Tetrahedron Letters,Vol.27,No.42,pp 5063-5066,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

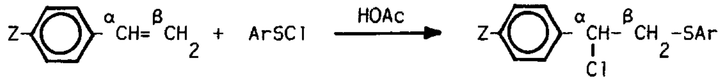
CARBON-14 KINETIC ISOTOPE EFFECTS AND MECHANISMS OF ADDITION OF 2,4-DINITROBENZENESULFENYL CHLORIDE TO SUBSTITUTED STYRENES IN THE PRESENCE OF LITHIUM PERCHLORATE[1]

Marianna Kanska and Arthur Fry*

Department of Chemistry and Biochemistry, University of Arkansas,
Fayetteville, AR 72701, U.S.A.

Abstract: The $k/{}^{\alpha}k$ isotope effect for addition of ArSCl to p-methylstyrene is small and unchanged by addition of $LiClO_4$; $k/{}^{\beta}k$ is high and unchanged. For styrene and p-chlorostyrene $k/{}^{\beta}k$ values are high and unchanged, while $k/{}^{\alpha}k$ increases from ~ 1.025 to ~ 1.04. p-Methylstyrene reacts through an open carbenium ion and the other two have cyclic intermediates.

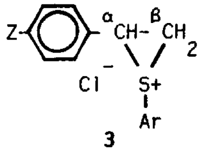
A few years ago we reported[2] the first case of the observation of a carbon isotope effect in a simple electrophilic addition reaction. 2,4-Dinitrobenzenesulfenyl chloride adds to styrenes with both ${}^{\alpha}C$ and ${}^{\beta}C$ carbon-14 isotope effects:



Ar = 2,4-dinitrophenyl **1** **2**

For Z = Cl, H, and CH_3, $k/{}^{\alpha}k$ = 1.027, 1.022, and 1.004; and $k/{}^{\beta}k$ = 1.035, 1.032, and 1.037.

The ${}^{\beta}C$ isotope effects do not change much with substituent, but the ${}^{\alpha}C$ isotope effects are smaller in all cases, and decrease with increasing electron donating ability of the substituent; for p-methylstyrene there is no measurable isotope effect within our experimental error of ± about 0.005. The Hammett plot[2] for rates of reaction of substituted styrenes is significantly curved: using σ^{+}, $\rho = -3.39$ for the electron donating end of the scale, and -1.82 for the electron withdrawing end. These data and other mechanistic information for the reaction, reviewed extensively in reference 2, led us to the tentative conclusion that there is a change over in mechanism from cyclic thiiranium ion intermediates, **3**, (probably ion pairs of various degrees of freedom--see below) to open carbenium ion intermediates, **4**, as Z becomes a better EDG. We reasoned that the constancy



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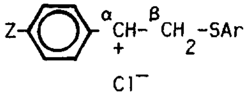

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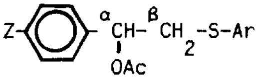

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of the $^{\beta}$C isotope effect was probably due to the change of the hybridization of that carbon from sp^2 to sp^3, regardless of which mechanism was followed. On the other hand, the bonding at the alpha carbon is very different for **3** and **4**, and the isotope effects would be expected to be different. For the cyclic mechanism the situation might be much like it is for the beta carbon (however, see below), but for the carbenium ion mechanism, the $^{\alpha}$C isotope effect would be expected to be small because the hybridization of that carbon remains sp^2 (no net bonding change means little or no isotope effect). Also, conjugation between the ring, with its EDG substituent, and the developing positive charge represents additional (isotope effect lowering) bonding in the activated complex.

Several groups of Russian workers have been directing their attention to the detailed nature of the cyclic intermediates in the reactions and especially to the interactions of the ion pairs in them.[2,3] They have found that the additions of arylsulfenyl halides to alkenes are much faster in more polar solvents, and in the presence of strong electrolytes, e. g., lithium perchlorate. It is clear from their work that the intermediate ion pairs become less associated with increasing polarity of the medium and added salts. There is very little discussion of the possibility of the intermediacy of open carbenium ions like **4** in this Russian work, but we believed that there would be a competition between mechanistic paths involving an open carbenium ion, **4**, and those involving cyclic intermediates, **3**, (of varying degrees of association of the positive center with the departing anion). We believed that the small (non-existent?) $^{\alpha}$C isotope effect for p-methylstyrene was due to the dominance of the formation of an open carbenium ion intermediate, and that the isotope effect characteristic of rate-determining formation of a cyclic intermediate would be higher as it is for the $^{\alpha}$C effect of styrene and p-chlorostyrene, or, better, as it is for the $^{\beta}$C effect for all three compounds. We reasoned that added lithium perchlorate probably would not change the isotope effect value for p-methylstyrene, but that it might transfer the mechanism for styrene and p-chlorostyrene toward dominance of the open carbenium ion intermediate, thus reducing further the $^{\alpha}$C isotope effect, perhaps to near unity. We even thought there might be inverse isotope effects. As it turns out (see below), the first expectation was correct but the second was "backwards".

