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Use of Kinetic Isotope Effects in Mechanism Studies. 3. Measurement of Hydrogen Isotope Effects on the Primary Chlorine Isotope Effect during Elimination Reactions[1]

Sir:

We have recently reported[2] that the excellent experimental data for the temperature dependence of the primary kinetic isotope effects measured for dehydrobromination of $C_6H_5C^iH(CH_3)CH_2Br$ (I-Br)[3,4] can be computer simulated by assuming that reaction proceeds via an internal-return mechanism, Scheme I. Since this elimination reaction is considered to be an example of a concerted E2 mechanism,[5] we initiated studies designed to help distinguish between the two possible interpretations of such isotope data. An elimination reaction offers additional methods which can be employed to help determine if reaction proceeds by a one-step or a two-step pathway, namely, leaving group isotope effects[6] and element effects.[7] We have questioned the validity of using the element effect when studying dehydrohalogenation reactions, and therefore wish to report a novel approach which measures the hydrogen isotope effect on a primary chlorine isotope effect to aid in assigning mechanisms for these eliminations.

The Arrhenius behavior and primary kinetic hydrogen isotope effects observed for ethoxide-promoted dehydrochlorination of $C_6H_5C^iH(CH_3)CH_2Cl$ (I-Cl) are similar to those reported for I-Br.[8] Both an E2 mechanism and the E1cb pathway with internal return should give measurable $^{35}Cl/^{37}Cl$ leaving group isotope effects;[9] however, measuring k^{35}/k^{37} for both the protio and deuterio compounds should in principle allow for experimental differentiation between the two mechanisms. Experimental results are summarized in Table I.

Scheme I

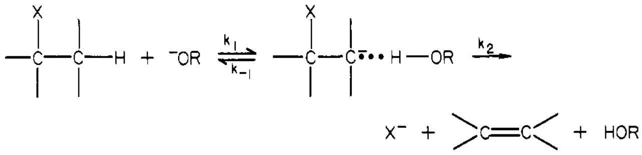

Table I. Chlorine Isotope Effects for Sodium Alkoxide Promoted Dehydrochlorination Reactions in Alcohol

compound[a]	solvent	k^{35}/k^{37} [b]	temp, °C
I-Cl-*h*	EtOH	1.00590 ± 0.00013	75
I-Cl-*d*	EtOH	1.00507 ± 0.00036	75
V	EtOH	1.00580 ± 0.00034	75
IV-*h*	EtOH	1.00908 ± 0.00008	24
IV-*d*	EtOH	1.00734 ± 0.00012	24
IV-*h*	MeOH	1.00978 ± 0.00020	21
IV-*d*	MeOH	1.00776 ± 0.00020	21
III-*h*	EtOH	1.01229 ± 0.00047	0
III-*d*	EtOH	1.01003 ± 0.00024	0
III-*h*	MeOH	1.01255 ± 0.00048	20
III-*d*	MeOH	1.01025 ± 0.00043	20

[a] I-Cl = $C_6H_5C^iH(CH_3)CH_2Cl$, III = $C_6H_5C^iHClCF_2Cl$, IV = $C_6H_5C^iHClCH_2Cl$, V = $C_6H_5CH_2CH_2Cl$. [b] k^{35}/k^{37} values were calculated as described by Hill, J. W.; Fry, A. *J. Am. Chem. Soc.* 1962, *84*, 2763.

If the elimination of I-Cl went by an E1cb mechanism with a moderate amount of internal return, there should be a dramatic difference in the observed k^{35}/k^{37} for I-Cl-*h* vs. I-Cl-*d*. When the same internal-return parameters needed to model the Arrhenius behavior of I-Br were used, we calculated an expected k^{35}/k^{37} of 1.00370 for I-Cl-*h*.[10] In this model, the forward step, k_2, is favored by a factor of 2.5 over the return step, k_{-1}, and it is not surprising to expect a measurable k^{35}/k^{37}. However, when reaction occurs with I-Cl-*d*, k_2 is now favored by a factor of 25, and a rather large drop in the chlorine isotope effect is expected, k^{35}/k^{37} = 1.000 50. These two values are readily distinguished from each other since measurements of $^{35}Cl/^{37}Cl$ are accurate enough to calculate k^{35}/k^{37} to better than 50 parts per 10^5.[9] Intuitively, we felt that k^{35}/k^{37} should be about the same for I-Cl-*h* and I-Cl-*d* if reaction proceeded by an E2 mechanism. This expectation was substantiated by model calculations of isotope effects for I-Cl-*h* and I-Cl-*d* by using methods described elsewhere.[11] The results from these calculations will be reported in the full paper.

