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Heavy Atom Isotope Effects in Elimination Reactions. An *ab initio* Study*

William H. Saunders Jr.

Department of Chemistry, University of Rochester, Rochester, New York 14627, USA
(E-mail: saunders@chem.rochester.edu)

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Heavy atom kinetic isotope effects (KIEs) in bimolecular elimination (E2) reactions, both *anti* and *syn*, were calculated for the leaving group (LG, $^{18}F/^{19}F$, $^{35}Cl/^{37}Cl$), the carbon attached to the leaving group (C-1, $^{12}C/^{13}C$), and the carbon bearing the proton removed in the reaction (C-2, $^{12}C/^{13}C$) by *ab initio* methods at the MP2/6-31+G*//MP2/6-31+G* level. The substrates examined were EtF, EtF solvated by one H_2O, and EtCl. The bases used were OH^-, OH^- solvated by one H_2O, LiOH, NaOH, F^-, and Cl^-. The KIEs found for each reaction were compared with bond orders calculated by the Pauling equation and changes in NPA charges from reactant to transition structure. Qualitative and semiquantitative but few truly quantitative correlations are found. Restricted subsets of the data (*e.g*, only *anti* eliminations of EtF) give best results, but even here the C-2 KIEs correlate poorly. LG KIEs correlate well with ΔQ(X) and n(CX), C-1 KIEs with n(CX) and n(CC) but with scatter, and C-2 KIEs with ΔQ(C-2) and n(CC) + n(CH) but with much scatter. The dependence of KIEs on transition structure appears too complex to be expressed well by simple relationships with bond orders and charge distributions.

Key words: E2, KIE, transition structure, bond order, charge, BEBOVIB method.

INTRODUCTION

Professor Ašperger collaborated with the present author on studies of sulfur isotope effects on the rates of elimination reactions of sulfonium salts.[1,2] Because this research was among the earliest utilizing heavy atom

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* Dedicated to Professor Smiljko Ašperger on the occasion of his 80th birthday.

isotope effects in eliminations, the calculations reported in the present paper seem appropriate for an issue honoring Professor Ašperger on the occasion of his 80th birthday.

Subsequent to the collaboration with Professor Ašperger, the present author studied heavy atom isotope effects in a number of elimination reactions, including more sulfur isotope effects,[3,4] nitrogen isotope effects,[5] and carbon isotope effects at the α and β positions relative to the leaving group.[3,4,6,7] Interpretation of such results at the time relied either on qualitative reasoning, or on calculations in which »mechanical« models were constructed possessing assumed geometries and with assumed force constants for stretching, bending, and torsional motions. The fundamental vibrational frequencies and isotope effects were calculated using the programs of Wolfsberg and Stern[8] or, later, the program of Sims, Burton, and Lewis.[9] These in turn are based on the isotope effect theory of Bigeleisen and Goeppert-Mayer.[10]

For comparison with experimental data the general procedure is to adopt a reasonable geometry for the transition state structure and then vary the force constants by means of assumed relationships with bond orders until the calculated values match the experimental. The name given to this approach is the BEBOVIB method because it assumes a relationship between bond energy and bond order. It is also possible to explore systematically the expected range of isotope effects for models ranging from reactant like to product like.[11,12] These procedures are rather laborious and possess the disadvantage that the number of parameters to be fixed substantially exceeds the number of experimental data. Consequently, one cannot be sure that a unique solution has been achieved.

Quantum chemical calculations are now sufficiently powerful that realistic results can be obtained on systems of modest size. The behavior of primary and secondary protium/deuterium isotope effects has been explored in a pioneering series of papers by Glad and Jensen.[13–15] No heavy atom (atoms heavier than the hydrogen isotopes) isotope effect calculations for elimination reactions have been reported except for a few for E1cB and E2 reactions by the present author.[16] The investigation reported here does not aim at a comparison of experimental and calculated kinetic isotope effects (KIEs), but rather an exploration of how calculated heavy-atom KIEs vary with bond orders and charge distributions in the transition structures.

COMPUTATIONAL METHODS

The calculations utilized Gaussian 94[17] and Gaussian 98.[18] The work utilized the standard basis set 6-31+G*. Correlation corrections utilized the Møller-Plesset method.[19–23] The enthalpies (ΔH) reported in the tables are corrected to constant pressure and for zero-point-energy differences from MP2/6-31+G*//MP2/6-31+G* calculations scaled to 0.95 to account for the overestimation of frequencies by Hartree-Fock methods.[24,25] The enthalpies were further corrected to 298 K for the contributions of the translational, rotational, and vibrational partition functions.[26] The vibrational contribution is not based on scaled frequencies, because inspection of numerous frequency calculations makes it doubtful that low-lying calculated frequencies (the only ones that contribute significantly to the vibrational partition functions) bear a predictable relation to experimental frequencies.[27] Isotope effects were calculated from vibrational frequencies, masses and moments of inertia by means of a program Iecalc[28] based on the Bigeleisen-Mayer equations for isotope effects.[10] Tunnel corrections are not included in any of the isotope effects.

