adiabatic or nonadiabatic, i.e., whether it is the π or the n orbital that is empty in the doubly excited state as illustrated in Figure 8.

From this point of view the main importance of the second crossing rests in the fact that if it does not occur then the n level will lie above the π level in the orbital diagram. The corresponding singly excited $\pi\pi^*$ state, Figure 9a, will then suffer a rapid radiationless transition in the sense of Kasha's rule[13] to the $n\pi^*$ state, Figure 9b. Due to the low oscillator strength of the $n \rightarrow \pi^*$ transition the latter state will rapidly decay into the ground state, presumably by intersystem crossing before radiation can take place. According to the HAM calculation the transition $34 \leftarrow 35$ of 3-aminophthalate should correspond to a wavelength of 416 nm, which compares very favorably with the observed value of 425 nm, the wavelength of maximum fluorescence in aqueous solutions. Similarly the radiative lifetime of the singlet is calculated to be 7.9 ns, which compares well with 18 ns as estimated from the quantum yield[14] and measured lifetime[15] of the fluorescence of 3-aminophthalate.

Since the second intersection, II, appears to be essential for the chemiluminescence to take place, we should expect that upon interchanging the amino group for other substituent groups only those molecules will chemiluminesce whose MO correlation diagrams contain a second intersection. This is, in fact, predicted for the OH-substituted molecule. On the other hand, e.g., the H- or CH_3-substituted molecules should not luminesce since their MO correlation diagrams like those of the model substance contain only a single intersection. All this is in agreement with experimental facts.[16]

As far as the quantitative aspect is concerned, the quantum chemical calculations are, of course, much too approximate to allow a reliable estimate of the efficiency of chemiexcitation exhibited by individual molecules. It is, however, easy to discern some of the decisive factors that determine this yield. Such a factor is the probability of a nonadiabatic transition at the first intersection, I. This probability depends in part on the exchange integral K_{ia} and in part on the rate $\dot{q}$ at which the crossing is passed. These two factors are dependent on the forms and energies of the orbitals i and a and may vary slightly but perhaps significantly from case to case.

In one of their publications, White et al.[17] have noticed a negative correlation between the efficiency with which the emitting state is populated and the energy gap between the HOMO and the LUMO of the corresponding phthalate. Such a dependence is easy to explain from the present model. An increase of the LUMO energy in the substituted phthalate would obviously force the first crossing point, I, to move to the left in the diagram toward lower O–O distances. The system velocity, $\dot{q}$, at the intersection point would then be lower with an attendant decrease in the probability of a nonadiabatic transition. The probability P_{12} of a nonadiabatic transition is, in fact, highly sensitive to a change in $\dot{q}$. If $\dot{q}$ is halved, P_{12} will, e.g., decrease from 24 to 5.76%. It is, however, too early to say whether this effect alone is sufficient to explain the negative correlation between the HOMO–LUMO gap and the chemiexcitation efficiency observed by the above authors or if this correlation is partly due also to other accompanying changes of the molecular properties not necessarily related to the HOMO–LUMO gap.

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Carbon-14 Kinetic Isotope Effects and Mechanisms of Addition of 2,4-Dinitrobenzenesulfenyl Chloride to Substituted Styrenes-*1*-^{14}C and Styrenes-*2*-^{14}C[1]

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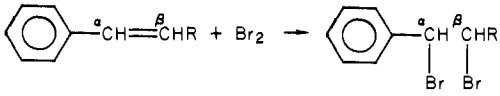
Abstract: As the first reported examples of carbon isotope effects in simple electrophilic addition reactions we have measured the carbon-14 kinetic isotope effects in the addition of 2,4-dinitrobenzenesulfenyl chloride to a series of para-substituted α- and β-labeled styrenes in acetic acid at 30.1 °C: for para substituents Cl, H, and CH_3 the $k/^{14}k$ values for α labeling are 1.027, 1.022, and 1.004, and the $k/^{14}k$ values for β labeling are 1.035, 1.032, and 1.037, all $\pm\sim$0.004. The kinetics of the reaction were measured for the *p*-CH_3O, *p*-CH_3, unsubstituted, *p*-Cl, and *m*-NO_2 styrenes; electron-donating groups strongly accelerate the reaction, and electron-withdrawing groups retard it. The Hammett plot is curved with ρ^+ values ranging from about −4.6 at the electron-donating group (EDG) end to about −1.8 at the electron-withdrawing group (EWG) end. Both the isotope effect and kinetic data, and related data from the literature, are interpreted in terms of a changing mechanism, with the activated complexes of the rate-determining steps having much open carbenium ion (ion pair) character for EDG-substituted styrenes and much cyclic thiiranium ion (ion pair) character for EWG-substituted styrenes.

We have been puzzled for many years[2] about the reported[3] lack of a carbon kinetic isotope effect in the addition of bromine to $^{\alpha}C$ and $^{\beta}C$ carbon-14 labeled styrene and methyl cinnamate (eq 1 and 2).



(1)

$^{12}k/^{14}k$ for $^{\alpha}C$ and $^{\beta}C = 1.00$[3] (2)

All of the mechanisms proposed for these electrophile addition reactions involve substantial bonding changes at $^{\beta}C$ and (perhaps—see below) at $^{\alpha}C$ in the rate-determining steps, and these changes should be reflected in carbon isotope effects. Since the main action involved is bond formation, it might be anticipated

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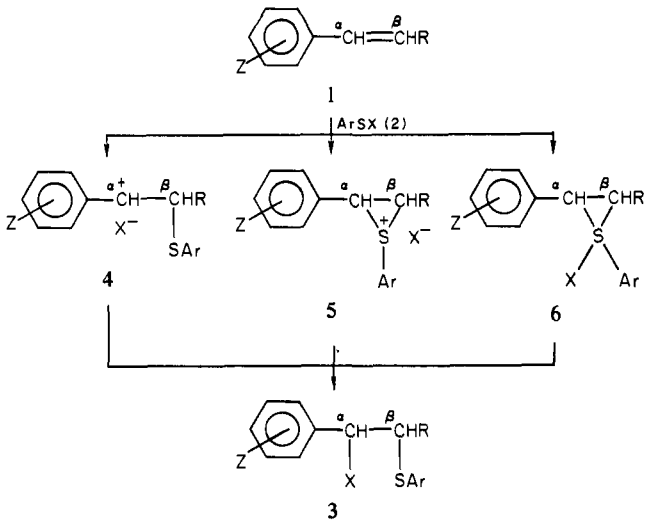
0002-7863/83/1505-7666$01.50/0

