are primarily due to other differences in the conformational requirements of the various cyclic transition states. For the cases of 1–3 and 1–4 H-transfers the necessary distortions of the C–H–C angle are sufficient to provide the major impediment to the reaction.

Acknowledgment. This work was supported in part by a BHE-PSC grant.

Registry No. $^\bullet CH_2CH_2CH_3$, 2143-61-5; $^\bullet CH_2(CH_2)_2CH_3$, 2492-36-6; $^\bullet CH_2(CH_2)_3CH_3$, 2672-01-7; $^\bullet CH_2(CH_2)_4CH_3$, 2679-29-0; $^\bullet CH_2(CH_2)_5CH_3$, 3356-67-0; $^\bullet CH_2(CH_2(_6CH_3$, 4606-96-6; $^\bullet CH_2(CH_2)_7CH_3$, 32757-65-6; $^\bullet CH_2CH_2CH(CH_3)(CH_2)_5CH_3$, 134848-03-6; $^\bullet CH_2(CH_2)_2CH(CH_3)(CH_2)_4CH_3$, 134848-04-7; $^\bullet CH_2 \rightleftarrows CH_2(CH_2)_3CH(CH_3)(CH_2)_3CH_3$, 65388-48-9; $^\bullet CH_2(CH_2)_4CH(CH_3)(CH_2)_2CH_3$, 134848-05-8; $^\bullet CH_2(CH_2)_5CH(CH_3)CH_2CH_3$, 134848-06-9; $^\bullet CH_2(CH_2)_6CH(CH_3)_2$, 134848-07-0.

Supplementary Material Available: Drawings and archive files for each of the 24 transition states optimized. They are organized in the following manner: drawing followed by archive files for each structure of type a (Figure 1) in order of increasing size; idem for type b and type c (36 pages). Ordering information is given on any current masthead page.

Calculated Double-Bond Stabilization by Bromine and Chlorine. Relevance to the k_{Br}/k_{Cl} Element Effect[†]

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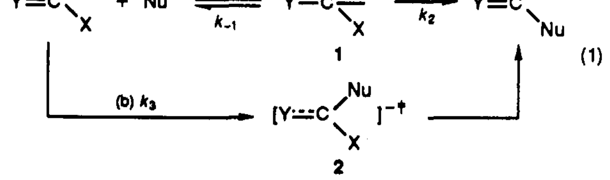
Received April 1, 1991

The relative stabilization of a carbon–carbon double bond by Cl and Br was obtained by ab initio MO calculations. The results at the MP2//RHF/CEP-21G* level corrected for differences in zero-point energy show that stabilization by Cl exceeds that by Br by ca. 1.3 kcal mol^{-1}. Consequences related to the use of k_{Br}/k_{Cl} ratios as mechanistic probes in vinylic substitution are discussed.

The halogen isotope effects $k(^{35}Cl)/k(^{37}Cl)$ or $k(^{79}Br)/k(^{81}Br)$ should serve as a powerful mechanistic tool for investigating the extent of cleavage of a bond to a leaving group in the transition state. In practice, however, the experimental difficulties associated with the accurate measurement of such small effects resulted in the application of the chlorine isotope effect in only a few cases.[1]

A substitute for a halogen isotope effect is the "element effect",[2] where the rate constants of two systems bearing different nucleofuges are compared. In order to be of mechanistic value, the nucleofuges compared in the element effect should resemble one another as much as possible. Hence, comparison between Cl and Br derivatives is frequently made. Heterolytic C–Br bond dissociation energies in alkyl bromides are several kcal mol^{-1} lower than the corresponding values for C–Cl,[3] and hence the k_{Br}/k_{Cl} ratios are expected to be >1 when the C–X bond is cleaved in the transition state of the rate-determining step.

Consequently, the element effect is a most valuable probe in an "all or nothing" situation, which occurs when the halogen is attached to an unsaturated center. As demonstrated in eq 1, the substitution of an aromatic, a vinyl, an acyl, or an imidoyl halogen (Y = C, O, NR) can proceed in a two-step mechanism via the negatively charged intermediate 1 (route a) where either k_1 or k_2 is rate limiting, or it can proceed via the concerted route b, where 2 is a transition state.



