

The Energetics of Halogenated Ethylenes (Ethyne)s and 1,3-Butadienes (Butadiynes): A Computational and Conceptual Study of Substituent Effects and “Dimerization”*

Carol A. Deakyne,^{a,**} Lawrence H. Warfel IV,^a Haunani M. Thomas,^a Dhananjaya Nauduri,^b Toyosi Esther A. Ajibowo,^c Nicole J. Carbonaro,^c Alec G. Simpson,^c and Joel F. Liebman^{c,**}

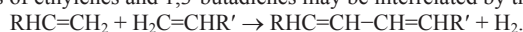
^aDepartment of Chemistry, University of Missouri-Columbia, Columbia, MO 65211-7600, USA

^bAnalytical Core Chemistry, Department of Pathology and Molecular Toxicology, University of Texas Medical Branch, Galveston, TX 77555, USA

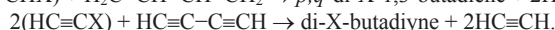
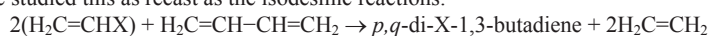
^cDepartment of Chemistry and Biochemistry, University of Maryland, Baltimore County, 1000 Hilltop Circle, Baltimore, MD 21250, USA

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Abstract. The energetics of ethylenes and 1,3-butadienes may be interrelated by the reaction:



Shown earlier to be nearly enthalpically thermoneutral for a variety of hydrocarbon cases, we are now interested in the related energetics of halogenated alkenes and alkynes. Using quantum chemical calculations, we have studied this as recast as the isodesmic reactions:



Here p,q - = 1,3-; 1,4- and 2,3- with X = F, Cl, Br, and I. The halogen and location-dependent deviations from near enthalpic thermoneutrality are discussed.

Keywords: dienes, diynes, halogenated compounds, resonance (conjugation) energy, isodesmic reactions, *ab initio* calculations

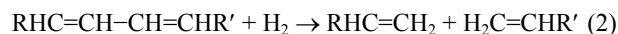
INTRODUCTION

In papers by Roth *et al.*¹ and Liebman² published nearly two decades ago, it was chronicled that the “dimerization” of two substituted ethylenes to form the correspondingly disubstituted 1,3-butadiene, reaction (1), was generally close to enthalpically thermoneutral as a gas phase process.

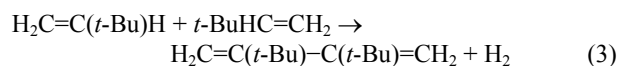


More precisely, this reaction was shown to be endothermic by only a few kcal mol⁻¹. To the best of the authors’ knowledge, examples of this reaction have yet to be observed. (This reaction where the hydrogen adds to another olefin molecule or is otherwise oxidized is, however, preceded in the transition metal literature, *e.g.* refs. 3–6).

Then again, the reverse reaction (2), the hydrogenolysis of dienes is also unobserved, although it is now the more thermodynamically favored direction. Although reactions can always be discussed in either direction, we opt to do so in terms of process (1). Writing the reaction this way emphasizes the uniquely conjugative interactions in the diene by having this species as the final product.



The most significant exception to the suggested near enthalpic thermoneutrality¹ was that of the dimerization of 3,3-dimethyl-1-butene (*i.e.*, *tert*-butyl-ethylene) to form 2,3-di-*tert*-butyl-1,3-butadiene, reaction (3).



* Dedicated to Professor Zvonimir Maksić on the occasion of his 70th birthday.

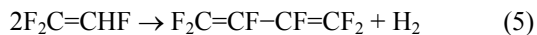
** Author to whom all correspondence about quantum chemical calculations should be addressed (E-mail: deakynec@missouri.edu). Author to whom all correspondence about qualitative chemical reasoning should be addressed (E-mail: jliebman@umbc.edu).

We are not surprised that this reaction is highly endothermic: the final diene is expected to be considerably strained -- the *tert*-butyl group is large and regardless of the conformation, there are considerable non-bonded repulsions and resulting destabilization.

Extending the analysis to acetylenes and butadiynes (reaction (4)), enthalpies of formation from the NIST Chemistry webbook⁷ indicate that there is congruity between the diene and diyne results when R = H and CH₃. That is, reaction (4) is endothermic by only a few kcal mol⁻¹ for both of these substituents. In particular, $\Delta_{\text{rxn}}H_{298}$ is 2.4 kcal mol⁻¹ when R = H and is 1.6 kcal mol⁻¹ when R = CH₃.



All of these examples involve substituted ethylenes (acetylenes) and butadienes (butadiynes) that are "solely" hydrocarbons -- what about other species, those with "hetero" atoms? The assumption of near enthalpic thermoneutrality is implicitly made in an empirical model for aromaticity of heterocycles.⁸ However, what do we find for the energetics of derivatives of the halogens? The experimental literature is bleak: we know of one example, that of trifluoroethylene and hexafluorobutadiene, reaction (5), for which there are the requisite gas phase data.