The observed k^{35}/k^{37} = 1.00590 at 75 °C for the ethoxide-promoted elimination of I-Cl-*h* coupled with a k^{35}/k^{37} = 1.00507 for I-Cl-*d* provides experimental evidence that strongly favors an E2 pathway for this dehydrochlorination reaction. The rather large element effect, I-Cl:I-Br = 1:64 at 50 °C, coupled with substantial isotope effects, k^H/k^D greater than 6 at 50 °C, should be convincing evidence that there is cleavage of both C–H and C–X bonds in what would be an E2 transition state;[5a] however, we have measured k^H/k^D values of 2–4 for the alkoxide-promoted dehydrohalogenations of $ArCHXCF_2X$ which appear not to proceed by a simple E2 mechanism and yet give k^{Br}/k^{Cl} ratios of 25–50.[12] This has led us to doubt the validity of using element effects to assign mechanisms to elimination reactions.

Kaldor and Saunders[13] cite our temperature-independent isotope effects for the ArC^iHXCF_2X systems as the only cases where observed Arrhenius behavior of an elimination reaction differs markedly from the E2 pattern as exemplified by the temperature dependence of k^H/k^D for I–Br and their own results. Using an internal-return mechanism as a model, it is possible to predict

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(1) (a) Other papers in this series are ref 12 (part 1) and ref 2 (part 2). (b) Presented in part at the IUPAC 5th International Symposium on Physical Organic Chemistry, Santa Cruz, CA, Aug 17–22, 1980.

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temperature-independent hydrogen isotope effects, k^H/k^D, similar to those reported for $C_6H_5C^iHBrCF_2Br$ (II) and $C_6H_5C^iHClCF_2Cl$ (III).[12a] However, the parameters chosen to mimic the k^H/k^D behavior will not allow calculation of the observed temperature dependence of k^D/k^T. Thus the experimental results appear not to agree with either an E2 mechanism or a simple E1cb pathway that features internal return.

In an attempt to understand this behavior better, we used both III-*h* and III-*d* for chlorine isotope effect studies. Experimental results are summarized in Table I. Alkoxide-promoted dehydrochlorination of III resulted in k^{35}/k^{37} values of 1.01255 (III-*h*) and 1.01025 (III-*d*) in methanol and 1.01229 (III-*h*) and 1.01003 (III-*d*) in ethanol. These values are much larger than those measured for I-Cl, and the k^{35}/k^{37} values for III-*h* appear to be the largest chlorine isotope effects reported to date. Although the reaction occurs 17 times faster in ethanol than in methanol and k^H/k^D differs in the two alcohols (2.3 in MeOH vs. 2.9 in EtOH), the observed chlorine isotope effects for III-*h* are within experimental uncertainty of each other when measured in each solvent. The same is true for III-*d*. On the other hand, differences between III-*h* and III-*d* are well outside the limits of experimental uncertainty. On the basis of values obtained for III-*h*, we anticipated that k^{35}/k^{37} should be between 1.00300 and 1.00600 for III-*d*. Thus the observed differences between III-*h* and III-*d* are too large for an E2 mechanism and much smaller than predicted by a simple E1cb with internal return.

Of special interest was $C_6H_5C^iHClCH_2Cl$ (IV) which features the activating β chlorine but has the eliminated chloride leaving from $-CH_2Cl$ (similar to I-Cl) rather than from $-CF_2Cl$ (similar to III). Primary hydrogen isotope effects for IV are $k^H/k^D = 3.2$ (MeOH) and 4.5 (EtOH) at 50 °C.[12b] The magnitudes of the chlorine isotope effects are smaller than those for III but larger than those for I-Cl (see Table I). The differences between k^{35}/k^{37} for IV-*h* and IV-*d* are similar to the observed differences for III-*h* and III-*d*.