Scheme I



that the isotope effects would be small. We have suggested[2] that the reported[3] lack of an isotope effect might be due to a balancing (accidental canceling) of bond formation and bond rupture effects and that the balance point might be changed by using substituted styrenes. The lack of a carbon isotope effect in these simple electrophilic addition reactions is particularly puzzling because other types of addition reactions to alkenes[4] (cycloadditions, catalytic hydrogenation, ozonization) give carbon isotope effects as expected. We have initiated[1] a program to investigate the relationship between mechanisms and carbon kinetic isotope effects in simple electrophilic addition reactions, using the successive labeling[5] approach.

Sulfenyl halides add to double bonds[6-9] to give halo sulfides (Scheme I). Additions to styrenes, **1**, of arylsulfenyl halides, **2**, give halo sulfides, **3**, presumably through carbenium ions, **4**, thiiranium ions (episulfonium ions), **5**, or sulfuranes, **6**.

The reactions are cleanly second order; first order each in **1** and **2**.[8,10] Appropriately substituted styrenes generally give stereospecific anti addition[8,9,11-17] (an exceptional case[15] is discussed later), showing that an intermediate is involved, that it is bridged, and that the activated complexes leading to its formation and its conversion to products are also bridged. The original proposal[7] for rate-determining formation of thiiranium ions (**5**) and their subsequent stereospecific and regiospecific decomposition to products (**3**) has been accepted[8] in general terms for many years. However, various intimate and/or solvent separated ion pairs with structures between **6** and **5**, **6** and **4**, and **5** and **4** also qualify as appropriate intermediates and activated complexes, and most recent mechanistic discussions are couched in terms of such ion pair intermediates[18-20] rather than "free" thiiranium ions.

Thiiranium ions are well-known as postulated intermediates in a variety of reactions,[21] and crystalline thiiranium salts were isolated many years ago.[22,23] These pre-formed salts, however, show behavior[24] (rearrangements, reactions with other nucleophiles present, etc.) not generally observed[24] in the addition reactions of sulfenyl halides to alkenes as ordinarily carried out in solution in acetic acid or relatively non-polar solvents.

In these usual addition reactions of arylsulfenyl halides, **2**, to substituted styrenes, **1**, the activated complexes for the rate-determining steps clearly have a substantial positive charge (some **4**-like character) at the α carbon as shown by the fairly large negative Hammett ρ values, mostly near −2.4, for additions of 2,4-dinitrobenzenesulfenyl chloride and bromide and of 4-methyl-, 4-chloro-, 4-nitro-, and unsubstituted benzenesulfenyl chlorides and thiocyantes to substituted styrenes and 1-phenylpropenes.[11,12,24-30] The view that there is also a (probably small) positive charge on sulfur in the activated complex of the rate-determining step has been supported by the (relatively small) negative ρ^+_{ArSX} value of near −0.7 for the addition of 4-substituted 2-nitrobenzenesulfenyl chlorides and bromides to cyclohexene.[31] However, recent work[20d,29,30] on the addition of 4-substituted benzenesulfenyl chlorides and thiocyanates to substituted styrenes shows that ρ_{ArSX} is variable and changes from negative to positive as the styrene substituents change from electron withdrawing to electron donating. (These Hammett plot data are discussed in more detail below.)

The partial positive charge at the α carbon in the activated complex of the rate-determining step noted above carries forward into the activated complex of the product-determining step, as can be deduced from the fact that additions of arylsulfenyl halides

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to styrenes are regiospecific, or at least highly regioselective, formation of **3** rather than $ZC_6H_4CN(SAr)CHRX$ for R = H or alkyl.[8-15,25-28,32,33] Substituted styrenes give regiospecific additions of other nucleophiles in this same (Markownikoff) sense when preformed thiiranium ions similar to **5** are used.[33]

From the above it is clear that in the simple additions of arylsulfenyl derivatives to styrenes, bridging exists in the activated complexes of both the rate-determining and product-determining steps, but in both cases the bridging is unsymmetrical with considerable **4**-like character.

By contrast, there is considerable[8b,34-43] (but disputed[44]) evidence that halogenations of styrenes (unlike aliphatic alkenes) generally proceed through open carbenium ions,[35] $Ar-{}^{+}CH-CHRX$, rather than through the bridged ions[36] characteristic of arylsulfenyl derivative additions. The Hammett ρ value for addition of bromine to styrenes,[37,38] ~ -4.8 using σ^{+}, is much more negative than the value (~ -2.4) for addition of arylsulfenyl derivatives. The addition of bromine to appropriately substituted styrenes is nonstereospecific[36,39] (although often substantially stereoselective). In the presence of other nucleophiles, additions of bromine and the nucleophile are regiospecific in the Markownikoff sense (bromine positive),[8b,34,39b,40-42] Furthermore, the secondary α-deuterium isotope effects[43] are very small, (inverse) ${}^{H}k/{}^{D}k \sim 0.99 \pm 0.01$, for addition of bromine to styrenes, but substantially more inverse, ${}^{H}k/{}^{D}k \sim 0.95 \pm 0.01$, for addition of 2,4-dinitrobenzenesulfenyl halides to styrenes. These results are interpreted in terms of no hybridization change at the α carbon for bromination (sp^2 π bond changes to sp^2 carbenium ion) but a more restrictive (bridged) bonding at the α carbon for addition of arylsulfenyl halides.