RESULTS AND DISCUSSION

The substrates chosen were ethyl fluoride and ethyl chloride. Bases for both substrates were hydroxide, fluoride, and chloride ions, as well as lithium hydroxide and sodium hydroxide. A somewhat more extensive list of calculations was done on ethyl fluoride than on ethyl chloride, including hydration of the leaving fluoride by a single water molecule, and hydration of the attacking hydroxide ion by a single water molecule. Both *syn* and *anti* transition structures were calculated in each case. All calculations were done at the MP2/6-31+G*//MP2/6-31+G* level, which Glad and Jensen[13–15] found gave sensible results on the protium/deuterium KIEs.

The measures of transition state structure used for comparison with the KIEs were bond orders and charges, the latter calculated by the natural population analysis (NPA) method.[29,30] Bond orders were calculated from bond distances by the Pauling equation (Eq. 1).[31] A value of 0.3 for the constant a has been found to give a good

$$n = \exp((r^0 - r) / a) \qquad (1)$$

correlation between bond order and bond length for bonds in stable molecules.[32] The best value (or values) to use for bonds in transition structures is not entirely clear. Glad and Jensen use 0.25 for the C–C bond and follow a previous recommendation of 0.6 for the partial bonds.[33] It is quite possible that the »constant« does vary with bond length, especially for very weak bonds. In the absence of knowledge of the form of this variation, the value of 0.3 is used throughout in the present work. Relative values of the bond orders are, of course, not changed by changes in a, and relative values suffice for the purposes of this study.

A major consideration in choosing reactions for inclusion in the test set was to achieve as wide a variety of transition structures as possible. Table I lists barriers to reaction, ΔH_{TS}, and heats of reaction, ΔH, for all of the reactions examined. There is obviously a very wide range in both barrier height and heat of reaction. It should be noted that gas-phase ion-dipole reactions

TABLE I

Barriers (ΔH_{TS}) relative to separated reactants and heats of reaction (ΔH) in E2 reactions of ethyl halides in the gas phase

System	ΔH_{TS} kJ mol^{-1}	ΔH kJ mol^{-1}
$HO^- + C_2H_5F$ (*anti*)	–37.95	–146.11
$HO^- + C_2H_5F$ (*syn*)	–11.88	–146.11
$H_3O_2^- + C_2H_5F$ (*anti*)	11.25	–30.67
$H_3O_2^- + C_2H_5F$ (*syn*)	8.12	–30.67
$HO^- + C_2H_5F \cdot HOH$ (*anti*)	–69.41	–129.33
$HO^- + C_2H_5F \cdot HOH$ (*syn*)	–76.65	–129.33
$H_3O_2^- + C_2H_5F \cdot HOH$ (*anti*)	–25.02	–13.89
$H_3O_2^- + C_2H_5F \cdot HOH$ (*syn*)	–21.84	–13.89
$LiOH + C_2H_5F$ (*anti*)	105.06	–89.41
$LiOH + C_2H_5F$ (*syn*)	15.44	–89.41
$NaOH + C_2H_5F$ (*anti*)	76.07	–67.78
$NaOH + C_2H_5F$ (*syn*)	27.74	–67.78
$Cl^- + C_2H_5F$ (*anti*)	162.55	–36.15
$Cl^- + C_2H_5F$ (*syn*)	182.34	–36.15
$F^- + C_2H_5F$ (*anti*)	–147.86	60.08
$F^- + C_2H_5F$ (*syn*)	–105.9	60.08
$OH^- + C_2H_5Cl$ (*anti*)	–48.58	–211.17
$OH^- + C_2H_5Cl$ (*syn*)	–15.06	–211.17
$LiOH + C_2H_5Cl$ (*anti*)	106.86	–104.98
$LiOH + C_2H_5Cl$ (*syn*)	28.53	–104.98
$NaOH + C_2H_5Cl$ (*anti*)	76.65	–111.71
$NaOH + C_2H_5Cl$ (*syn*)	24.56	–111.71
$F^- + C_2H_5Cl$ (*anti*)	–176.19	–294.34
$F^- + C_2H_5Cl$ (*syn*)	–125.6	–294.34
$Cl^- + C_2H_5Cl$ (*anti*)	91.29	1.51
$Cl^- + C_2H_5Cl$ (*syn*)	138.24	1.51

first result in an ion-dipole complex that then passes over a central barrier. The barrier ΔH_{TS} is defined as the difference in enthalpy between reactants and the transition structure at the top of the barrier. The result of this definition is that ΔH_{TS} is negative in cases where the central barrier is below the separated reactants, a not uncommon situation in such reactions. When the barrier is defined with respect to the ion-dipole complex it is always positive, but it also contains an unpredictable contribution from the stability of the complex, which may depend in rather specific ways on the shapes and charge distributions of the components.

Although the geometric arrangements of the atoms in the transition structures is not a major focus of this investigation, some comment on the three-dimensional structures is worthwhile. Optimized *syn* and *anti* structures for the reaction of hydroxide ion and lithium hydroxide with ethyl fluoride previously reported[34] exemplify the important features of most of the transition structures in the present study. In the hydroxide ion reactions, the *anti* transition structure is coplanar, indicating developing p-orbital overlap between the two carbon atoms. In contrast, the *syn* transition structure is not coplanar. Apparently eclipsing effects cost more than any energy gained from overlap. The situation is the reverse with a metal hydroxide as base. The metal ion can coordinate with the leaving group as the hydroxide attacks the β-hydrogen, powerfully stabilizing the *syn* transition structure. The *anti* transition structure cannot enjoy such stabilization and is adversely affected by the weaker basicity of the hydroxide coordinated with the metal ion.