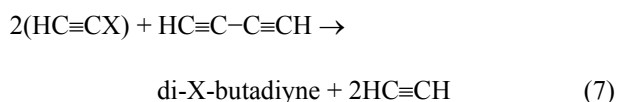
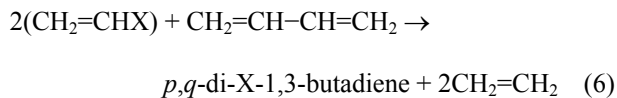


If we accept the enthalpies of formation of trifluoroethylene from archival ref. 9 and that of hexafluorobutadiene (-225 kcal mol⁻¹) from ref. 10, we find this reaction to be endothermic by *ca.* 9 kcal mol⁻¹. However, this is a big "if". From thermal equilibration studies¹¹ it was found that hexafluorobutadiene is less stable than the corresponding cyclobutene by 11.6 kcal mol⁻¹. From a recent review on the thermochemistry of cyclobutanes and cyclobutenes¹² we find the suggestion that the enthalpy of formation of hexafluorocyclobutene is -269 kcal mol⁻¹ and hence that of the desired butadiene is -258 kcal mol⁻¹. This value is some 44 kcal mol⁻¹ more negative than the earlier one. The discrepancy is painful and makes us suspicious of both values.

We thus conclude there is but little information and insight as to the energetics of reactions (1) and (4) from the experimental literature to guide us for the energetics of halogenated species. Reports in the literature on electronic structure calculations on halogenated 1,3-butadienes and butadiynes are also somewhat limited. East *et al.*¹³ have investigated length-scrambling and substituent-scrambling reaction energies of halogen-substituted polyynes, X = F, Cl, Br, I, in order to assess the effect of the substitution pattern on polyne

stability. With respect to halogen-substituted 1,3-butadienes, fluorine substitution has been studied most extensively. Craig *et al.*,¹⁴ Hu *et al.*¹⁵⁻¹⁷ and Xi *et al.*¹⁸ have calculated the relative energies (*cis* effect^{19,20}),¹⁴⁻¹⁸ rotational barriers,^{16,18} and internal rotation potential energy curves¹⁸ for the three isomers of 1,4-difluoro-1,3-butadiene. Xi *et al.*¹⁸ have also examined internal rotations about the C-C bond in 2,3-difluoro-1,3-butadiene and Senthilkumar and Kolandaivel²¹ have examined the *cis* effect for the 1,4-dichloro-1,3-butadienes. To the authors' knowledge, however, no calculations have been carried out at the same high level of theory on dihalogenated butadiyne and the complete set of 1,3-; 1,4-; and 2,3-dihalogenated 1,3-butadiene isomers, for all four halogens F, Cl, Br and I.

Let us now consider the reactions of species of the type H₂C=CHX and HC≡CX, where X = H, F, Cl, Br and I -- other substituents will be considered in later studies. How close to enthalpic thermoneutrality are these reactions? In order to address this question, we have performed quantum chemical calculations on the relevant butadiynes and on all six possible butadiene products. More precisely, we have considered the (*Z*)-1,3-disubstituted butadiene and its stereoisomer (*E*)-1,3-, the (*Z,Z*)-1,4-, (*Z,E*)-1,4-, (*E,E*)-1,4- and 2,3-regioisomers. Additionally, we have recast reactions (1) and (4) in terms of the isodesmic reactions (6) and (7), which will maximize the cancellation of errors. Here the *p* and *q* denote the site of substitution as well as the stereochemistry.



COMPUTATIONAL DETAILS

For purposes of comparison with the dihalogenated butadiynes, all possible planar configurations of the dihalogenated butadienes were considered. Fully optimized geometries (tight convergence criteria) and normal mode vibrational frequencies were computed with the B3LYP method as implemented in the Gaussian 03 (ref. 22) program package. The double- ζ plus polarization (DZP) quality cc-pVDZ basis set was used for the C, H, F and Cl atoms^{23,24} and the corresponding cc-pVDZ-PP basis set, with small-core relativistic pseudopotentials, was used for the Br and I atoms.^{25,26} Computed energies were then improved by evaluating sin-

gle-point energies at the coupled cluster CCSD(T) level with the aug-cc-pVTZ basis set for C, H, F and Cl^{24,27} and the aug-cc-pVTZ-PP basis set for Br and I.^{25,26} These two levels of calculation will be designated B3LYP/cc-pVDZ-(PP) and CCSD(T)/aug-cc-pVTZ-(PP) in the following. The need for tight d-orbitals on the Cl atoms²⁸ was assessed for 2,3-dichlorobutadiene, (Z,Z)-1,4- and (E,E)-1,4-dichlorobutadiene and dichlorobutadiyne. At both levels of calculation, reaction energies, enthalpies and free energies differ by no more than 0.2 kcal mol⁻¹ with and without the tight d-orbitals. Thus, the tabulated thermochemical data give the results of the calculations without tight d-orbitals on the Cl atoms. All optimized geometries were found to be true minima by analysis of harmonic vibrational frequencies, all of which are real. The unscaled vibrational frequencies were used to calculate thermal correction terms.

