# ISOTOPE EFFECTS AND MECHANISM IN THE BASE-PROMOTED DEHYDROCHLORINATION OF 1,1-DICHLORO-2,2-DIARYLETHANES-1-$^{14}$C[1]
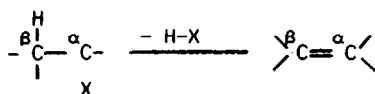
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**Abstract:** In the base-promoted dehydrochlorination of 1,1-dichloro-2,2-diphenylethane-1-$^{14}$C and its p-nitro analog, the isotope effects, $k/^{14}k$, are 1.045 and 1.024, respectively. These results support an Elcb-like E2 mechanism for both elimination reactions.

Isotope effect studies in elimination reactions,[2,3] especially carbon isotope studies[4,5] have become a mainstay of the effort to establish details of mechanisms (reaction coordinate motions and activated complex structures) of these reactions. In particular, for irreversible E1, E2, and Elcb mechanisms the expected carbon isotope effect consequences are as follows (extension of the arguments to reversible cases is straightforward):[2]

$$-\underset{\underset{\displaystyle X}{|}}{\overset{\overset{\displaystyle H}{|}}{\underset{\beta}{C}}}-\overset{\alpha}{C}- \xrightarrow{\ -\ H-X\ } \ \overset{\beta}{C}=\overset{\alpha}{C}\diagup$$

Isotope Effect Expectations

| Mechanism | $\alpha$C IE | $\beta$C IE |
|-----------|:---:|:---:|
| E1 | yes | no |
| E2 | yes | yes |
| Elcb | no | yes |

McLennan's research group has carried out extensive studies[6-10] of the mechanisms of base-promoted elimination of HCl from DDD-type compounds (1,1-dichloro-2,2-diarylethanes), and have concluded that the compounds react mainly by the E2 mechanism, with varying degrees of Elcb character, depending on the nature of the ring substituent, with the p-nitro compound

being at the Elcb limit. In particular, this last conclusion is based primarily on their intramolecular chlorine isotope effect data:[7,9] for ring substituents, $CH_3O-$, $H-$, $Cl-$, and $NO_2$; $^{35}k/^{37}k$ = 1.0038, 1.0035, 1.0023, and 1.0000 (all ± about 0.0002). The trend in the data, and the lack of a chlorine isotope effect for the p-nitro compound are claimed to be what would be expected[11] for an Elcb-like E2 mechanism changing over (at the p-nitro compound) to a limiting Elcb mechanism.

We have been searching for some time[4] for a convenient "Elcb calibration case" for our carbon-14 isotope effect studies of elimination reaction mechanisms, and it appeared that this p-nitro case might be it. One notes from the table above that an $^\alpha C$ isotope effect is to be expected for the E2 mechanism, but not for the Elcb mechanism. Accordingly, we have now measured the $^\alpha C$ isotope effects for the unsubstituted and p-nitro DDD-type compounds:

$$(Z-\underset{2}{\bigcirc}-)_2CH-^\alpha CHCl_2 \xrightarrow[-\ HCl]{base} (Z-\underset{2}{\bigcirc}-)_2C=^\alpha CHCl$$
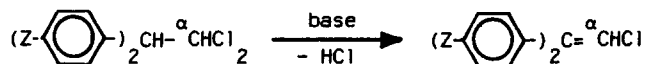
$$k/^\alpha k = 1.045 \pm 0.003 \text{ for } Z = H, \text{ and } 1.024 \pm 0.002 \text{ for } Z = NO_2$$

The carbon-14 labeled unsubstituted reactant was synthesized by relatively conventional means from commercially available sodium acetate-2-^{14}C through the acid chloride, acetophenone, dichloroacetophenone, and 2,2-dichloro-1-phenylethanol, followed by treatment with benzene and sulfuric acid. The nitro compound was prepared by nitration of the unsubstituted compound. Full details will be published later. The elimination reactions were carried out in $CH_3ONa/CH_3OH$ at 30 ($Z = NO_2$) or 60 ($Z = H$) °C using a limited amount of base to control the fraction of reaction, f. The recovered reactant and product alkene were separated by column chromatography and recrystallized to constant radioactivity. Radioactivities of the starting material, $R_o$, the recovered reactant, $R_r$, and the product alkene, $R_p$ were measured by liquid scintillation counting[12], and the kinetic isotope effects, $k/^\alpha k$, were calculated by the Tong and Yankwich equations[13]. The results for the critical p-nitro compound are presented in detail in **Table 1** below. Similar data (from 5 fractions of reaction) were obtained for the unsubstituted compound, and data for both compounds are summarized under the equation above.