There remain the transition structures in which water molecules are coordinated with the base, the leaving group, or both. These are shown in structures **1–6**, Figure 1. In **1** and **2**, the water coordinated to the hydroxide seems mainly to act by weakening its base strength. In **3** and **4**, on the other hand, the water aids the departure of the leaving group. **3** is a conformer of **1**, but the cyclic arrangement in **3** provides only a few kJ stabilization compared to **1**. Water is coordinated to both the base and the leaving group in the *syn* and *anti* transition structures **5** and **6**. The *syn* transition structure **5** seems to be somewhat stabilized by a cyclic arrangement analogous to that in **3**, though the cycle is folded and the hydrogen bond connecting the two water molecules is longer in **5** than in **3**.

Bond orders are listed in Table II and the difference in charge between each heavy atom and the corresponding atom in the reactant ethyl halide in Table III. The minimum and maximum values of each of these parameters are listed in Table IV. It is obvious that the range in each case is wide enough that a really meaningful range of transition structures has been achieved, as one would expect from the wide range of thermodynamic quantities listed in Table I.

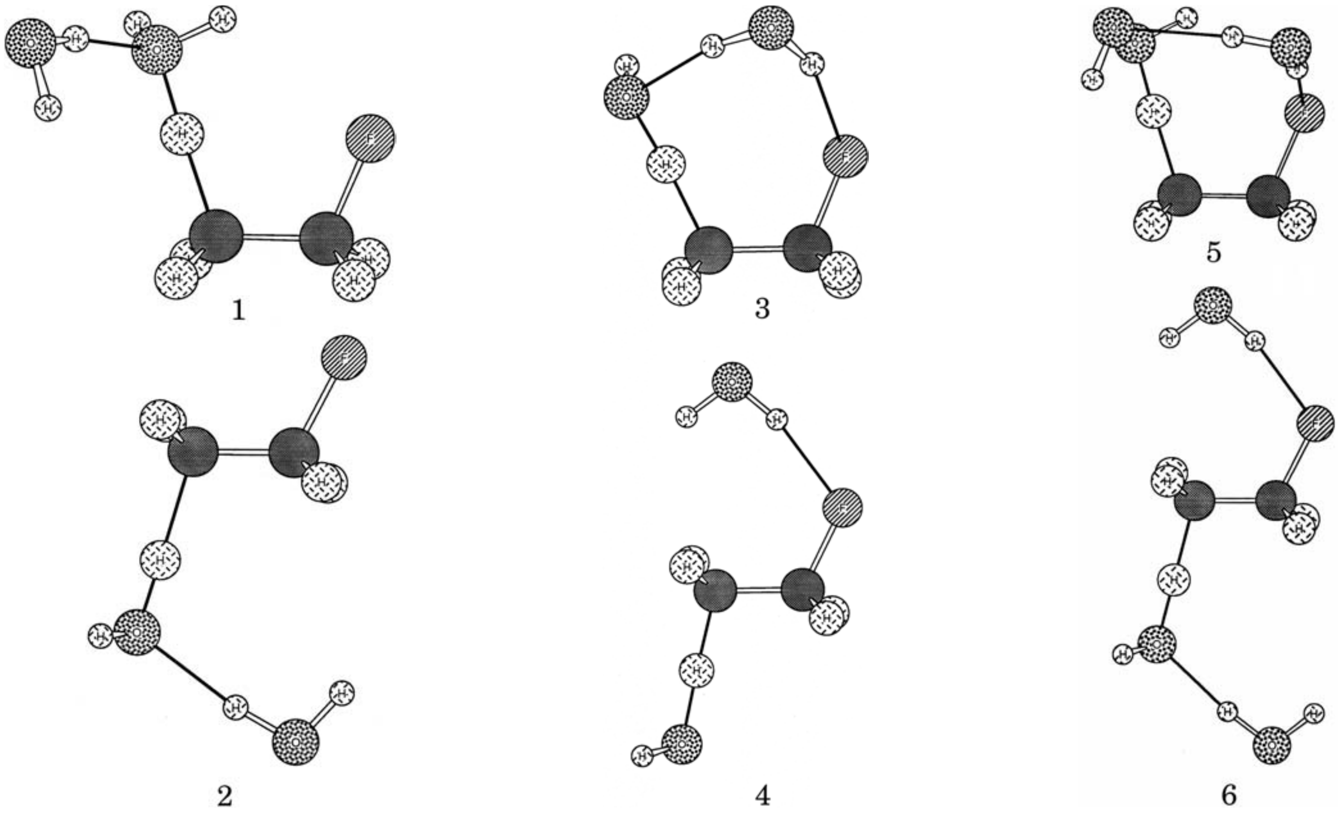

Figure 1. Transition structures (**1–6**) in which water molecules are coordinated with the base, the leaving groups or both.