We have now measured several $^{\alpha}$C and $^{\beta}$C isotope effects for these three compounds in the presence of varying amounts of lithium perchlorate (various ratios of salt to arylsulfenyl chloride--see tables). The labeled compounds were available from our previous work[2], and the reaction and workup procedures used were similar in most respects. However, in the presence of LiClO$_4$ substantial amounts of the acetate, **5**, as well as the normal addition product, **2**, were found. The Russian workers had also observed this. Of course this is related to the higher degree of ion pair separation in the more polar medium, enabling the solvent to compete effectively with the chloride ion in further reactions with the positive ions present (cyclic or open). For styrene and *p*-chlorostyrene, almost no acetate was found in the absence of the salt; with *p*-methyl styrene 10 % of the product was acetate in the absence of salt. For *p*-chlorostyrene, for instance, the % acetate changed from 3 to 36 to 48 to 61 to 63 as the $LiClO_4$/ArSCl ratio changed from 0 to 2 to 4 to 6 to 8.

Products **2** and **5** were separated from each other and from the recovered reactant by column chromatography, and isotope effects were measured for both products **2** and **5**. The radioassays were made by our standard procedure,[2,4] and the ratios of rate constants were calculated using the Tong and Yankwich equations[5]. Some of the measurements were carried out in 1984, and some in 1985; we also deliberately repeated some of the original 1982 measurements in both years to assure ourselves that the earlier values were reproducible. They were. For example, for *p*-chlorostyrene $k/{}^{\alpha}k$ (no added salt) was 1.027 ± 0.004 in 1982 and 1.026 ± 0.001 in 1985; the corresponding $k/{}^{\beta}k$ values were 1.035 ± 0.005 and 1.038 ± 0.003. For styrene itself, the ${}^{\alpha}C$ isotope effects in 1982, 1984, and 1985 were 1.022, 1.025, and 1.022; and for *p*-methylstyrene the corresponding values in 1982 and 1984 were 1.004 and 1.002. A very significant mechanistic factor is that the measured isotope effects were the same within experimental error for the acetate, **5**, and the normal addition product, **2**, in every case investigated. These results are tabulated at the right below. The variations of isotope effects with salt concentration are tabulated at the left below.

Variation of Isotope Effects with Lithium Perchlorate Concentration: Values ± about 0.005

Z	Salt/ArSCl Ratio	$k/{}^{\alpha}k$	$k/{}^{\beta}k$
Cl	0	1.026	1.038
	2	1.035	1.036
	4	1.039	1.034
	8	1.044	1.034
H	0	1.022	1.032
	2	1.027	
	4	1.038	
	8	1.038 **2**	
		1.044 **5**	
CH_3	0	1.002	1.037
	4	1.004 **2 & 5**	

Agreement in values for 2 and 5
1985 Values ± about 0.005

Z	$k/{}^{\alpha}k$	$k/{}^{\beta}k$	**Product**
Salt/ArSCl Ratio = 2			
H	1.027		**2**
H	1.026		**5**
Cl	1.035	1.036	**2**
Cl	1.035	1.032	**5**
Salt/ArSCl Ratio = 4			
H	1.038		**2**
H	1.033		**5**
Cl	1.039	1.034	**2**
Cl	1.040	1.036	**5**

Several important conclusions may be drawn from these results. **(1)** The isotope effect results are consistent over time; reagent purities and experimental procedures are satisfactory. **(2)** The increased amount of acetate with increased salt concentration shows that the ion association is decreasing--the reaction is becoming "more ionic". **(3)** The $^{\beta}$C isotope effects are **high and constant with substituent and salt concentration**; having the reaction become more ionic doesn't affect the bonding at $^{\beta}$C. The observed effect is probably characteristic of $^{\beta}$C changing from sp^{2} to sp^{3}, regardless of the bonding situation at $^{\alpha}$C. **(4)** The most notable finding is that the $^{\alpha}$C isotope effect **behavior of p-methylstyrene**, both in the presence and absence of added salt **is radically different** from that of styrene and p-chlorostyrene; **the reaction mechanisms must be different.** The k/$^{\alpha}$k values for p-methylstyrene are small (or non-existent) **with or without added salt**; while for the other two compounds added salt causes am increase in an already substantial isotope effect. p-Methylstyrene probably reacts by an open carbenium ion mechanism through intermediate **4**, and the other two by a cyclic mechanism through intermediate **3**. **(5)** The $^{\alpha}$C and $^{\beta}$C isotope effects for acetate **5** and chloride **2** are almost identical; a common mechanistic path is probably involved. The isotope effect is probably decided in the intermediate formation step, and is therefore independent of the nucleophile in the product-determining step. **(6)** For styrene and p-chlorostyrene the increase in the $^{\alpha}$C isotope effect with increasing salt concentration probably is caused by decreasing association ("bond rupture") of the leaving chloride ion with the alpha carbon. (An alternative is reversible formation of the cyclic intermediate, followed by rate-determining ring opening by acetate or chloride; isotope effects should be similar and high for the S$_{N}$2-like ring openings.)

References and Notes

1. The financial support of U.S. NSF Grant CHE-8314767 is gratefully acknowledged.
2. See Kanska, M.; Fry, A. J. Am. Chem. Soc. **1983**. 105, 7666-7672, **1982**, 104, 5512-5514 for this initial work, and for a review of the literature on isotope effects and mechanisms of simple electrophilic addition reactions.
3. Much of this early research is reviewed in reference 2; an excellent summary of this work, with many leading references is Smit, W. A.; Zefirov, N. S.; Bodrikov, I. V.; Krimer, M. Z. Acc. Chem. Res. **1979**, 12, 282-288.
4. Hasan, T.; Sims, L.B.; Fry, A. J. Am. Chem. Soc. **1983**, 105, 3967-3975.
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(Received in USA 23 June 1986)