Both $^{\alpha}C$ and $^{\beta}C$ carbon isotope effects would be expected for both the bridged and open carbenium ion mechanisms, since there are bonding changes at both labeled positions for both mechanisms. But the bonding charges are quite different for the different mechanisms, and these differences would be expected to give rise to different values for the $^{\alpha}C$ and/or $^{\beta}C$ isotope effects. It is hard to predict what these values should be because both bond rupture and bond formation (including, for C_α, additional ring–C_α bonding by positive charge delocalization) are involved at both C_α and C_β. In view of the α deuterium isotope effect results[43] quoted in the last paragraph, it is tempting to speculate that there is little net bonding change at C_α in the addition of bromine to styrene (open carbenium ion-like activated complex) which should result in a small $^{\alpha}C$ isotope effect but a greater bonding change at C_α in the addition of arylsulfenyl halides to styrene (bridged activated complex) which should result in larger[45] $^{\alpha}C$ isotope effect. The best answer to such mechanistic questions is comparison of experimental and calculated[46] isotope effects. Our future program includes isotope effect calculations using these different mechanistic assumptions, and the present research is our first[1] effort to provide $^{\alpha}C$ and $^{\beta}C$ isotope effect calibration data for the addition of 2,4-dinitrobenzenesulfenyl chloride to substituted styrenes. Work is in progress to obtain similar calibration data for bromination reactions.

Table I. Rate Constants for the Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with Substituted Styrenes in Anhydrous Acetic Acid at 30.1 °C

substituent	k, M^{-1} s^{-1}	correl coeff	k, lit.[25] value, M^{-1} s^{-1}
p-CH_3O	(0.31)[a]	0.9749	(0.5)[a,b]
p-CH_3	2.09×10^{-3}	0.9990	3.2×10^{-3} [c]
H	7.11×10^{-4}	0.9987	11.3×10^{-4} [c]
p-Cl	2.31×10^{-4}	0.9900	1.6×10^{-4} [c]
m-NO_2	3.01×10^{-5}	0.9978	
p-NO_2			1.7×10^{-5} [c]

[a] Minimum value; reaction too fast for reliable measurement. [b] 25.0 °C. [c] Interpolated or extrapolated from data at other temperatures.

Procedure and Results

As a preliminary to the isotope effect experiments, the kinetics of the addition reaction of 2,4-dinitrobenzenesulfenyl chloride to a series of substituted styrenes (Scheme I: **1**, R = H; Z = p-CH_3O, p-CH_3, H, p-Cl, m-NO_2) were determined in anhydrous acetic acid at 30.1 °C under a blanket of dry nitrogen according to the procedure of Orr and Kharasch.[10] The data gave linear second-order plots with no noticeable nonlinearity even at 80–96% completion. Rate constants were calculated from the slopes of the lines by least-squares methods and are summarized in Table I, where they are compared with the literature values of Orr and Kharasch.[25] The reaction of the p-CH_3O compound was 78.4% complete at the time of first sampling, 30 s, and the rate constant reported is calculated from data taken between 30 s (78.4%) and 7.5 min (90.2%). Clearly it is not a reliable rate constant, but the value reported is a minimum (see Discussion).

The $^{\alpha}C$ and $^{\beta}C$ carbon-14 labeled styrenes for the isotope-effect experiments (Scheme I; **1**, R = H, Z = p-CH_3, H, p-Cl) were prepared from commercially available $^{\alpha}C$ and $^{\beta}C$ carbon-14 labeled sodium acetate, sodium cyanide-^{14}C and benzoic-7-^{14}C acid by procedures described elsewhere.[47,48]

For the isotope effect experiments the same procedures were used as for the kinetics measurements, except that the desired fractions of reaction were obtained by using appropriate limited amounts of 2,4-dinitrobenzenesulfenyl chloride. The starting styrenes and those recovered after partial reaction were converted quantitatively to the styrene dibromides for radioactivity determination. The radioactivity of the addition product was measured directly. In about one-third of the samples the styrene recovered after partial reaction polymerized during workup and could not be used for radioactivity determination (see Experimental Section). All radioactivity measurements were made by liquid scintillation counting with a Beckman DPM-100 instrument and a dioxane–

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(48) Eubanks, J. R. I. Ph.D. Dissertation, University of Arkansas, 1981. Eubanks, J. R. I.; Sims, L. B.; Fry, A. *J. Am. Chem. Soc.*, to be submitted.

Table II. Carbon-14 Kinetic Isotope Effects for the Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with *p*-Methyl, Unsubstituted, and *p*-Chloro α- and β-Labeled Styrenes in Anhydrous Acetic Acid at 30.1 °C

substituent	isotope effect position	$^{12}k/^{14}k$ ± std dev from R_0, R_r R_p	f, R_0, R_r	f, R_0, R_p	f, R_r R_p	$^{12}k/^{14}k$ av all methods
p-CH_3[a]	$k/^{\alpha}k$	1.005 ± 0.004	1.005 ± 0.003	1.005 ± 0.004	1.002 ± 0.002	1.004 ± 0.003
H[b]	$k/^{\alpha}k$	1.022 ± 0.003	1.023 ± 0.004	1.022 ± 0.005	1.022 ± 0.003	1.022 ± 0.004
p-Cl[c]	$k/^{\alpha}k$	1.026 ± 0.003	1.026 ± 0.004	1.028 ± 0.005	1.026 ± 0.002	1.027 ± 0.004
p-CH_3[d]	$k/^{\beta}k$	1.038 ± 0.004	1.042 ± 0.001	1.036 ± 0.005	1.037 ± 0.002	1.037 ± 0.004
H[e]	$k/^{\beta}k$	1.031 ± 0.002	1.034 ± 0.005	1.031 ± 0.002	1.031 ± 0.002	1.032 ± 0.003
p-Cl[f]	$k/^{\beta}k$	1.036 ± 0.003	1.031 ± 0.006	1.038 ± 0.001	1.034 ± 0.004	1.035 ± 0.004

[a] From six fractions of reaction; recovered styrene polymerized in two cases. [b] From five fractions of reaction; recovered styrene polymerized in two cases. [c] From six fractions of reaction; recovered styrene polymerized in one case. [d] From six fractions of reaction; recovered styrene polymerized in four cases. [e] From five fractions of reaction; in no case did the recovered styrene polymerize. [f] From six fractions of reaction; recovered styrene polymerized in one case.

base cocktail–fluor solution, using the external standard ratio method.[47]

The carbon-14 isotope effect values ($k/^{\alpha}k$ and $k/^{\beta}k$ values) were calculated for each fraction of reaction (five or six fractions ranging from ~20% to ~70% for each of the six labeled compounds) by using the equations of Tong and Yankwich.[49] These equations permit calculation of $k/^{\alpha}k$ or $k/^{\beta}k$ in four ways by using any three of the measured parameters, fraction of reaction, f, activity of the product, R_p, and activity of the styrene used, R_0, and that recovered after partial reaction, R_r. In those cases (10 of 32, including 6 of 12 for the *p*-CH_3 compound) where the recovered styrene polymerized during workup, only the equation using f, R_0, and R_p could be used. The isotope effect values calculated in this way are summarized in Table II. There were no discernible trends in the isotope effect with fraction of reaction (cf. the standard deviations in Table II), and there is good agreement in all cases among the values calculated by the four different equations. These two facts provide good evidence of the high chemical and radiochemical purities of the reactants and of the satisfactory nature of the procedures used in making the measurements.