TABLE II

Bond orders of transition structure bonds in E2 reactions of ethyl halides

LG, base, stereoch.	n(C–X)	n(C–C)	n(C–H)
F^-, OH^-, *anti*	0.710	1.178	0.304
F^-, OH^-, *syn*	0.819	1.088	0.407
F^-, $H_3O_2^-$, *anti*	0.631	1.235	0.157
F^-, $H_3O_2^-$, *syn*	0.752	1.133	0.291
$FHOH^-$, OH^-, *anti*	0.669	1.187	0.389
$FHOH^-$, OH^-, *syn*	0.742	1.137	0.286
$FHOH^-$, $H_3O_2^-$, *anti*	0.619	1.227	0.277
$FHOH^-$, $H_3O_2^-$, *syn*	0.691	1.163	0.282
F^-, LiOH, *anti*	0.894	1.069	0.137
F^-, LiOH, *syn*	0.313	1.350	0.385
F^-, NaOH, *anti*	0.865	1.088	0.125
F^-, NaOH, *syn*	0.386	1.294	0.398
F^-, Cl^-, *anti*	0.087	1.626	0.078
F^-, Cl^-, *syn*	0.256	1.502	0.095
F^-, F^-, *anti*	0.148	1.569	0.092
F^-, F^-, *syn*	0.377	1.424	0.094
Cl^-, OH^-, *anti*	0.562	1.230	0.412
Cl^-, OH^-, *syn*	0.702	1.129	0.342
Cl^-, LiOH, *anti*	0.838	1.072	0.136
Cl^-, LiOH, *syn*	0.216	1.378	0.516
Cl^-, NaOH, *anti*	0.789	1.100	0.129
Cl^-, NaOH, *syn*	0.277	1.345	0.480
Cl^-, Cl^-, *anti*	0.098	1.586	0.263
Cl^-, Cl^-, *syn*	0.143	1.506	0.326
Cl^-, F^-, *anti*	0.341	1.367	0.323
Cl^-, F^-, *syn*	0.431	1.295	0.273

The calculated KIEs are listed in Table V. Before proceeding to a more quantitative discussion it is worthwhile to point out a few regularities. The leaving group KIE is larger for *anti* than for *syn* eliminations in all cases where the barrier to *syn* elimination is higher. The *syn* elimination barrier is lower for the reactions with LiOH and NaOH, and here the leaving group

TABLE III

Changes in NPA charges[a] (TS – reactant) in E2 reactions of ethyl halides

LG, base, stereoch.	ΔQ(X)	ΔQ(C-1)	ΔQ(C-2)
F^-, OH^-, *anti*	–0.0987	–0.0182	–0.2174
F^-, OH^-, *syn*	–0.0623	–0.0069	–0.2304
F^-, $H_3O_2^-$, *anti*	–0.1214	0.4653	–0.2316
F^-, $H_3O_2^-$, *syn*	–0.0957	0.4692	–0.2682
$FHOH^-$, OH^-, *anti*	–0.1068	0.4797	–0.2010
$FHOH^-$, OH^-, *syn*	–0.0823	0.4748	–0.2648
$FHOH^-$, $H_3O_2^-$, *anti*	–0.1214	0.4653	–0.2316
$FHOH^-$, $H_3O_2^-$, *syn*	–0.0957	0.4692	–0.2682
F^-, LiOH, *anti*	–0.0346	–0.0127	–0.4072
F^-, LiOH, *syn*	–0.2720	0.0022	–0.2443
F^-, NaOH, *anti*	–0.0444	–0.0234	–0.3725
F^-, NaOH, *syn*	–0.2236	0.0039	–0.2404
F^-, Cl^-, *anti*	–0.4431	0.3049	–0.0365
F^-, Cl^-, *syn*	–0.3016	0.3634	–0.2001
F^-, F^-, *anti*	–0.3876	0.3390	–0.113
F^-, F^-, *syn*	–0.2289	0.3919	–0.2834
Cl^-, OH^-, *anti*	–0.2710	0.1403	–0.1806
Cl^-, OH^-, *syn*	–0.1754	0.0988	–0.2380
Cl^-, LiOH, *anti*	–0.0884	0.0378	–0.4036
Cl^-, LiOH, *syn*	–0.5129	0.3451	–0.2344
Cl^-, NaOH, *anti*	–0.1175	0.0471	–0.3624
Cl^-, NaOH, *syn*	–0.4746	0.2998	–0.2356
Cl^-, Cl^-, *anti*	–0.7026	0.3157	–0.1062
Cl^-, Cl^-, *syn*	–0.6148	0.3024	–0.2027
Cl^-, F^-, *anti*	–0.4313	0.2221	–0.2014
Cl^-, F^-, *syn*	–0.3360	0.1756	–0.2876

[a] Calculated by the natural population analysis (NPA) method.

KIE is smaller for the *anti* elimination. The reason that the *syn* elimination is easier in these cases is that the metal ion can assist the departure of the leaving group as the hydroxide attacks the β-hydrogen.[34] The KIE at C-2 is usually larger for the *syn* than for the *anti* reactions, again except for the LiOH and NaOH reactions. Thus the more difficult reaction is also the less

TABLE IV

Ranges of the bond orders and charge differences in the E2 transition structures

Quantity	Minimum	Maximum
n(CF)	0.09	0.89
n(CCl)	0.10	0.84
n(CC)	1.07	1.63
n(CH)	0.08	0.52
ΔQ(F)	–0.44	–0.03
ΔQ(Cl)	–0.70	–0.09
ΔQ(C-1)	–0.02	0.48
ΔQ(C-2)	–0.41	–0.11

concerted one. There is little apparent regularity in the KIE at C-1, except that the reactions with halide ion as base give unusually large KIEs.