Bunnett introduced the use of the "element effect" in the study of nucleophilic aromatic substitution.[2] A comparative study of the reactivity of aryl chlorides and bromides resulted in k_{Br}/k_{Cl} ratios that were close to unity.[2,4] Based on the assumption that the electronic effects of Cl and Br are similar, this observation provides a strong evidence for the intermediacy of the anionic σ-Meisenheimer complexes (route a) with k_1 being rate determining in S_NAr reactions.

The k_{Br}/k_{Cl} element effect is also frequently used in nucleophilic vinylic substitution reactions where its value is around, or slightly higher than, unity for systems of largely different activation.[5] Again, this observation is considered to be the strongest evidence for the multistep nature of these reactions (i.e., eq 1, route a, Y = C).[6]

[†] Dedicated to Professor Joseph F. Bunnett on the occasion of his 70th birthday.

[1] E.g.: (a) Grout, A.; McLennan, D. J.; Spackman, I. H. *J. Chem. Soc., Chem. Commun.* **1976**, 775. (b) *J. Chem. Soc., Perkin Trans. 2* **1977**, 1758. (c) Koch, H. F.; McLennan, D. J.; Koch, J. G.; Tumas, W.; Dobson, B.; Koch, N. H. *J. Am. Chem. Soc.* **1983**, *105*, 1930.

[2] Bunnett, J. F.; Garbisch, E. W., Jr.; Pruitt, K. M. *J. Am. Chem. Soc.* **1957**, *79*, 385.

[3] Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 5th ed.; Allyn and Bacon: Boston, 1987; p 22.

[4] Miller, J. *Aromatic Nucleophilic Substitution*; Elsevier: London, 1968.

[5] (a) First systems investigated: Campagni, A.; Modena, G.; Todesco, P. E. *Gazz. Chim. Ital.* **1960**, *50*, 694. (b) Reviews of many values: Rappoport, Z. *Adv. Phys. Org. Chem.* **1969**, *7*, 1. (c) Modena, G. *Acc. Chem. Res.* **1971**, *4*, 73. (d) Rappoport, Z. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 309. (e) Rappoport, Z.; Topol, A. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1823. (f) Rappoport, Z.; Rav-Acha, C. *Tetrahedron Lett.* **1984**, *25*, 117.

0022-3263/91/1956-5424$02.50/0

Table I. Calculated Total Electronic Energies at the RHF/CEP-21G* and MP2//RHF/CEP-21G* Levels (au) and STO-3G Zero-Point Energies (kcal mol^{-1})

	CH_3Cl	CH_3Br	$CH_2{=}CHCl$	$CH_2{=}CHBr$	$CH_2{=}CH_2$	CH_4
RHF	-21.8526	-20.3108	-27.2846	-25.7407	-13.2064	-7.7779
MP2//RHF	-22.0678	-20.5138	-27.5746	-26.0185	-13.3699	-7.8706
ZPE	28.03	27.87	31.29	31.15	37.67	33.91

However, the quote "the element effect is the poor man's isotope effect"[7] reflects the feeling that this probe is not without flaws. One problem is the difficulty to distinguish between route a and route b having an early transition state involving only a slight C–X bond cleavage.[8] Another deficiency relates to the different extent of solvation of incipient Cl^- and Br^- in the transition state.[9] Steric effects that seem to be important in nucleophilic vinylic substitution will also reduce the k_{Br}/k_{Cl} ratio.[10,11] In this paper we will address the basic assumption of the near identity of the overall electronic effects of the halogens in the ground state. This assumption, which is essential to the interpretation of the k_{Br}/k_{Cl} element effect, is supported by the fact that σ_m, σ_p, σ_I, and σ_R values are almost the same, although not identical, for Br and Cl.[12]