RESULTS AND DISCUSSION

A. 1,3-Butadienes

For each X, all six possible *trans*-1,3-butadiene configurations and one possible *cis*-1,3-butadiene configuration, *cis*-(Z,E)-1,4-di-X-butadiene, are minima on the B3LYP/cc-pVDZ-(PP) potential energy hypersurfaces of the four disubstituted dienes (Figure 1). For F, a second *cis* configuration, *cis*-(Z)-1,3-difluorobutadiene, is also a minimum. (It should be noted that in this article, the *cis* prefix will be written for the *cis* conformers but no prefix will be written for the *trans* conformers.) As reported by others^{17,18,21} for X = F, Cl the (E,E)-1,4-;

(Z,Z)-1,4-; and 2,3- regioisomers have C_{2h} symmetry. All remaining isomers have C_s symmetry.

Table 1 gives B3LYP/cc-pVDZ-(PP) and CCSD(T)/aug-cc-pVTZ-(PP) enthalpies of isodesmic reaction (6) at 298 K ($\Delta_{rx6}H_{298}$, in kcal mol⁻¹) and free energies of reaction at 298 K ($\Delta_{rx6}G_{298}$, in kcal mol⁻¹). The same information has also been tabulated for reaction (1). CCSD(T)/aug-cc-pVTZ-(PP) data are provided for each of the disubstituted butadiene minima except *cis*-(Z,E)-1,4-dibromobutadiene, *cis*-(Z,E)-1,4-diiodobutadiene, (Z)-1,3-dibromobutadiene and (Z)-1,3-diiodobutadiene. Single-point energies were not obtained for these isomers because they are among the least stable Br and I substituted butadienes at the B3LYP/cc-pVDZ-(PP) level of theory, and the analogous F and Cl substituted butadienes are not stabilized significantly at the higher level of theory.

Table 2 presents the relative stabilities of the isomeric disubstituted butadienes in terms of the individual halogens. For those dihalogenated butadienes with two (0.0) entries in the table, the total energies of the two isomers differ by a few hundredths of a kcal mol⁻¹.

What patterns do the data show? To begin with, at both levels of theory there is little difference between whether we consider just the energy of reaction (6), or that corresponding to enthalpy at 298 K by thermal corrections including the ZPE. With the exception of the 2,3-dihalobutadienes, these thermochemical values for a given choice of halogen and of isomeric dihalobutadiene are the same to within 0.3 kcal mol⁻¹ (data not shown). The discrepancy is no larger than 0.6 kcal mol⁻¹

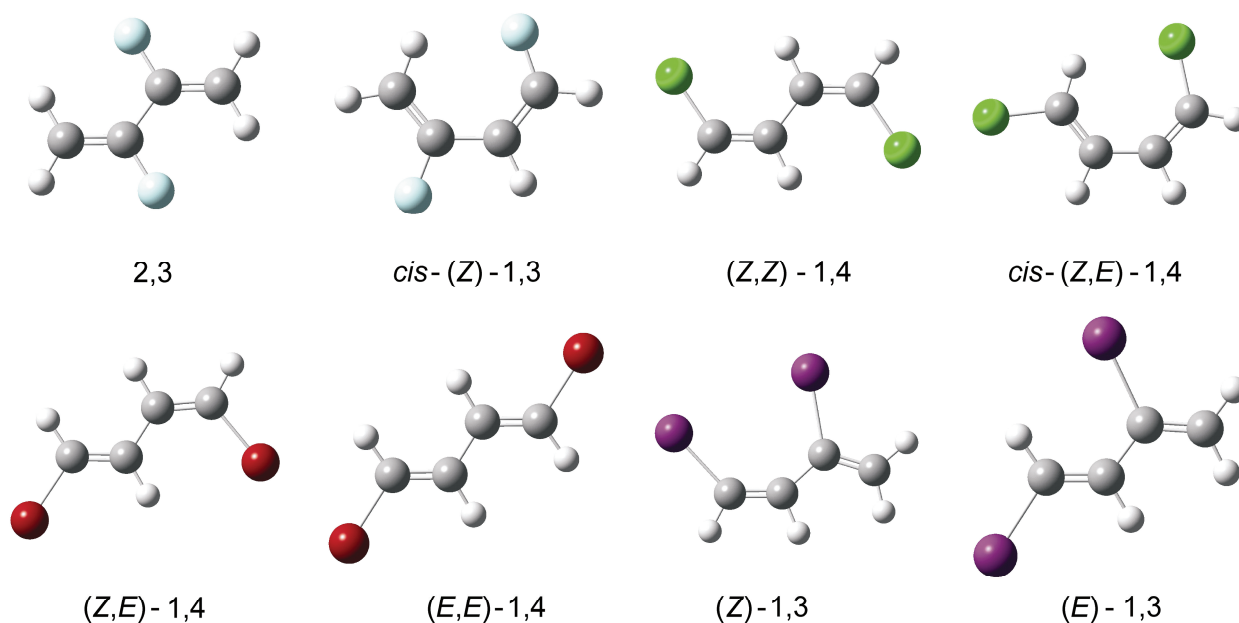


Figure 1. Diagram of the eight minima located on the B3LYP/cc-pVDZ-(PP) potential energy surfaces of *p,q*-di-X-1,3-butadiene. Here *p,q*- = 1,3-, 1,4- and 2,3- with X = F, Cl, Br, and I. Two isomers are given for each X: F, blue; Cl, green; Br, red; I, purple; C, gray; H, white.