The most important question to be addressed by this study is whether there is any quantitative correlation between the KIEs and the chosen measures of structure. There is no good reason to expect any particular form for such a correlation, so linear least squares plots were chosen to test the goodness of fit. A very large number of plots were done, too many to fit within an article of reasonable size, so the main summary of the results is given in Table VI, where the square of the correlation coefficient (R) and slope of the plot are listed as the most important parameters. The data are grouped as follows. First are given the correlations including all of the ethyl fluoride reactions, then correlations including only the *anti* and then only the *syn* reactions of ethyl fluoride. Finally the correlations including all of the ethyl chloride reactions are given. The degree of fit in the entire set of correlations ranges from fairly good at one end to scatter plots at the other. In order to keep the Table to reasonable length, only those plots with $R^2 > 0.5$ ($R > 0.71$) are listed except where no correlation meets this criterion. In those two cases the best correlations are listed.

It is evident that few of the correlations are as good as one would expect for a typical linear free energy relationship. The best set of correlations is that for the *anti* eliminations of ethyl fluoride. Even here the KIEs at C-2 do not correlate really well with any parameter. The most successful correlations overall are those of the leaving group isotope effects with ΔQ(X) and n(CX). The correlations of the KIEs at C-1 with n(CX) and n(CC) show more scatter, and the KIEs at C-2 correlate with few parameters and with even fewer of those reasonably well. It should be emphasized again that correlations not listed all have R^2 values below 0.5, some of them far below. It is

TABLE V

Rate constant ratios in E2 reactions of ethyl halides at 20 °C calculated at MP2/6-31+G*//MP2/6-31+G*

LG, base, stereoch.	$k(^{12}C) / k(^{13}C)$		
	LG	1-^{13}C	2-^{13}C
F^-, OH^-, *anti*	1.00883	1.01814	1.01882
F^-, OH^-, *syn*	1.00563	1.01505	1.02127
F^-, $H_3O_2^-$, *anti*	1.01941	1.02621	1.02926
F^-, $H_3O_2^-$, *syn*	1.00731	1.01862	1.02353
$FHOH^-$, OH^-, *anti*	1.00839	1.01699	1.01571
$FHOH^-$, OH^-, *syn*	1.00700	1.01723	1.02365
$FHOH^-$, $H_3O_2^-$, *anti*	1.00983	1.02069	1.01858
$FHOH^-$, $H_3O_2^-$, *syn*	1.00776	1.01919	1.02329
F^-, LiOH, *anti*	1.00384	1.00988	1.03134
F^-, LiOH, *syn*	1.01168	1.02547	1.01497
F^-, NaOH, *anti*	1.00521	1.01339	1.03735
F^-, NaOH, *syn*	1.01143	1.01185	1.01680
F^-, Cl^-, *anti*	1.03783	1.06028	1.01764
F^-, Cl^-, *syn*	1.02321	1.04402	1.04584
F^-, F^-, *anti*	1.03669	1.06635	1.01741
F^-, F^-, *syn*	1.02477	1.04096	1.06036
Cl^-, OH^-, *anti*	1.00457	1.01693	1.01399
Cl^-, OH^-, *syn*	1.00341	1.01635	1.02185
Cl^-, LiOH, *anti*	1.00230	1.01098	1.03189
Cl^-, LiOH, *syn*	1.00443	1.01596	1.01334
Cl^-, NaOH, *anti*	1.00336	1.01512	1.03640
Cl^-, NaOH, *syn*	1.00460	1.01699	1.01508
Cl^-, Cl^-, *anti*	1.00764	1.04188	1.01138
Cl^-, Cl^-, *syn*	1.00693	1.04270	1.01603
Cl^-, F^-, *anti*	1.00625	1.04871	1.01531
Cl^-, F^-, *syn*	1.00623	1.04304	1.03257

clear that no quantitative correlations can be expected except with a limited range of reactions such as the *anti* reactions of ethyl fluoride, and even in these cases some correlations show significant scatter. The KIEs evidently