Replacement of the benzylic chloride of IV with hydrogen, $C_6H_5CH_2CH_2Cl$ (V), causes both hydrogen and chlorine isotope effects to revert back to values quite similar in magnitude to those observed for I-Cl. Values of k^H/k^D are 5.59 (V) and 5.37 (I-Cl) at 75 °C,[8] and the observed k^{35}/k^{37} of 1.00580 is virtually the same as that reported for I-Cl-*h*. Reaction of V with ethanolic sodium ethoxide results in 4–5% substitution competing with the elimination reaction. Therefore, chlorine isotope effects were not measured by using $C_6H_5CD_2CH_2Cl$, since substitution now accounts for ~25% of the reaction product.[14]

This unique method of measuring a hydrogen isotope effect on the heavy-atom isotope effect and using it to assign mechanisms to elimination reactions need not be limited to leaving groups. Carbon atoms directly involved in the elimination could be used in a similar manner. Results for dehydroiodination of $C_6H_5C^iH(CH_3){}^*CH_2I$ (I-I) give k^{12}/k^{14} values of 1.034 ± 0.007 (I-I-*h*) and 1.028 ± 0.004 (I-I-*d*) when reaction is carried out in methanolic sodium methoxide at 50 °C, and these values also support an E2 mechanism for this reaction. The magnitude of either α or β carbon isotope effects is difficult to predict for an elimination reaction since the atoms are not only involved in more than one bond making and breaking but are also undergoing hybridization changes. The advantage of making use of both protio and deuterio compounds is that one could determine a mechanism prior to attempting to interpret the magnitude of the heavy-atom isotope effect.

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(14) A substitution reaction competing with the elimination process is also observed for I-Cl-*d* (3–4%). Reactions of IV are also subject to wrong way elimination, $PhCHClCH_2Cl \rightarrow PhCCl{=}CH_2$, which occurs with IV-*h* (1–2%) and IV-*d* (3–8%) depending on temperature and alcohol used as solvent. These minor amounts of side products will not alter k^{35}/k^{37} significantly and k^H/k^D is readily corrected for the competing reaction.

Photoinduced Electron-Transfer Reactions. Radical Cations of the 1,2-Diphenylcyclopropanes

Sir:

The photosensitized geometric isomerization of diarylcyclopropanes may involve either a triplet state, generated by triplet energy transfer, a radical ion, generated by electron transfer, or a cyclopropyl radical, generated by hydrogen abstraction, as a key intermediate.[1] While the structure of the cyclopropyl radical appears to be understood,[2] those of the triplet state and the radical ion are open to question. They could be "closed", having the charge and/or the unpaired spin(s) localized in one aryl group, or they could attain an "open" form where the tertiary–tertiary cyclopropane bond is broken or weakened so that charge and/or spin(s) are delocalized over both aryl groups.

We have studied the reaction of *cis*- and *trans*-1,2-diphenylcyclopropane (**1**) with photoexcited acceptors, such as tetrachlorobenzoquinone (chloranil, **2**), and have applied the CIDNP technique[3] in an attempt to identify the nature of the intermediates. This technique is a sensitive tool for radical pair[3] and radical ion pair reactions[4] and has been useful, inter alia, in establishing the intermediacy of aminium radical ions in the photoreaction of ketones with tertiary amines[5] and in studying the mechanism involved in the electron-transfer-induced isomerization of olefins.[6] CIDNP effects reflect the signs and magnitudes of the hyperfine coupling constants (hfc) of the intermediate in which the polarization is generated and, therefore, can be used to differentiate between potential intermediates provided that their hfc patterns are sufficiently different.

The irradiation of chloranil in acetonitrile or acetone solutions containing either *cis*- or *trans*-**1** resulted in strong CIDNP effects for the reactant. The aromatic and the benzylic protons showed enhanced absorption (A) whereas the secondary protons appeared in emission (E; Figure 1). However, neither experiment showed any evidence for a polarized rearrangement product.

The nature of the reactants and key experimental observations allow us to eliminate some intermediates from consideration. Since chloranil has a lower triplet energy[7] than other sensitizers, whose reactions with **1** have been studied, and since it fails to cause any

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