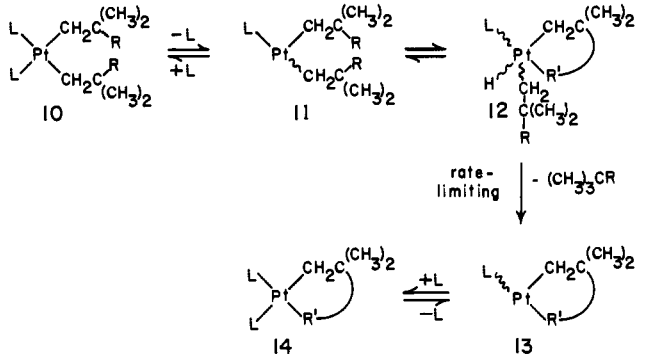
Metallacycloalkanes have been identified as intermediates in a variety of metal-catalyzed reactions,[2-8] but little is known about the thermodynamic or electronic characteristics of these species. We have described previously the mechanism of conversion of dineopentylbis(triethylphosphine)platinum(II) (**1**) to bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (**2**) by thermal cyclometallation.[9] Here we summarize product yields and activation parameters (Table I) indicating that similar mechanisms also describe analogous reactions forming platinacyclopentanes and platinacyclohexanes and interpret these data as evidence that the platinacyclobutanes are much less strained (ring strain $\lesssim 5$ kcal mol^{-1} greater than that of an analogous platinacyclopentane) than cyclobutane itself (ring strain = 26 kcal mol^{-1}).[10]

Scheme I. Mechanism of Cyclometallation Reactions Generating Platinacycloalkanes (L = Et_3P; R = CH_3, CH_2CH_3, $CH_2CH_2CH_3$)



Compounds **1**, **3**, and **6** and their deuterated analogues were prepared, characterized, and decomposed thermally following techniques described previously.[9,11] Kinetics of decomposition followed rate eq 1 (L = Et_3P). The activation parameters sum-

$$-d[L_2PtR_2]/dt = k[L_2PtR_2][L]^{-1} \quad (1)$$

marized in Table I were obtained by following the disappearance of **1**, **3**, and **6** from cyclohexane solutions containing added triethylphosphine;[12] similar numbers were obtained in the absence of added phosphine. Isotope effects are those observed or inferred[13] for deuterium substitution at the positions indicated in Table I. The similarity in products and activation parameters and the magnitudes of the kinetic isotope effects indicate that the same mechanism is followed in all of these cyclometallations.

If the reasoning described in detail for **1** → **2** is followed,[9] we propose that the rate-limiting step for each of the transformations

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(10) Benson, S. W. "Thermochemical Kinetics"; 2nd ed.; Wiley: New York, 1976; p 273. Strain energies are (kcal mol^{-1}): C_3H_6, 27.6; C_4H_8, 26.2; C_5H_{10}, 6.3; C_6H_{12}, 0.2.

(11) Kinetic studies were carried out at temperatures between 69 and 157 °C (depending on the compound) by using cyclohexane solutions originally 0.08 M in organoplatinum compound, 0.02 M in triethylphosphine, and 0.16 M in triethylphosphate as internal standard. The rate of disappearance of starting material was determined by following the change in its concentration relative to internal standard by $^{31}P\{^1H\}$NMR and was equivalent to the rate of production of alkane monitored by gas chromatography. Metallacyclic products were identified either by comparison with independently synthesized samples or by a combination of ^1H and $^{31}P\{^1H\}$NMR spectroscopy, elemental analysis, and chemical reactions.

(12) Reactions in the presence of added triethylphosphine were more reproducible than those in its absence.

(13) The kinetic isotope effect for **6** → **8** was determined by setting the rate of formation of **8** equal to 68% of the rate of disappearance of **6** (the relative yield of **8** from the reaction is 68%). A similar treatment of the rate of decomposition of deuterated **6** (for which the yield of **8** is 43%) yielded the rate of formation of deuterated **8**. These calculated rates were used to determine k_H/k_D. The relative yields of **7**, **8**, and **9** did not change over the course of the reaction.

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