TABLE VI

Linear least squares correlations of KIE[a] with various parameters

Isotope, site	Parameter	R^2	Slope
$^{18}F/^{19}F$, all RF	$\Delta Q(F)$	0.823	–7.91
$^{18}F/^{19}F$, all RF	$n(CF)$	0.769	–3.68
$^{18}F/^{19}F$, all RF	$n(CC)$	0.892	5.80
1-$^{12}C/^{13}C$, all RF	$n(CF)$	0.721	–5.62
1-$^{12}C/^{13}C$, all RF	$n(CC)$	0.861	8.98
2-$^{12}C/^{13}C$, all RF	$n(CH)$	0.357	–6.05
$^{18}F/^{19}F$, *anti* RF	$\Delta Q(F)$	0.944	–8.59
$^{18}F/^{19}F$, *anti* RF	$n(CF)$	0.943	–4.43
$^{18}F/^{19}F$, *anti* RF	$n(CC)$	0.959	6.43
$^{18}F/^{19}F$, *anti* RF	$n(CC)+n(CF)$	0.877	–13.75
1-$^{12}C/^{13}C$, *anti* RF	$n(CF)$	0.953	–7.04
1-$^{12}C/^{13}C$, *anti* RF	$n(CC)$	0.966	10.21
1-$^{12}C/^{13}C$, *anti* RF	$n(CC)+n(CF)$	0.893	–21.95
2-$^{12}C/^{13}C$, *anti* RF	$\Delta Q(C\text{-}2)$	0.626	–5.29
2-$^{12}C/^{13}C$, *anti* RF	$n(CC)+n(CH)$	0.820	–3.94
$^{18}F/^{19}F$, *syn* RF	$\Delta Q(F)$	0.616	–6.14
$^{18}F/^{19}F$, *syn* RF	$n(CF)$	0.626	–2.58
$^{18}F/^{19}F$, *syn* RF	$n(CC)$	0.860	4.53
1-$^{12}C/^{13}C$, *syn* RF	$n(CC)$	0.704	6.59
2-$^{12}C/^{13}C$, *syn* RF	$\Delta Q(C\text{-}2)$	0.684	40.43
2-$^{12}C/^{13}C$, *syn* RF	$n(CH)$	0.864	–11.76
$^{35}Cl/^{37}Cl$, all RCl	$\Delta Q(Cl)$	0.747	–0.74
$^{35}Cl/^{37}Cl$, all RCl	$n(CCl)$	0.742	–0.59
1-$^{12}C/^{13}C$, all RCl	$n(CC)$	0.486	6.13
2-$^{12}C/^{13}C$, all RCl	$\Delta Q(C\text{-}2)$	0.770	–9.40
2-$^{12}C/^{13}C$, all RCl	$n(CC)$	0.515	–3.92
2-$^{12}C/^{13}C$, all RCl	$n(CH)$	0.558	–5.42
2-$^{12}C/^{13}C$, all RCl	$n(CC)+n(CH)$	0.759	–3.24

[a] $((k_L / k_H) - 1) \times 100$.

depend on structure in ways that cannot be quantitatively expressed in simple relationships with bond orders or charge distributions.

The picture is brighter for qualitative relationships. Examination of the last column of Table VI shows a number of useful regularities. The leaving group KIE increases as the charge on the leaving group increases and as n(CX) decreases. The KIE at C-1 increases as n(CX) decreases and as n(CC) increases. The least useful of the heavy atom KIEs is that at C-2, though even it shows some qualitative regularities. It goes up in most cases as the charge on C-2 becomes more negative and down as n(CC) + n(CH) goes up. These are all intuitively reasonable trends even where they are not quantitative.

The present results point up a potential pitfall in BEBOVIB calculations, that what appear to be perfectly reasonable transition structures may not be chosen by real systems. For example, none of these reactions shows an n(CH) value larger than 0.52, though possibly such values could be attained with better leaving groups. The result is that all of the C-2 KIE values are normal (light faster than heavy), whereas BEBOVIB calculations predict inverse C-2 KIEs for reactant-like transition structures (n(CH) values larger than 0.5) in the absence of tunneling.[11,12]

In order to provide visual impressions of the results, selected correlations are displayed graphically in Figures 2–7. In Figure 2 the fluorine KIE is plotted against ΔQ(F) and in Figure 3 the carbon KIE at C-1 is plotted against n(CC). Some of the measures of structure correlate with each other; n(CF) correlates very well with n(CC) (Figure 4), and ΔQ(F) correlates well with n(CF) (not shown). Interestingly, a plot of n(CC) *vs*. n(CH) shows no significant correlation; it is essentially a scatter plot. Most of the transition structures in this study can best be characterized as carbanion like, so it is not possible to predict whether this lack of correlation would be true for all E2 reactions.

The first three figures show plots that are among the best found in any of the reactions. Figure 5 provides an example of a poorer correlation, that of the carbon KIE at C-2 with n(CC) + n(CH), which is actually one of the more successful correlations of C-2 KIEs with any of the parameters. Efforts to find good plots of a wider range of KIEs against various parameters meet with distinctly limited success. Figures 6 and 7 show the results when all of the ethyl fluoride reactions, both *anti* and *syn*, are included in the plots. The correlations would be improved if the *syn* eliminations promoted by LiOH and NaOH were removed from the data set (both fall well below the lines in both plots), but significant scatter still remains. Plots of the ethyl chloride data show similar scatter. The figures taken as a whole reinforce the point made earlier, that only within a restricted range of reactions can quantitative correlations of KIEs with bond orders or charge distributions be expected.

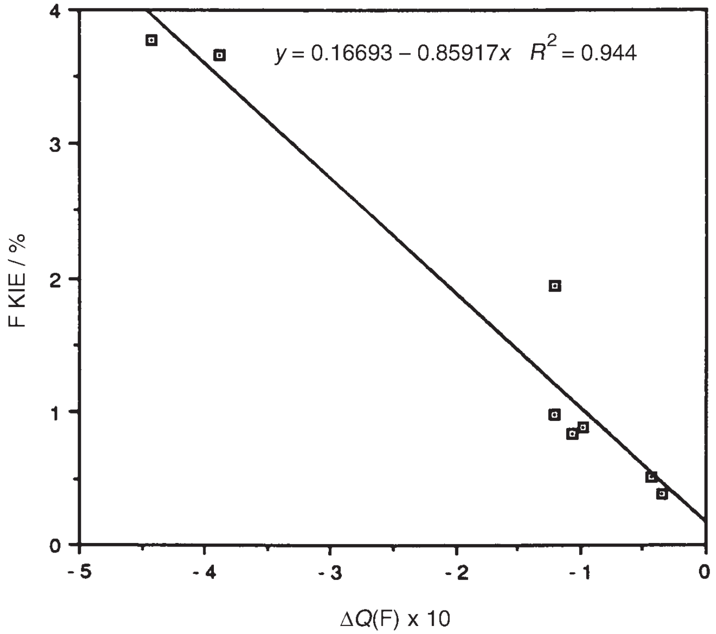

Figure 2. ^{18}F/^{19}F KIE *vs.* Δ*Q*(F) for *anti* EtF eliminations.