Discussion

In agreement with previous work[11,12,24–30] it is clear from our data in Table I that the additions of arylsulfenyl halides to substituted styrenes are strongly accelerated by electron-donating groups (EDG), supporting the thesis that there is a substantial positive charge at the α carbon in the activated complex of the rate-determining step. Our data in Table I are in acceptable agreement with the corresponding data of Orr and Kharasch,[25] but whereas they chose to show a linear Hammett plot, omitting the *p*-methoxystyrene point, we choose to include the *p*-methoxystyrene point and show a curved Hammett plot, solid line, Figure 1.[50] We interpret their omission of the *p*-CH_3O point and our inclusion of it to give a curved Hammett plot to mean the same thing, a mechanism changing with substituent from one with a large positive charge at C_α for styrenes containing EDG (activated complex **4**-like, Scheme I for the rate-determining step) to one with a less positive charge at C_α and a smaller responsiveness to EDG (activated complex **5**-like or **6**-like, Scheme I). The dotted line for the top four points in Figure 1 gives $\rho = -3.39$, correlation coefficient 0.9797, while the dashed line for the bottom four points in Figure 1 gives $\rho = -1.82$, correlation coefficient 0.9879. When only the *p*-CH_3O and *p*-CH_3 points are used, $\rho = -4.62$, about the same value as that for the bromination of styrenes which presumably involves an open carbenium ion-like activated complex for the rate-determining step (see introductory material above).

The point of inclusion or exclusion of the *p*-CH_3O point in the Hammett plot deserves more discussion. Neither our value nor that of Orr and Kharasch[25] is a reliable rate constant, but both

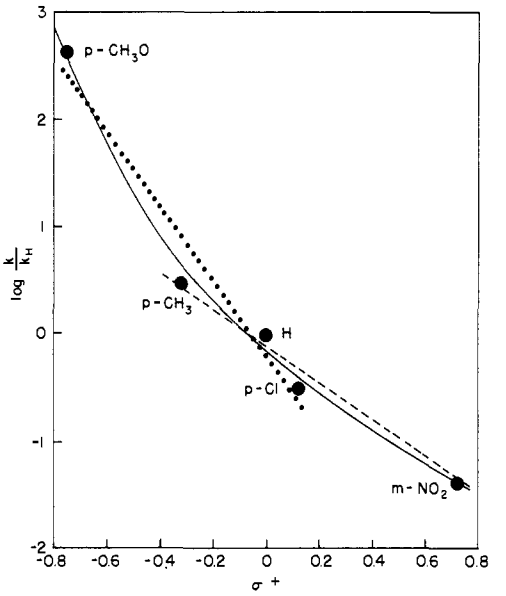
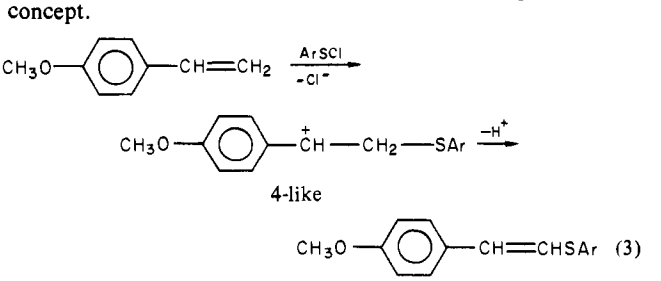


Figure 1. Hammett plot for the addition of 2,4-dinitrobenzenesulfenyl chloride to substituted styrenes in acetic acid at 30.1 °C.

are acceptable as *minimum* values. Thus, even the minimum rate constant values for the *p*-CH_3O compound lie far above the linear Hammett plot established by the other substituents, even when σ^+ constants are used. Even though *p*-methoxystyrene is a bad actor as far as polymerization is concerned, we saw no sign of polymerization with it in our kinetics experiments where we followed the rate of disappearance of 2,4-dinitrobenzenesulfenyl chloride to 90.2%. However, in agreement with the findings of Orr and Kharasch,[25] we found that the product of this reaction is not the usual chlorosulfide, *p*-CH_3O—C_6H_4—$CHClCH_2$—SAr, but rather the vinyl sulfide, *p*-CH_3O—C_6H_4—CH=CHSAr. Orr and Kharasch[25] were able to make the chlorosulfide at lower temperatures and to show that it is stable and does not form the vinyl sulfide under the normal addition reaction conditions. The vinyl sulfide undoubtedly arises from the carbenium ion by loss of an adjacent proton (eq 3), in line with the changing mechanism concept.



Thus the reaction of 2,4-dinitrobenzenesulfenyl chloride with substituted styrenes in acetic acid is easily interpreted in terms of rate-determining formation of an open carbenium ion–chloride

(49) Tong, J. Y.; Yankwich, P. E. *J. Phys. Chem.* **1957**, *61*, 540–543.
(50) Izawa, Okuyama, and Fueno[11] omitted the *p*-CH_3O points, and thus obtained linear Hammett plots for the addition of 2,4-dinitrobenzenesulfenyl chloride to *cis*- and *trans*-1-arylpropenes in acetic acid. Curved lines similar to Figure 1, solid line, also fit their data well.

ion pair (or pair of ions) (Scheme I, **4**-like) for styrenes containing strong EDG and in terms of a somewhat unsymmetrical thiiranium ion–chloride ion pair (or pair of ions) (Scheme I, **5**-like) or a sulfurane (Scheme I, **6**-like) for styrenes not containing a strong EDG. These particular kinetic data do not speak directly to the question of intimacy of the ion pairs, but it is clear that a simple thiiranium ion-like (**5**-like) activated complex is inadequate to explain the variation of mechanism with substituent.