Table 1. Energies, enthalpies and free energies of reactions (1) and (6) (kcal mol⁻¹) for the dihalogenated butadienes^(a)

X	Isomer	$\Delta_{\text{rx1}}H_{298}^{(b)}$ kcal mol ⁻¹	$\Delta_{\text{rx1}}G_{298}^{(c)}$ kcal mol ⁻¹	$\Delta_{\text{rx6}}H_{298}^{(b)}$ kcal mol ⁻¹	$\Delta_{\text{rx6}}G_{298}^{(c)}$ kcal mol ⁻¹
	1,3-Butadiene	1.9 (1.4)	4.2 (3.6)		
F	(<i>E</i>)-1,3-difluorobutadiene	1.9 (0.5)	5.7 (4.3)	0.0 (-0.9)	1.5 (0.7)
F	(<i>Z</i>)-1,3-difluorobutadiene	4.6 (2.5)	8.3 (6.2)	2.7 (1.2)	4.1 (2.6)
F	(<i>E,E</i>)-1,4-difluorobutadiene	4.9 (3.8)	8.9 (7.7)	3.0 (2.5)	4.7 (4.2)
F	(<i>Z,E</i>)-1,4-difluorobutadiene	4.3 (2.9)	7.8 (6.5)	2.4 (1.6)	3.7 (2.9)
F	(<i>Z,Z</i>)-1,4-difluorobutadiene	3.5 (1.9)	7.4 (5.9)	1.5 (0.6)	3.2 (2.3)
F	2,3-difluorobutadiene	1.0 (-0.6)	5.4 (3.8)	-0.9 (-1.9)	1.3 (0.3)
F	<i>cis</i> -(<i>Z,E</i>)-1,4-difluoro- butadiene	6.1 (4.8)	9.6 (8.3)	4.1 (3.5)	5.4 (4.7)
F	<i>cis</i> -(<i>Z</i>)-1,3-difluoro- butadiene	3.7 (2.5)	7.3 (6.1)	1.7 (1.1)	3.1 (2.5)
Cl	(<i>E</i>)-1,3-dichlorobutadiene	1.8 (3.6)	5.7 (7.4)	-0.1 (2.2)	1.5 (3.8)
Cl	(<i>Z</i>)-1,3-dichlorobutadiene	6.4 (8.4)	10.1 (12.0)	4.5 (7.0)	5.9 (8.4)
Cl	(<i>E,E</i>)-1,4-dichlorobutadiene	2.8 (2.8)	6.7 (6.7)	0.8 (1.4)	2.6 (3.2)
Cl	(<i>Z,E</i>)-1,4-dichlorobutadiene	2.4 (2.7)	5.9 (6.2)	0.4 (1.3)	1.8 (2.7)
Cl	(<i>Z,Z</i>)-1,4-dichlorobutadiene	1.7 (2.3)	5.7 (6.3)	-0.2 (1.0)	1.6 (2.8)
Cl	2,3-dichlorobutadiene	2.4 (6.1)	6.8 (10.5)	0.4 (4.7)	2.7 (7.0)
Cl	<i>cis</i> -(<i>Z,E</i>)-1,4-dichloro- butadiene	5.5 (6.2)	8.9 (9.5)	3.5 (4.8)	4.7 (6.0)
Br	(<i>E</i>)-1,3-dibromobutadiene	-0.2 (4.1)	3.6 (7.9)	-2.2 (2.8)	-0.6 (4.4)
Br	(<i>Z</i>)-1,3-dibromobutadiene	(9.7)	(13.2)	(8.4)	(9.6)
Br	(<i>E,E</i>)-1,4-dibromobutadiene	1.4 (2.8)	5.3 (6.7)	-0.6 (1.5)	1.1 (3.2)
Br	(<i>Z,E</i>)-1,4-dibromobutadiene	0.8 (2.8)	4.4 (6.4)	-1.2 (1.5)	0.2 (2.8)
Br	(<i>Z,Z</i>)-1,4-dibromobutadiene	0.0 (2.6)	4.0 (6.6)	-2.0 (1.3)	-0.2 (3.0)
Br	2,3-dibromobutadiene	-0.5 (7.0)	3.9 (11.4)	-2.5 (5.7)	-0.3 (7.8)
Br	<i>cis</i> -(<i>Z,E</i>)-1,4-dibromo- butadiene	(6.7)	(10.0)	(5.4)	(6.5)
I	(<i>E</i>)-1,3-diiodobutadiene	-0.5 (4.3)	3.3 (8.1)	-2.5 (3.0)	-0.9 (4.6)
I	(<i>Z</i>)-1,3-diiodobutadiene	(10.9)	(14.1)	(9.6)	(10.5)
I	(<i>E,E</i>)-1,4-diiodobutadiene	0.7 (2.5)	4.6 (6.4)	-1.2 (1.2)	0.5 (2.9)
I	(<i>Z,E</i>)-1,4-diiodobutadiene	0.2 (2.7)	3.8 (6.3)	-1.7 (1.3)	-0.4 (2.7)
I	(<i>Z,Z</i>)-1,4-diiodobutadiene	-0.5 (2.5)	3.5 (6.5)	-2.5 (1.2)	-0.7 (3.0)
I	2,3-diiodobutadiene	-0.3 (7.4)	4.0 (11.7)	-2.2 (6.1)	-0.2 (8.1)
I	<i>cis</i> -(<i>Z,E</i>)-1,4-diiodo- butadiene	(7.2)	(10.1)	(5.8)	(6.5)