Hine and co-workers[13] had evaluated the stabilization of a double bond by various substituents attached to it from the equilibrium data for the isomerization reaction 2 corrected for the allylic interaction. When X = halogen

$$trans\text{-}XCH_2CH{=}CHY \overset{K}{\rightleftharpoons} trans\text{-}XCH{=}CHCH_2Y \qquad (2)$$

this gives the stabilization of the double bond by a halogen. Contrary to the aforementioned assumption, they found that Cl stabilizes a double bond more than Br by 1.5 kcal mol^{-1} at 25 °C. However, this conclusion is based only on a single value for Br and Cl, taken from the gas-phase isomerization data of Abell and Adolph[14] for allyl halides (i.e., when Y = H). The only other relevant data that we were able to find are from Taskinen and Sainio's work[15] on the isomerization of the α-haloethyl vinyl ethers 3 to (E)-β-halovinyl ethers 4 (eq 3). The $\Delta G°$, $\Delta H°$, and $\Delta S°$

3 4 (3)

values for the 3 ⇌ 4 isomerizations are −0.12 and −0.46 kcal mol^{-1} and −1.2 cal K^{-1} mol^{-1} for X = Cl and 0.9 and 0.33 kcal mol^{-1} and −1.9 cal K^{-1} mol^{-1} for X = Br. Thus, although chlorine is still more stabilizing than bromine, the differences between them are smaller than in the absence of the β-ethoxy group.[16]

Chart I. RHF/CEP-21G* Geometries

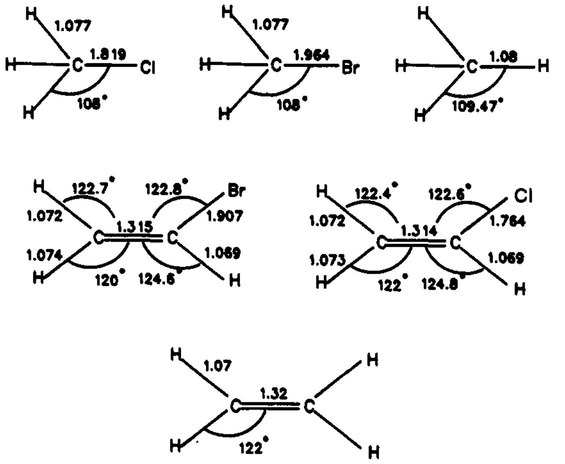


Table II. Energies (kcal mol^{-1})^a of the Isodesmic Reaction of eq 4 at Various Levels of Calculations

		MP2//RHF/CEP-21G*	
X	RHF/CEP-21G*	no ZPE	ZPE^b
Cl	2.1 (0.00347)	4.7 (0.00749)	5.2 (0.00829)
Br	0.9 (0.00143)	3.3 (0.00529)	3.8 (0.00606)

^{a} Values in au in parentheses. ^{b} Corrected by adding 90% of the STO-3G calculated ZPE to the MP2//RHF/CEP-21G* calculated energies.

These results prompted us to calculate the double-bond stabilizing effect of the two halogens by ab initio calculations. In the isodesmic reaction of eq 4, the stabilization of the double bond by the halogen is measured relative to that of CH_3X. The optimal geometries of the species in

$$H_2C{=}CH_2 + CH_3X \rightleftharpoons H_2C{=}CHX + CH_4 \qquad (4)$$
$$(X = Cl, Br)$$

eq 4 were calculated ab initio with the restricted Hartree–Fock (RHF) self-consistent field method in a CEP-21G* basis set.[17–19] Single-point energies were calculated at the MP2 level using the RHF optimized geometries. Zero-point energies (ZPE) were obtained from frequency calculations using STO-3G optimized geometries. All calculations were performed with GAUSSIAN 88.[20] The total electronic energies calculated for the species in eq 4 are given in Table I and the geometries are depicted in Chart I. The energies of the isodesmic reactions at the two (RHF and MP2) levels of computation are given in the first two columns of Table II. The data in the third column of

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(6) Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7.

(7) Koch, H. F. ESOR II, Padova, Italy, Sept. 1989, Abs. p 64, lecture C-1.

(8) For references, see: Avramovitch, B.; Weyerstahl, P.; Rappoport, Z. *J. Am. Chem. Soc.* **1987**, *109*, 6687.

(9) Bird, R.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans 2*, **1973**, 1221.