Our $^{\alpha}$C and $^{\beta}$C isotope effect data, Table II, also lead us to the conclusion that the mechanism of addition of 2,4-dinitrobenzenesulfenyl chloride to substituted styrenes changes with substituents. While the $^{\beta}$C isotope effects remain approximately constant, $k/^{\beta}k$ = 1.035, 1.032, and 1.037 for substituents *p*-Cl, H, and *p*-CH_3; the $^{\alpha}$C isotope effects decrease as the substituent becomes a better EDG, with a dramatic change between the unsubstituted and *p*-methylstyrenes, $k/^{\alpha}k$ = 1.027, 1.022, and 1.004 for substituents *p*-Cl, H, and *p*-CH_3. These isotope effects constitute the first reported example of carbon isotope effects in a simple electrophilic addition reaction and are in sharp contrast to the "no isotope effect" reports in the brominations of styrene and methyl cinnamate.[3] Experiments are planned to extend these addition reaction isotope effect studies to the halogenations of substituted styrenes (and, perhaps, methyl cinnamates).

The $^{\beta}$C isotope effects are probably characteristic of conversion of the sp^2-hybridized β carbon to the sp^3-hybridized β carbon of an activated complex similar either to intermediate **4** *or* to cyclic intermediates **5** or **6** (Scheme I). Since both bond rupture, i.e., double bond conversion to a single bond, and C_β–S bond formation are involved at C_β for both types of mechanism, it is not surprising that the $^{\beta}$C isotope effects are relatively small and unchanging with substituent; no direct interaction of C_β with the ring is possible in either case.

On the other hand, at C_α the bonding changes would be expected to be quite different for the two types of mechanisms. For a **5**-like or **6**-like activated complex, the bonding changes at C_α are similar to those at C_β, and a similar $^{\alpha}$C isotope effect might be expected to the one for $^{\beta}$C, $k/^{*}k \sim 1.035$. To the extent that there is any **4**-like nature to the activated complex, the smaller amount of C_α–S bond formation should lead to an increased $^{\alpha}$C isotope effect, while the larger amount of C_α–ring bonding (delocalization of the positive charge into the ring) should lead to a decreased $^{\alpha}$C isotope effect. There is clearly some **4**-like character to the activated complex of the rate-determining step as deduced from the large negative Hammett ρ values for the reaction (see the preceding kinetics discussion). Evidently the C_α–ring bonding effect is dominant over the C_α–S (less) bonding effect, since the $^{\alpha}$C isotope effects are lower than the $^{\beta}$C effects. The C_α–ring bonding (delocalization) isotope effect lowering factor is largest just where it would be expected to be, for the compound (*p*-methylstyrene) with the substituent best able to stabilize a developing positive charge (best able to support a **4**-like activated complex). The break in the Hammett curve, Figure 1, was interpreted above in the some way, a **4**-like activated complex for electron-donating substituents.

Much of the discussion in the last two paragraphs is speculative, since there are as yet no comparison or "calibration" carbon isotoe effect data. Experiments are planned to collect the data on other reactions needed to test these ideas. The present isotope effect data do not speak directly to the question of intimacy of the ion pairs, but additional planned isotope effect measurements under other experimental conditions[24] may throw light on that question. Hammett ρ values do not change much when these addition reactions are carried out in the presence of $LiClO_4$, but the rates increase substantially.[24]

The interpretation of the secondary α-deuterium isotope effect data[43] for the addition of bromine and 2,4-dinitrobenzenesulfenyl chloride to styrene mentioned in the introduction was that a larger inverse effect is characteristic of a **5**-like activated complex whereas a smaller inverse effect is characteristic of a **4**-like activated complex (less change in C_α hybridization so less change in C_α–H_α bonding). Measurements were made[43] for the addition of 2,4-dinitrobenzenesulfenyl chloride to several substituted styrenes, but none of them contained strong EDG. If our interpretation of the kinetic and $^{\alpha}$C isotope effect data is correct, one would expect a smaller inverse α-deuterium isotope effect for addition of 2,4-dinitrobenzenesulfenyl chloride to *p*-methylstyrene than was observed[43] for other substituted styrenes.

The research of Schmid and Nowlan[12,15] on the addition of 2,4-dinitrobenzenesulfenyl chloride to a series of cis- and trans-substituted 1-phenylpropenes, **1**, R = Me, in 1,1,2,2-tetrachloroethane also provides evidence that the mechanism of the reaction changes with substituent. For the cis compounds containing EDG the reactions, while still somewhat stereoselective anti, do not show the nearly stereospecific anti behavior of the cis compounds containing EWG or the trans compounds containing either EDG or EWG. Thus it appears that at least in the activated complexes for the *product-determining* steps for the EDG-containing cis compounds there is substantial **4**-like character. On the basis of *linear* Hammett plots (considerable scatter, especially for EDG-containing compounds) for *both* the cis and trans series, Schmid and Nowlan conclude that the activated complexes for all the rate-determining steps are bridged. However, ρ = −3.7 for the trans series and only −2.7 for the cis series, and the authors, logically, favor more **4**-like character for the activated complexes of the *rate-determining* steps for the trans (faster reacting) series than for the cis series. It may be that the trans compounds have fairly tight ion pair-like activated complexes for both rate-determining *and* product-determining steps (unsymmetrical bridging, leading to and from an intermediate somewhere between **4** and **5**), while the cis compounds have more **5**-like activated complexes for the rate-determining steps (steric factors may inhibit the coplanarity of the ring and double bond required for **4**-like structures). If this is the case then the mechanism for transfer of the chlorine to the back side of the α carbon must be less hindered in the trans than in the cis series (as would probably be expected), requiring a more **4**-like activated complex for the *product-determining* step for cis than for trans compounds (especially EDG-containing ones which would stabilize **4**-like species), leading to decreased stereoselectivity, as observed. If our interpretation (see above) that the lower $^{\alpha}$C isotope effect for addition of 2,4-dinitrobenzenesulfenyl chloride to *p*-methylstyrene rather than unsubstituted or *p*-chlorostyrene results from more **4**-like character in the activated complex of the rate-determining step is correct, it should follow from the discussion earlier in this paragraph that *cis*-1-(4-methoxyphenyl)propene should have a *higher* $^{\alpha}$C isotope effect than its trans isomer, since the activated complex for the *rate-determining* step for the cis compound presumably has *less* **4**-like character (in spite of the fact that the subsequent activated complex for the *product-determining* step has *more* **4**-like character). Such an isotope effect experiment is planned as a test of both the isotope effect and Hammett plot stereochemical interpretations.