^(a) CCSD(T)/aug-cc-pVTZ-(PP)//B3LYP/cc-pVDZ-(PP) and B3LYP/cc-pVDZ-(PP) (parentheses) data. See text for explanation of absent CCSD(T) data. ^(b) Reaction enthalpy at 298 K. ^(c) Reaction free energy at 298 K.

Table 2. Relative stabilities (kcal mol⁻¹) of the dihalogenated butadienes^{(a)(b)}

X	(<i>E</i>)-1,3	(<i>E,E</i>)-1,4	(<i>Z,E</i>)-1,4	(<i>Z,Z</i>)-1,4	2,3
F	0.9 (1.0)	3.9 (4.4)	3.3 (3.5)	2.4 (2.5)	0.0 (0.0)
Cl	0.1 (1.2)	1.0 (0.4)	0.6 (0.3)	0.0 (0.0)	0.6 (3.7)
Br	0.3 (1.5)	1.9 (0.2)	1.3 (0.2)	0.5 (0.0)	0.0 (4.4)
I	0.0 (1.8)	1.3 (0.0)	0.8 (0.1)	0.0 (0.0)	0.3 (4.9)

^(a) Relative enthalpies at 298 K. ^(b) CCSD(T)/aug-cc-pVTZ-(PP)//B3LYP/cc-pVDZ-(PP) and B3LYP/cc-pVDZ-(PP) (parentheses) data.

for the 2,3-dihalobutadienes. This is a welcome simplification in that we can pay attention solely to stereoelectronic aspects of chemical energetics, and not those borne of statistical thermodynamics. We may thus maintain our most customary language for discussion of these species.

When X = Cl, Br and I improving the calculational level from B3LYP/cc-pVDZ-(PP) to CCSD(T)/aug-cc-

pVTZ-(PP) makes reaction (6) more exothermic and, therefore, more exoergic, for all isomers (Tables 1 and 2). Doing so also preferentially stabilizes the (*E*)-1,3- and 2,3-species with respect to the other species and expands the gaps in the stabilities of the 1,4-species with respect to each other. The opposite trends are observed when X = F. Since omitting diffuse functions from the basis set and the dispersion interaction term

from the total energy alters the trends for even the isodesmic reaction (6), the remainder of the discussion on the butadienes will address only the CCSD(T)/aug-cc-pVTZ-(PP) results.

As the halogen changes from F to Cl to Br to I, reaction (6) becomes increasingly more exothermic for all types of butadiene products but the 2,3-dihalobutadienes. For the latter products, in which the halogens are near each other, the exothermicity of the reaction follows the trend $\text{Cl} < \text{F} < \text{I} \leq \text{Br}$ (Table 1). A partial explanation for the comparative stability of 2,3-difluorobutadiene is found in terms of $\text{C}-\text{H}\cdots\text{F}-\text{C}$ hydrogen bond formation, earlier suggested^{29,30} for (*E*)-1,3-difluorobutadiene. With respect to the three heavier halogens, where the $\text{C}-\text{H}\cdots\text{X}-\text{C}$ hydrogen bonding is expected to be weaker, the different trend for the 2,3-dihalobutadienes can be rationalized as follows. From considerations of electronegativity we may conclude that electrostatic interhalogen repulsion is presumably greatest in the case of Cl – chlorines are the most negative, and bromine and iodine decrease in that order. Concomitantly, Cl is the least polarizable and I the most polarizable of the three atoms. From steric considerations, we may conclude that “bulk” repulsion (*cf.* the *tert*-butylated case above) is the greatest for I – the size of iodine is rather much larger than bromine and chlorine in turn. These stereoelectronic contributors run countercurrent and the calculations suggest that the polarizability, perhaps combined with the weak hydrogen bonding, is the more important contributor, especially for Cl and Br.