(10) Bernasconi, C. F.; Fassberg, J.; Killion, R. B., Jr.; Rappoport, Z. *J. Am. Chem. Soc.* **1991**, *113*, 4937.

(11) However, comparison of the solid-state geometries of p-$MeC_6H_4C(X){=}C(CO_2Me)_2$, X = Cl, Br, had shown that the steric effect in this system is small. (Rappoport, Z.; Gazit, A. *J. Org. Chem.* **1986**, *51*, 4107).

(12) Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; Chapter 10, p 439.

(13) (a) Hine, J.; Flackskam, N. W. *J. Am. Chem. Soc.* **1973**, *95*, 1179. (b) Hine, J.; Skoglund, M. J. *J. Org. Chem.* **1982**, *47*, 4766. (e) Hine, J. *Structural Effects on Equilibria in Organic Chemistry*; Wiley: New York, 1975; p 275.

(14) Abell, P. I.; Adolf, P. K. *J. Chem. Thermodyn.* **1969**, *1*, 333. See also Alfassi, Z. B.; Golden, D. M.; Benson, S. W. *J. Chem. Thermodyn.* **1973**, *5*, 411.

(15) Taskinen, E.; Sainio, E. *Tetrahedron* **1976**, *32*, 593.

(16) Interestingly, fluorine is 1.5 kcal mol^{-1} more stabilizing than Cl in eq 2, but less stabilizing by 1.8 kcal mol^{-1} in eq 3.

(17) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026.

(18) The compact effective potentials (CEP) for carbon and chlorine were taken from ref 17 and the relativistic CEP for the bromine atom from ref 19. Special CEP-21G atom basis sets were generated for the purpose of this work. The single Gaussian d-type polarization exponents on chlorine and bromine are 0.5140 and 0.3890, respectively.

(19) Stevens, W. J.; Jasien, P.; Krauss, M.; Basch, H., to be published.

(20) Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, A. GAUSSIAN Inc.; Pittsburgh, PA, 1988.

Table II were obtained by adding 90% of the ZPE to the MP2//RHF/CEP-21G* energies of the individual species.[21] As can be be seen from Table II, at all the levels of calculations examined, Cl stabilization of a vinylic moiety is larger than that of Br by ca. 1.3 kcal mol^{-1}.

The similarity between the observed 1.5 kcal mol^{-1} $\Delta G°$ value[13] and the calculated (isolated molecule) difference in double-bond stabilization energies by bromine and chlorine is remarkable. The important consequence of the greater double-bond stabilization by Cl is that the reactivity of the vinyl chloride may be reduced by up to ca. 10-fold compared with the vinyl bromide. Since the observed element effect in many cases is actually close to unity, a compensating effect, reducing the relative reactivity of the vinyl bromide, has to exist. Several causes are possible: (a) The transition state leading to the carbanion 1, X = C, is stabilized better with X = Cl than with X = Br. A recent calculation of the negative hyperconjugative abilities of the two halogens in carbanions CH_2CH_2X showed somewhat higher stabilization of chlorine than of bromine.[22a] If this also applies for the total stabilization of 1, and for the transition state leading to it, then preferential Cl stabilization should decrease the k_{Br}/k_{Cl} value.[22b] (b) The larger bulk of bromine should result in a larger steric hindrance to approach of a nucleophile to the double bond, as found for other bulky substituents.[10] This factor, which was observed in the k_{Br}/k_{Cl} ratio for nucleophilic attack on halo bicyclo[1.1.0]butanes[23] should also reduce the k_{Br}/k_{Cl} ratios. (c) β-Electron-withdrawing substituents may reduce the differential double-bond stabilization as is the case with the β-ethoxy group.[15] However, these groups should enhance the XC=C resonance interaction in contrast to the ether functionality. These three possible causes may compensate for the ground-state stabilization effect, bringing the k_{Br}/k_{Cl} ratios to near unity.

Double bond stabilization by the halogens should be important in other types of reactions of vinyl halides. A literature search for radical additions to vinyl chlorides and bromides gave no relevant data. The k_{Br}/k_{Cl} ratios of 0.23 and 0.46 for the electrophilic addition of CF_3COOH to 2-halopropenes[24a] and for the acetolysis of α-halo-p-methoxystyrene[24b] are dominated by stabilization of the transition state for α-halocarbocation formation by the halogen.