The question of exactly how the chlorine gets from the sulfur to the back side of the α carbon has received but scant attention in the literature;[18,20a,51] it is not even known for sure that the product-determining step is intramolecular, although that is generally assumed to be the case. Crossover exchange experiments are planned to test this point, using chlorine-36. Arylsulfenyl chlorides that do not contain *o*-nitro groups do not undergo rapid exchange of organic chlorine with $Li^{36}Cl$ in acetic acid,[52] so the crossover experiments may be practical.[53]

One further line of evidence that bears on the changing with substituent of the mechanism of addition of arenesulfenyl derivatives to substituted styrenes is the variation of rate and even sign of the Hammett ρ_{ArSX} for substituted arenesulfenyl deriva-

(51) Kartashov, V. R.; Bodrikov, I. V.; Skorobogatova, E. V.; Zefirov, N. S. *Zh. Org. Khim.* **1976**, *12*, 297–304. Csizmadia, V. M.; Schmid, G. H.; Mezey, P. G.; Csizmadia, I. G. *J. Chem. Soc., Perkin Trans. 2*, **1977**, 1019–1024. Zefirov, N. S.; Sadovaya, N. K.; Akhmedova, R. S.; Bodrikov, I. V.; Morrill, T. C.; Nersisyan, A. M.; Rybakov, V. B.; Saraceno, N. D.; Struchkov, Y. T. *Zh. Org. Khim.* **1980**, *16*, 580–588.

(52) Andreeva, L. A.; Zefirov, N. S.; Fedoseev, V. M.; Churilin, V. S. *Tetrahedron Lett.* **1982**, *23*, 3797–3798.

(53) For related research, see: Schmid, G. H.; Fitzgerald, P. H. *J. Am. Chem. Soc.* **1971**, *93*, 2547–2548.

tives.[20d,29-31] The original ρ_{ArSX} values for the additions of 4-substituted-2-nitrosulfenyl chlorides and bromides to cyclohexene[31] were all around −0.7, showing that there is some buildup of positive charge at sulfur in the rate-determining step. However, the fact that these ρ_{ArSX} values are not more negative than they are supports the contention that the activated complex does not have a structure with a lot of free thiiranium ion character (like **5**, taken as an unassociated ion pair). The more recent work[20d,29,30] with substituted arenesulfenyl derivatives and substituted styrenes shows even smaller values of ρ_{ArSX}, and the sign of ρ_{ArSX} changes from negative to positive as the substituent on the styrene changes from an EWG to an EDG. The simplest interpretation of these data is in line with the mechanistic arguments presented above: When an EDG is present in the styrene, the activated complex is **4**-like, with no buildup of positive charge at S and a positive ρ_{ArSX}. When an EWG is present in the styrene, the activated complex is **5**-like, with some buildup of positive charge at S and a negative ρ_{ArSX}. A sulfur isotope effect study of this phenomenon would be most interesting.

Experimental Section

The general outline of the experimental approach is given in the Procedure and Results section. Many of the experimental procedures were essentially identical with those described in our previous work.[47,48]

Kinetic Procedures. The kinetics of the reactions of 2,4-dinitrobenzenesulfenyl chloride with *p*-methoxy-, *p*-methyl-, unsubstituted, *p*-chloro-, and *m*-nitrostyrenes were measured in anhydrous acetic acid at 30.1 ± 0.2 °C in a system continuously flushed with dry nitrogen following the general procedure of Orr and Kharasch.[10] The styrenes were commercially available products and were distilled at reduced pressure just prior to use. The acetic acid was dried by following the procedure of Wilkins and Regulski.[43a] The 2,4-dinitrobenzenesulfenyl chloride was commercial material recrystallized twice from carbon tetrachloride. Separate solutions of the styrene and sulfenyl chloride in acetic acid were brought to temperature in the constant temperature bath and then mixed as rapidly as possible. Concentrations of the styrenes, after mixing, averaged about 0.05 M, and those of the sulfenyl chloride averaged about 0.06 M. Aliquots were removed at appropriate intervals and analyzed for remaining sulfenyl chloride.[10] Good second-order plots (followed to at least 80% reaction) were obtained in all cases; rate constants were calculated from the slopes of these plots by least-squares methods, and these values, together with their correlation coefficients, are given in Table I. The general good agreement with the results of Orr and Kharasch[25] (see Table I) gives us confidence that our procedures are satisfactory and that our rate constant values are valid. The rate constant for *p*-methoxystyrene is clearly not reliable, but it is also, clearly, a minimum (see Discussion).

Preparations and Purities of Carbon-14 Labeled Compounds.[47,48] α and β carbon-14 labeled *p*-methyl- and *p*-chlorostyrenes were prepared by methods described in detail by Hasan, Sims, and Fry[47] involving the following reaction sequence: commercial sodium acetate-*1*-^{14}C or -*2*-^{14}C, acetyl chloride, substituted acetophenone, substituted α-phenylethyl alcohol, substituted α-phenylethyl chloride, substituted styrene-*1*-^{14}C or -*2*-^{14}C.