Note that there are no trends in the data in the table as the fraction of reaction changes, or as the equation by which the calculation is made is changed. The same applies to the data for the unsubstituted compound. This gives us high confidence in the chemical and radiochemical purities of the starting materials and products and demonstrates that our reaction and workup procedures are adequate. Also, the activities of the starting materials agreed closely with the activities of the products at 100 % reaction, as they should.

Table 1. Fractions of Reaction, Molar Activities,[a] and Carbon-14 Kinetic Isotope Effects in the $CH_3ONa$-Promoted Dehydrochlorination of 1,1-Dichloro-2,2-di(4-nitrophenyl)ethane-1-^{14}C in Methanol at 30 °C.

| Fraction of Reaction f | $R_r$ mCi/mole | $R_p$ mCi/mole | $k/^{\alpha}k$ obtained from:[b] | | | |
|---|---|---|---|---|---|---|
| | | | $R_o$, $R_r$, $R_p$ | $R_o$, $R_r$, f | $R_o$, $R_p$, f | $R_r$, $R_p$, f |
| 0.30 | 0.28353 | 0.27597 | 1.0239 | 1.0188 | 1.0248 | 1.0230 |
| 0.50 | 0.28690 | 0.27729 | 1.0240 | 1.0273 | 1.0228 | 1.0250 |
| 0.70 | 0.28899 | 0.27765 | 1.0254 | 1.0218 | 1.0280 | 1.0237 |

[a] $R_o$ = 0.28167; [b] Overall mean: $k/^{\alpha}k$ = 1.0240 ± 0.0024 (standard deviation).

The lower $^{\alpha}C$ isotope effect for the p-nitro compound than for the unsubstituted one shows the expected trend as the reaction becomes more E1cb-like, but the fact that there is an $^{\alpha}C$ isotope effect at all shows that the E1cb limit has not been reached at the p-nitro compound-- it still reacts by an E1cb-like E2 mechanism. The expectations for the magnitude of the $^{\alpha}C$ isotope effect are difficult to analyze in a qualitative fashion, since both bond formation and bond rupture at the alpha carbon must necessarily be involved in an E2 activated complex. The isotope effect for the unsubstituted compound is similar in magnitude to those observed[4] in other E2 systems; that for the p-nitro compound is considerably smaller than average. Clearly the p-nitro group influences the reaction path by stabilizing both the alkene and the carbanion, making the activated complex more reactant-like and more carbanion-like, both of which result in reduced carbon-chlorine bond rupture, and thus a lower isotope effect.

One should consider the possibility of the observed $^{\alpha}C$ isotope effect being the result of isotopic fractionation in the second step of a reversible E1cb mechanism. Such a mechanism would be expected to have qualitative results similar to those of the E2 mechanism as far as the $^{\alpha}C$ (and $^{\beta}C$) isotope effects are concerned. To our knowledge, no exchange experiments have been carried out on the p-nitro compound (they have been carried out on the unsubstituted compound[8], and there is no exchange). However, there is indirect evidence that any exchange is slower than the elimination reaction, since it was possible to measure[8] a deuterium isotope effect for the p-nitro compound, and if exchange had been rapid, the deuterium would have been "washed out" and no deuterium isotope effect measurement would have been possible. Substantial reaction by a reversible E1cb mechanism is thus ruled out as the reason for there being an $^{\alpha}C$ isotope effect. Reversibility (internal return) too fast to show up in exchange experiments would probably lead to the same isotope effect consequences as the E2 mechanism. This becomes largely a semantics question in the absence of appropriate experimental evidence.

The chlorine isotope effect data do not really bear directly on the critical question of whether or not the mechanism for the p-nitro compound has reached the Elcb limit--one would expect there to be intramolecular isotope effects for both the E2 and Elcb mechanisms (see note 11). However, they do bear indirectly on it, since all the effects are so small, and since the one for the p-nitro compound is nil. The most obvious way for this to be true is for there to be very little carbon-chlorine bond rupture in the E2 activated complex, meaning that the basic E2 mechanism is always quite Elcb-like, and is taking on more Elcb character as the substituent becomes more electron withdrawing. A solvation leveling[14] effect may also be contributing to the low values of these chlorine isotope effects.

### References and Notes

1. The financial support of U.S. NSF Grant CHE-8314767 is gratefully acknowledged.

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11. It is our view that an **intramolecular** chlorine isotope effect would normally be expected even if the mechanism were limiting Elcb; the choice would be between elimination of $^{35}Cl^-$ and $^{37}Cl^-$ **from within the same molecule** from an irreversibly formed carbanion, and if that is an activated process, (and it must be by the mechanistic definition) isotopic discrimination should result. And for the E2 mechanism, of course, both intermolecular (not measured) and intramolecular isotope effects would be expected.

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(Received in USA 23 June 1986)