The most important consequence of our result is for cases where the k_{Br}/k_{Cl} value is appreciably higher than unity. In reactions proceeding by nucleophilic addition, these cases would have been regarded as authentic examples of either a stepwise mechanism (eq 1, route a) with k_2 rate determining or a single-step substitution (eq 1, route b). Our theoretical calculations, which corroborate Hine's data, suggest that such interpretation of the data could be erroneous. That is, $k_{Br}/k_{Cl} > 1$ can be obtained even when route a with k_1 being the rate-determining step is the operative mechanism. In this case the element effect will reflect the greater loss of ground-state stabilization for the vinyl chloride than for the vinyl bromide rather than involvement of C–X bond cleavage at the transition state.[25]

Registry No. CH_3Cl, 74-87-3; CH_3Br, 74-83-9; CH_4, 74-82-8; $H_2C=CHBr$, 593-60-2; $H_2C=CH_2$, 74-85-1; $H_2C=CHCl$, 75-01-4; Br, 7726-95-6; Cl, 7782-50-5.

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[21] Hehre, W. H.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley: New York, 1986.

[22] (a) Data for Cl: Apeloig, Y.; Karni, M.; Rappoport, Z. *J. Am. Chem. Soc.* **1983**, *105*, 2784. Rappoport, Z.; Avramovitch, B.; Karni, M.; Apeloig, Y. *Isr. J. Chem.* **1988**, *29*, 267. Data for Br: Apeloig, Y.; Karni, M.; Rappoport, Z., unpublished results. (b) However, due to certain assumptions in the calculations and the small differences between Cl and Br, this should be regarded as an auxiliary rather than a main argument.

[23] Hoz, S.; Aurbach, D. *J. Am. Chem. Soc.* **1983**, *105*, 7685.

[24] (a) Peterson, P. E.; Bopp, R. I. *J. Am. Chem. Soc.* **1967**, *89*, 1283. Peterson, P. E.; Bopp, R. I.; Ajo, M. M. *Ibid.* **1970**, *92*, 2834. (b) Rappoport, Z.; Gal, A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 301.

[25] A referee commented that likewise it would seem that a k_{Br}/k_{Cl} ratio of ca. unity is no longer firm evidence for route a.

Substituent Effects on the Geometry of the Cyclooctatetraene Ring

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Received January 23, 1991

Cyclooctatetraene can achieve a variety of geometries, tub, crown, chaise, and octagonal or distorted planar forms, depending on the system's charge and spin multiplicity. Our ab initio computations, which produce optimum geometries, relative energetics, and vibrational frequencies, provide a coherent story of the influences of charge and spin, consistent with a Walsh analysis. Since acceptor and donor substituents may alter the net charge on a cyclooctatetraene ring, such substituents might affect the geometry of the ring. We used the AM1 model for the wave function and electronic energy to evaluate the impact of substituents on charge distribution in the ring and on the inversion barrier. Qualitative perturbation molecular orbital analysis suggests that substituents would force charge alternation in the ring, reduce bond length alternation, and lower the inversion barrier. These predictions were borne out for a model donor ($-CH_2$ anion) and a model acceptor ($-CH_2$ cation). However, more easily accessible substituents, the donor methoxy and the acceptor formyl, had minor effects on the inversion barrier. Multiple acceptor or donor substitution and push–pull substituents exaggerated the charge alternation, but had little impact on inversion barriers. Fused-ring derivatives, such as the biscyclopentacyclooctatetraenes, suffered less of the bias arising from σ-system strain toward a puckered singlet cyclooctatetraene ring, and in these systems electron donors were particularly effective in flattening the ring.

The cyclooctatetraene (COT) ring can take on a number of forms, which we characterize as crown, chaise, tub, and plane (Figure 1). The planar ring can be a regular octagon or take on a 4-fold symmetry. We report calculations on various ions of the hydrocarbon ring, substituted forms of the neutral ring, and fused-ring systems that bear on the

0022-3263/91/1956-5426$02.50/0