α and β carbon-14 labeled styrene could easily have been prepared by the same methods,[47] but because some of the labeled intermediates were available from other research,[48] these compounds were prepared by using the following reaction sequence:[1,48] ($^{\alpha}$C-labeled) commercial benzoic-*7*-^{14}C acid, benzyl alcohol, benzyl chloride, (for $^{\beta}$C-labeling, commercial $Na^{14}CN$) phenylacetonitrile, (2-phenylethyl)amine, (2-phenylethyl)dimethylamine, (2-phenylethyl)trimethylammonium bromide, styrene-*1*-^{14}C or -*2*-^{14}C.

For each of the intermediates in the preparations of each of the above six labeled compounds the physical properties, chemical yields, and radiochemical purities and yields were in agreement with literature values and/or expectations based on prior experiments with unlabeled compounds. In particular, radiochemical and chemical yields were essentially identical (taking into account dilutions with inactive reagents at some stages), showing both high chemical and high radiochemical purities. Full details for all of these reactions are available from the authors.

Carbon-14 Isotope Effect Measurement Procedures. The general procedures are outlined in the Procedures and Results section. The labeled styrenes were freshly distilled just prior to each set of experiments. The desired fractions of reaction, *f*, were controlled by using limited amounts of 2,4-dinitrobenzenesulfenyl chloride. After appropriate times (as estimated from the kinetics experiments), the completeness of the reactions was demonstrated by testing small aliquots for unreacted 2,4-dinitrobenzenesulfenyl chloride with use of potassium iodide and starch (absence of a blue color).[7] The insoluble addition products were then recovered by filtration and recrystallized three times from absolute ethanol (*p*-chloro and unsubstituted compounds) or benzene (*p*-methyl compound) to constant molar activity (for instance, for the $^{\beta}$C *p*-chlorostyrene case, for $f = 0.294$, $R_p = 0.7569 \pm 0.0037$ and 0.7562 ± 0.0037 mCi/mol after the second and third recrystallizations.) The purities were also checked by TLC and melting point (less sensitive methods). These samples were used for radioactivity assay, giving the recovered product, R_p, values.

The above filtrates were diluted with ice water and filtered again to remove the small additional amounts of adduct precipitated. These second filtrates were extracted with pentane (5 × 100 mL) to remove the unreacted styrene. The combined pentane–styrene solutions were washed three times with water and dried with $MgSO_4$. Since the styrenes are prone to polymerize, no attempt was made to isolate them in pure form; instead, excess bromine was added to the styrene–pentane solutions at 3 °C in the dark under a stream of dry nitrogen to give the styrene dibromides. After destroying the excess bromine with saturated sodium bisulfite solution, the pentane solutions were washed with water, dried with $MgSO_4$, and concentrated to give styrene dibromide residues. For the *p*-chloro and unsubstituted compounds, the solid styrene dibromides were recrystallized three times from ethanol–water to constant molar activity and finally vacuum sublimed. (For instance, for the $^{\beta}$C *p*-chlorostyrene case for $f = 0.294$, $R_r = 0.7908 \pm 0.0068$ mCi/mol after three recrystallizations and 0.7905 ± 0.0023 mCi/mol after the final sublimation.) These samples were used for radioactivity assay, giving recovered reactant, R_r, values. In a few cases (4 of 22, footnotes *b*, *c*, *e*, and *f*, Table II) no styrene dibromide samples were recovered; instead, styrene polymers were noted after concentration of the pentane solutions remaining after the brominations. No reasons were apparent for when the polymer formed and when it did not.

When the above bromination procedure was tried for *p*-methylstyrene, the "dibromide" proved to be an intractable oil which could not be recrystallized. For that reason, the recovered *p*-methylstyrene was derivatized by using 2,4-dinitrobenzenesulfenyl chloride. The dry pentane–*p*-methylstyrene solution was concentrated to a few milliliters at low temperature under vacuum and then treated with excess 2,4-dinitrobenzenesulfenyl chloride in anhydrous acetic acid under a stream of dry nitrogen at 30.1 °C for 20 half-lives. The precipitated adduct was purified as before and was used for radioactivity assay, R_r, values. In six (of 12) cases (footnotes *a* and *d*, Table II) no adduct precipitate was formed; apparently the *p*-methylstyrene had polymerized in these six cases. Fortunately, these "missing" R_r values are not critical to any of our arguments.

Several approaches were taken to measure the fourth parameter needed for the isotope-effect calculations, R_0, the activity of the starting material (which is necessarily equal to the activity of the product at 100% reaction). These approaches (measuring R_0 several ways) also serve as appropriate "control" experiments, demonstrating the chemical and radiochemical purities of reactants and products and the adequacy of the procedures used in derivative preparations. For the *p*-methylstyrene the R_0 value was measured for the neat starting material and for the 2,4-dinitrobenzenesulfenyl chloride adduct after 100% reaction (excess sulfenyl chloride, 20 half-lives, usual workup): For $^{\alpha}$C, R_0(neat) = 0.8470 ± 0.0020 mCi/mol and R_0(adduct) = 0.8479 ± 0.0101 mCi/mol; for $^{\beta}$C, R_0(neat) = 0.5735 ± 0.0012 mCi/mol and R_0(adduct) = 0.5778 ± 0.0104 mCi/mol. For the *p*-chlorostyrene, the R_0 value was measured for the neat starting material, for the adduct after 100% reaction, and for the 100% reaction dibromide prepared in the usual manner from the starting material: For instance, for $^{\beta}$C, R_0(neat) = 0.7874 ± 0.0008 mCi/mol, R_0(adduct) = 0.7749 ± 0.0039 mCi/mol, and R_0(dibromide) = 0.7804 ± 0.0065 mCi/mol. For the unsubstituted styrene the R_0 value was measured for the adduct after 100% reaction, for the 100% reaction dibromide, and for the (2-phenylethyl)trimethylammonium bromide salt from which the styrene was prepared: For instance, for $^{\beta}$C, R_0(adduct) = 0.5677 ± 0.0069 mCi/mol, R_0(dibromide) = 0.5712 ± 0.0036 mCi/mol, and R_0(salt) = 0.5638 ± 0.0036 mCi/mol. These values demonstrate the precision and accuracy of the radioactivity measurements and give us confidence in the isotope effect values reported in Table II.