Overall, at the CCSD(T)/aug-cc-pVTZ-(PP) level of calculation reaction (6) is at least mildly exothermic for the most stable butadiene isomer of all four halogens (Table 1). In fact, the CCSD(T) results indicate that when X = Br or I, halogenation stabilizes the diene for all five substitution patterns considered. When X = F or Cl, however, only the 2,3 fluorination is definitively stabilizing. The difference in these two sets of results is presumably caused by the greater conjugation possible between Br, I and the diene than between F, Cl and the diene.

In any case, since both experiment⁷ and calculation (Table 1, refs. 1 and 2) indicate that “dimerization” reaction (1) is endothermic by a few kcal mol^{-1} for the parent case of two ethylenes to form butadiene, by thermochemical (Hess) cycle reasoning “dimerization” reaction (1) for the halogenated olefins is always more endothermic than isodesmic reaction (6). Thus, for most of the fluorine isomers and perhaps all of the chlorine isomers, reaction (1) will not be thermoneutral to within a few kcal mol^{-1} . In contrast, formation of the 2,3-, (*Z,Z*)-1,4, and (*E*)-1,3 dibromo- and diiodobutadienes *via* reaction (1) is likely to be nearly thermoneutral and

may be exothermic rather than endothermic, as found for alkyl substitution.^{1,2} Quantitative support for this qualitative analysis is provided by the $\Delta_{\text{rxn}}H_{298}$ values in Table 1.

The entropies of reaction $\Delta_{\text{rxn}6}S_{298}$ and $\Delta_{\text{rxn}1}S_{298}$ are negative and of sufficient magnitude that $\Delta_{\text{rxn}6}G_{298}$ is more positive than $\Delta_{\text{rxn}6}H_{298}$ by 1–2 kcal mol^{-1} (Table 1). Likewise, $\Delta_{\text{rxn}1}G_{298}$ is more positive than $\Delta_{\text{rxn}1}H_{298}$ by 3–4 kcal mol^{-1} . Consequently those reactions involving bromine or iodine that are both exothermic and exoergic are exoergic by less than a kcal mol^{-1} .

For each of the halogen substituents, the 1,4 species for which the isodesmic reaction is most endothermic is the (*E,E*)-1,4 species, followed by the (*Z,E*)- and (*Z,Z*)-1,4 species in turn (Table 1). This trend reflects the literature findings for 1,4-difluorobutadiene and 1,4-dichlorobutadiene (experimental and calculational)^{14,17–21} of the relative stabilities of the three species: (*E,E*) < (*Z,E*) < (*Z,Z*). Our CCSD(T)/aug-cc-pVTZ-(PP) enthalpies of (*E,E*)-1,4-difluorobutadiene and (*Z,E*)-1,4-difluorobutadiene relative to that of (*Z,Z*)-1,4-difluorobutadiene are 1.5 and 0.9 kcal mol^{-1} , respectively, in excellent agreement with the experimentally determined values of 1.6 and 0.9 kcal mol^{-1} (ref. 14) and the G3B3 values of 1.4 and 0.8 kcal mol^{-1} .¹⁷ Our relative enthalpy values of 1.0 and 0.6 kcal mol^{-1} for the (*E,E*)- and (*Z,E*)-1,4-dichlorobutadienes, respectively, are less compressed than those of 0.6 and 0.5 kcal mol^{-1} found at the MP2/6-311++G(d,p) level of theory.²¹ Our corresponding values for the 1,4-bromobutadienes (1.4 and 0.8 kcal mol^{-1}) and 1,4-iodobutadienes (1.3 and 0.8 kcal mol^{-1}) are similar in magnitude to the above values, indicating that the so-called “*cis* effect”^{19,20} is nearly independent of the nature of the halogen (Tables 1 and 2).

One of the more surprising results, perhaps, is the competitive stability of the 2,3-, (*E*)-1,3- and (*Z,Z*)-1,4-isomers of the dibromobutadienes, diiodobutadienes and, to a lesser extent, the dichlorobutadienes. Again, the results differ for fluorine in that, although these three isomers are still the most stable, the enthalpy gap between 2,3-difluorobutadiene and the second most stable isomer, (*E*)-1,3-difluorobutadiene, is considerably larger (Table 2). That the 2,3-isomer is more stable than, or even similar in stability to, its 1,3- and 1,4-counterparts is counter to intuition based on destabilization due to steric and Coulombic repulsion of one halogen with the other halogen. Is there precedent in the literature to help us understand this result? Let us briefly discuss this in terms of 1- and 2-substituted propenes.