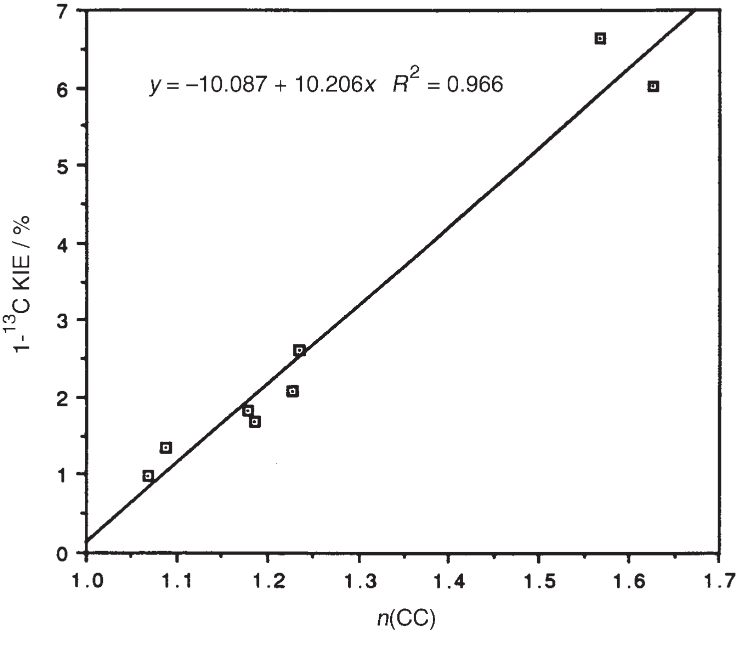

Figure 3. 1-^{12}C/^{13}C KIE *vs.* *n*(CC) for *anti* EtF eliminations.

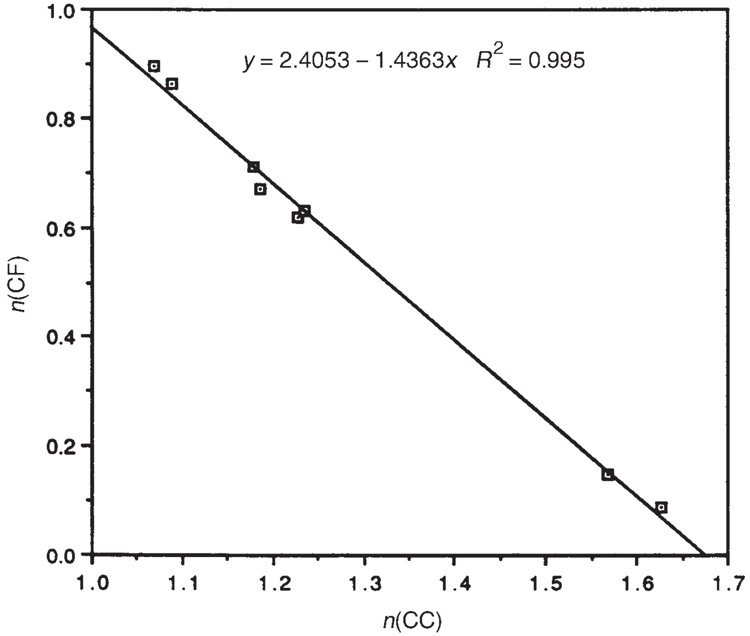

Figure 4. n(CF) *vs.* n(CC) for *anti* EtF eliminations.

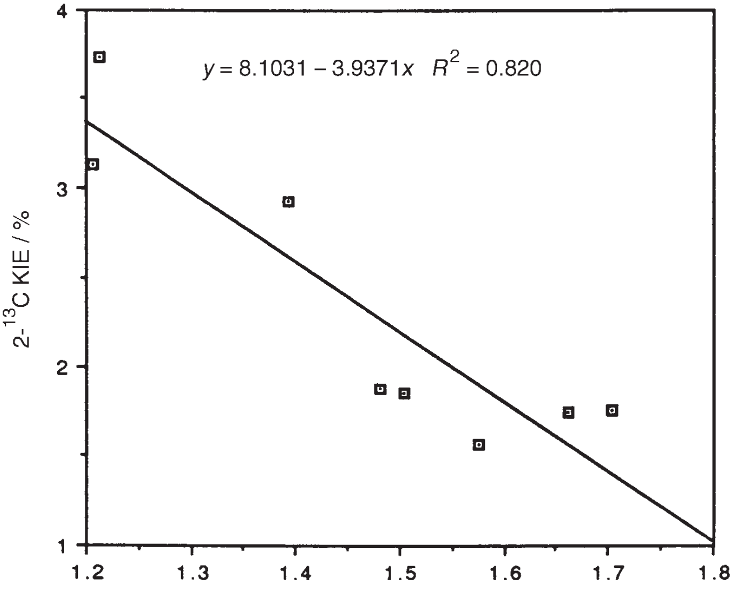

Figure 5. 2-^{12}C/^{13}C KIE *vs.* n(CC) + n(CH) for *anti* EtF eliminations.