The procedures used for the radioactivity measurements and for the isotope effect calculations are the same as those described in detail by Hasan, Sims, and Fry[47] with the two exceptions noted below. (1) Because the 2,4-dinitrobenzenesulfenyl chloride–styrene adducts were not very soluble in toluene, the toluene–base cocktail solution was replaced by a dioxane–base cocktail solution, made up of 6 g of 2,5-diphenyloxazole, 0.2 g of 1,4-bis[2-(4-methyl-5-phenyloxazolyl)]benzene, 100 g of naphthalene, and 1 L of dioxane. A new (not very different) quench calibration curve for the new cocktail solution was prepared and used. (2) The reaction products, $ZC_6H_4CHClCH_2SC_6H_3(NO_2)_2$, are yellow, and even small samples caused serious quenching problems. Accordingly,

higher than usual activity levels were used with a dilution-aliquot procedure to give appropriate counting rates. The usual size (10–20 mg) samples of the adducts were dissolved in the cocktail solution in a volumetric flask, and aliquots of a convenient size to give negligible quenching were then counted in the usual way. For these compounds dilution by a factor of about 3 gave suitable results.

Because the low value of the ^{a}C isotope effect for *p*-methylstyrene-*1*-^{14}C is so critical to our mechanistic conclusions, the original data from which the isotope effect values in Table II are derived are presented here in text format (R_0 = 0.8474 ± 0.0006), *f*, R_r (mCi/mol), R_p (mCi/mol): 0.1537, 0.8481 ± 0.0039, 0.8397 ± 0.0058; 0.2183, 0.8485 ± 0.0090, 0.8455 ± 0.0040; 0.3226, missing (polymer problem), 0.8395 ± 0.0113; 0.4173, missing, 0.8438 ± 0.0081; 0.4872, 0.8506 ± 0.0040, 0.8466 ± 0.0079; 0.7001, missing, 0.8469 ± 0.0083. To demonstrate that the constancy of the R_0, R_r, and R_p values (leading to the low value of the ^{a}C isotope effect) was not some abnormal characteristic of the (different) procedures used for the *p*-methylstyrene, we give the corresponding original data for the *p*-methylstyrene-2-^{14}C (R_0 = 0.5756 ± 0.0030 mCi/mol) (same format as above): 0.1555, missing 0.5590 ± 0.0029; 0.2290, 0.5816 ± 0.0063, 0.5556 ± 0.0071; 0.3607, missing, 0.5621 ± 0.0014; 0.5083, 0.5929 ± 0.0017, 0.5631 ± 0.0075; 0.6592, missing, 0.5624 ± 0.0083; 0.7253, missing, 0.5655 ± 0.0054.

Acknowledgment. We are indebted to Dr. John R. I. Eubanks for preparation of the benzyl-7-^{14}C chloride and to Professor L. B. Sims for many helpful discussions. Support of this research by National Science Foundation Grant CHE-8016398 is gratefully acknowledged. We wish to thank Warsaw University for support of a study leave for M.K.

Registry No. Carbon-14, 14762-75-5; 2,4-dinitrobenzenesulfenyl chloride, 528-76-7; *p*-methoxystyrene, 637-69-4; *p*-methylstyrene, 622-97-9; styrene, 100-42-5; *p*-chlorostyrene, 1073-67-2; *m*-nitrostyrene, 586-39-0.

Mechanisms of Epoxidations and Chlorinations of Hydrocarbons by Inorganic Hypochlorite in the Presence of a Phase-Transfer Catalyst[1]

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Abstract: Inorganic hypochlorite in the presence of a quaternary ammonium salt (phase-transfer catalyst) not only epoxidizes several arenes to arene oxides in high yields but also converts toluene to α-chlorotoluene, anisole to ring chlorinated anisoles, and alkenes to a complex mixture of chlorinated and oxidized products, including the epoxide. More detailed studies with this system indicate the following: (1) the high-yield conversion of toluenes to benzyl chlorides proceeds with a deuterium isotope effect of 3.6 and a ρ^+ value of −1.7; (2) *p*-chloroanisole is the major product from anisole and is formed in a 22-fold greater quantity than *o*-chloroanisole; (3) the epoxidation of *cis*- and *trans*-alkenes is stereoselective but not completely stereospecific; (4) the chlorination of saturated hydrocarbons occurs with a selectivity that is experimentally identical with that of chlorine monoxide. These and other results lead us to propose that the epoxidations and chlorinations observed in this system proceed by a free-radical mechanism involving chlorine monoxide and the ClO· radical. The relevance of this work to enzymic oxygenations is briefy considered.

As a result of our continuing interest in the mechanisms of organic and biological oxidations that proceed by the transfer of an oxygen atom or oxenoid species,[2] we report here a recent investigation of the mechanisms of some reactions that occur when various hydrocarbons are treated with inorganic hypochlorite in the presence of a phase-transfer catalyst (PTC). In 1977, we reported[3] that a number of arene oxides can be prepared in high yield by direct oxidation of arenes by this hypochlorite–PTC system, i.e., by reacting for a few hours at room temperature a solution of the arene in $CHCl_3$ or CH_2Cl_2 with aqueous commercial bleach (adjusted to pH 8–9) in the presence of a PTC such as tetrabutylammonium hydrogen sulfate. Although the arene oxide is the predominant product in most of those cases reported,[3] it was subsequently noted that some arenes give mainly chlorinated products under similar conditions. The present study was initiated to investigate the scope and mechanism of the epoxidations and chlorinations. Most of the data reported here were obtained from the reaction of toluenes, alkanes, alkenes, and anisole. The results strongly imply that all the reactions are proceeding by a free-radical mechanism with the chloroxy radical (ClO·) as an important chain-carrying species. The possibilities that the acylperoxy radical may be participating in some related epoxidations[4,5] and that the present system may be a reasonable model for oxygenations by cytochrome P-450 enzymes are briefly considered.

Results

Chlorination of Toluene. The reaction of toluene with the hypochlorite–PTC system under the conditions described in the

(1) (a) This research was partially supported by a research grant (AM 13448) from the National Institute of Arthritis, Diabetes, and Digestive and Kidney Diseases, Public Health Service. (b) Taken in part from the Ph.D. theses of S. Krishnan (1977) and H. E. Fonouni (1983), Department of Chemistry, The Pennsylvania State University.

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