The enthalpy of formation data for the fluorine and iodine substituted propenes is absent. However, in that there is roughly a constant enthalpy of formation difference for gaseous iodo and methylalkane deriva-

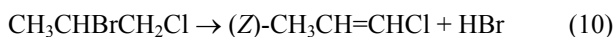
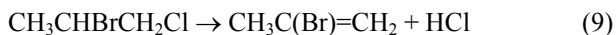
Table 3. Enthalpies and free energies of reactions (4) and (7) (kcal mol⁻¹) for the dihalogenated butadiynes^(a)

X	Isomer	$\Delta_{rx4}H_{298}^{(b)}$ kcal mol ⁻¹	$\Delta_{rx4}G_{298}^{(c)}$ kcal mol ⁻¹	$\Delta_{rx7}H_{298}^{(b)}$ kcal mol ⁻¹	$\Delta_{rx7}G_{298}^{(c)}$ kcal mol ⁻¹
	butadiyne	1.0 (-3.6)	2.7 (-1.8)		
F	difluorobutadiyne	3.6 (-0.9)	5.9 (1.4)	2.6 (2.6)	3.2 (3.3)
Cl	dichlorobutadiyne	0.6 (-4.2)	3.2 (-1.6)	-0.4 (-0.7)	0.5 (0.2)
Br	dibromobutadiyne	-0.9 (-4.6)	1.8 (-2.0)	-1.8 (-1.1)	-0.9 (-0.1)
I	diiodobutadiyne	-2.2 (-5.2)	0.4 (-2.6)	-3.2 (-1.6)	-2.3 (-0.8)

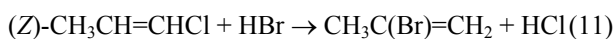
^(a) CCSD(T)/aug-cc-pVTZ-(PP)//B3LYP/cc-pVDZ-(PP) and B3LYP/cc-pVDZ-(PP) (parentheses) data. ^(b) Reaction enthalpy at 298 K. ^(c) Reaction free energy at 298 K.

derivatives³¹ and for gaseous fluoro and hydroxyalkane derivatives,³¹ we mimic F with OH and I with CH₃. Then, starting with F, or more precisely OH as mimic, 2-propenol is 2 kcal mol⁻¹ more stable than its 1-isomer.³² The thermochemical literature tells us that 2-chloropropene³³ has a more negative enthalpy of formation by 2 kcal mol⁻¹ than its (*Z*)-1-chloro isomer,³⁴ (in turn more stable than its (*E*)-counterpart).

For 2-bromopropene, there are again no direct data. However, we may invoke the liquid phase enthalpies (9) and (10) from ref. 35.



Let us take the difference of these equations, and then assume that the difference of these enthalpies is roughly phase independent. Accordingly, reaction 11 is exothermic by *ca.* 3 kcal mol⁻¹.



From the well-known enthalpies of formation of HCl and HBr, we find a value of *ca.* 7 kcal mol⁻¹ for the enthalpy of formation of gaseous 2-bromopropene; by contrast that of (*Z*)-1-bromopropene³⁴ is *ca.* 10 kcal mol⁻¹, some 3 kcal mol⁻¹ higher. For the iodo species of interest, we use mimicry to address the comparison of 2-iodopropene and its 1-isomers by that of 2-methylpropene and 2-butene.³¹ We so find that 2-methylpropene is somewhat less than 2 kcal mol⁻¹ more stable than either 1-methylpropene, where in this case the (*Z*)-isomer is less stable than the (*E*)-isomer unlike the halogenated case.

Accepting that the XC=CH₂ group in the 1,3-butadienes is analogous to the CH₃ group in the propenes, the environment of each halogen in the 2,3-diX-1,3-butadienes is similar to that of the halogen in the 2-propenes. Putting all of the above information together, then, does help to rationalize why the 2,3-isomer gains stability relative to our intuition based on steric repulsion. If the “2-propene-like” interactions were the do-

minant stabilizing interactions in the 1,3-butadienes, the expected order of stability would be 2,3-isomers > 1,3-isomers > 1,4-isomers, which is what is observed for X = F (Tables 1 and 2). That the 2,3-, (*E*)-1,3- and (*Z,Z*)-1,4-isomers are of comparable stability for X = Cl, Br and I is further indication that competing stabilizing interactions, such as reduced X⋯X repulsion and internal hydrogen bonding, are present in the 1,3-butadiene systems.

B. Butadiynes

With the results reported above on the “dimerization” of two substituted ethylenes, the question arises as to whether the near thermoneutrality of reactions (1) and (2) (for many substitution patterns) is an “accident”. That is, is there support for our diene results from an analysis of the corresponding reactions for diynes and doubled alkynes (reactions (4) and (7))? Table 3 gives for each of the disubstituted butadiynes the B3LYP/cc-pVDZ-(PP) and CCSD(T)/aug-cc-pVTZ-(PP) enthalpies of isodesmic reaction (7) at 298 K ($\Delta_{rx7}H_{298}$, in kcal mol⁻¹) and free energies of reaction at 298 K ($\Delta_{rx7}G_{298}$, in kcal mol⁻¹). The same thermochemical data for reaction (4) has also been tabulated.