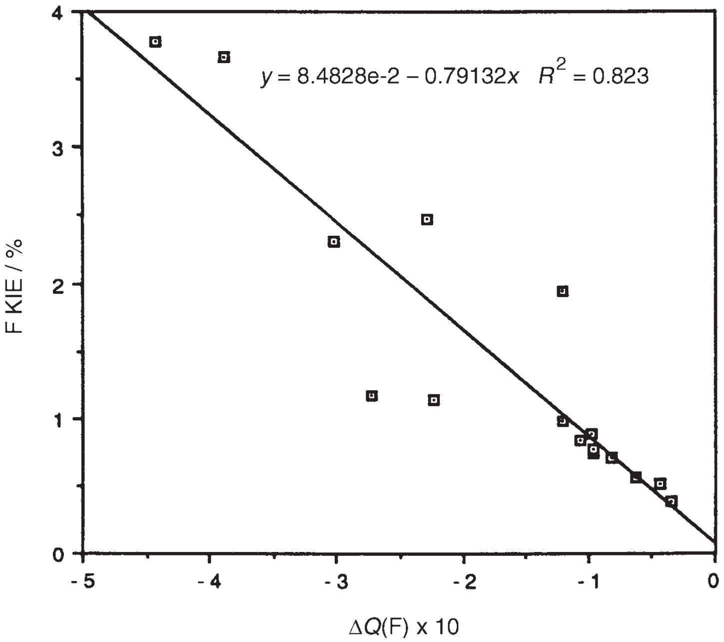

Figure 6. ^{18}F/^{19}F KIE *vs.* ΔQ(F) for all EtF eliminations.

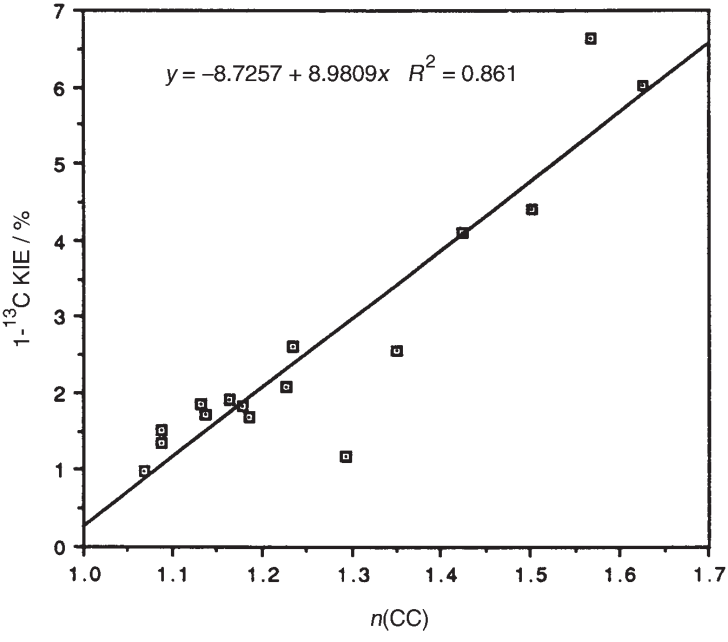

Figure 7. 1-^{12}C/^{13}C KIE *vs.* n(CC) for all EtF eliminations.

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SAŽETAK

Izotopski efekt teškog atoma u eliminacijskim reakcijama. *Ab initio* studija

William H. Saunders Jr.

Kinetički izotopski efekti (KIE) teškog atoma u bimolekularnim *syn-* i *anti-*eliminacijskim (E2) reakcijama izračunani su *ab initio* metodama na MP2/6-31+G*//MP2/6-31+G* razini za odlazeću skupinu (OS, ^{18}F/^{19}F, ^{35}Cl/^{37}Cl), za ugljik vezan na odlazeću skupinu (C-1, ^{12}C/^{13}C) i za ugljik koji nosi proton uklonjen u reakciji (C-2, ^{12}C/^{13}C). Ispitivani supstrati bili su EtF, EtF solvatiran s jednom molekulom H_2O i EtCl. Korištene baze bile su OH^-, OH^- solvatiran jednom H_2O, LiOH, NaOH, F^- i Cl^-. Nađeni KIE za svaku reakciju uspoređeni su s redom veze izračunanim Paulingovom jednadžbom i promjenama naboja NPA na putu od reaktanta do strukture prijelaznog stanja. Nađene su kvalitativne i polukvantitativne, ali rijetko stvarno kvantitativne korelacije. Ograničeni podskupovi podataka (npr. samo *anti*-eliminacije EtF) daju najbolje rezultate, ali i ovdje C-2 KIE koreliraju slabo. OS KIE koreliraju dobro s ΔQ(X) i n(CX), C-1 KIE s n(CX) i n(CC) ali uz rasipanje, a C-2 KIE s ΔQ(C-2) i n(CC) + n(CH) ali uz jako rasipanje. Ovisnost KIE o prijelaznoj strukturi čini se presloženom da bi se mogla dobro izraziti jednostavnim relacijama s redovima veze i raspodjelom naboja.