Several of the general points noted for the butadienes in the previous section also apply to the butadiynes. The enthalpies and uncorrected energies of isodesmic reaction (7) are the same to within 0.3 kcal mol⁻¹. The entropies of reaction are negative for both reactions (4) and (7), and only the isodesmic reactions for dibromobutadiyne and diiodobutadiyne are exoergic (Table 3). On the other hand, the B3LYP/cc-pVDZ-(PP) calculations reproduce the CCSD(T)/aug-cc-pVTZ-(PP) thermochemical values for reaction (7) significantly better than those for reaction (6). As a result, the trends in the thermochemical values as a function of X are the same for the two levels of calculation. However, the B3LYP reaction enthalpy for the parent “dimerization” reaction (4) of two acetylenes forming butadiyne is exothermic rather than endothermic as found from experiment⁷ (*ca.* 2.4 kcal mol⁻¹) and the CCSD(T) calculations (Table 3). Again, we will limit our discussion of diynes to only the CCSD(T)/aug-cc-pVTZ-(PP) data, allowing direct quantitative comparisons between the

diene and diyne results.

As for most of the diene species, the diyne reactions monotonically increase in exothermicity and thereby preferentially provide stabilization for the diyne as X proceeds from F to I. The enthalpy values for reaction (7) span a range of some 6 kcal mol⁻¹ (Table 3), which is larger than the range for most of the analogous diene reactions including that of the (*E*)-1,3-butadienes (*ca.* 4 kcal mol⁻¹, Table 1), species that presumably minimize the steric and electronic consequences of dihalogenation. The dihalodiyne reactions are more exothermic than are the corresponding diene reactions. In other words, alkynes and related diynes are somewhat more sensitive to halogen substitution than olefins and related dienes.

Using thermochemical (Hess) cycle reasoning, with $\Delta_{\text{rxn}}H_{298} > 0$ for the parent case, reaction (4) for the halogenated butadiynes is equivalently always more endothermic than isodesmic reaction (7). Therefore, the CCSD(T) calculations indicate that for all X but F, reaction (4) will be nearly thermoneutral (Table 3) and provide support for the diene results.

CONCLUSIONS

The near thermoneutrality of “dimerization” reactions for alkyl-substituted butadiynes and 1,3-butadienes is supported by our *ab initio* quantum chemical calculations on analogous halogenated systems. Large basis sets and inclusion of electron correlation are required to obtain accurate thermochemistry, even for the isodesmic reactions examined. The *cis* effect^{19,20} reported in the literature for fluorine^{14,17} and chlorine²¹ also holds for bromine and iodine. However, other results found in this work for X = F differ from those for the other halogens.

The energetics of the dihalobutadienes, as probed by the isodesmic reactions and the “dimerization” of olefins, exhibit numerous competing trends. Strong C–H···F hydrogen bonding and F···“other” double bond interactions in the difluorobutadienes stabilize the two fluorines when they are near each other on the diene chain. However, the high electronegativity of F and resulting high negative atomic charges suggest strong electrostatic repulsions between nearby fluorines. These effects combine to make 2,3-difluorobutadiene the most stable of its isomers and the other species of rather much similar total energy. These effects are smaller for the other halogens and so the isomers are more comparable in their stability. In fact, the weak hydrogen bonds, increasing steric size Cl < Br < I and decreasing negative charges Cl > Br > I conspire to make the 2,3-, 1,4-(*Z,Z*)- and 1,3-(*E*)-isomers essentially equal in stability. In the absence of these hydrogen bonds and “other”

stabilizing interactions involving halogens, difluorobutadiene is the most destabilized of these dihalogenated diynes. Further disentangling of the opposing trends awaits study of the saturated dihalobutanes and of mixed dihalogenated species.

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SAŽETAK

Energetski profil halogeniranih etilena (etina) i 1,3-butadiena (butadiina): računski i konceptualna studija supstituentskih efekata i “dimerizacije”

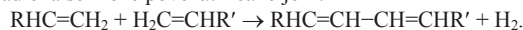
Carol A. Deakyne,^a Lawrence H. Warfel IV,^a Haunani M. Thomas,^a Dhananjaya Nauduri,^b Toyosi Esther A. Ajibowo,^c Nicole J. Carbonaro,^c Alec G. Simpson^c i Joel F. Liebman^c

^aDepartment of Chemistry, University of Missouri-Columbia, Columbia, MO 65211-7600, USA

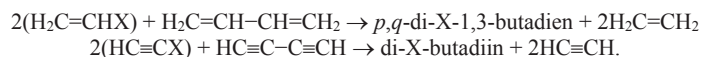
^bAnalytical Core Chemistry, Department of Pathology and Molecular Toxicology, University of Texas Medical Branch, Galveston, TX 77555, USA

^cDepartment of Chemistry and Biochemistry, University of Maryland, Baltimore County, 1000 Hilltop Circle, Baltimore, MD 21250, USA

Energetski profil etilena i 1,3-butadiena se može povezati reakcijom:



Ranije je pokazano da je reakcija entalpijski skoro termoneutralna za različite ugljikovodike, a sada su proučavane s njom povezane energetike halogeniranih alkena i alkena. Korištenjem kvantno-kemijskih računa, studirane su izodezmičke reakcije:



Ovdje je p,q - = 1,3-; 1,4- i 2,3-, te X = F, Cl, Br i I. Diskutirani su izbor halogenog atoma i položajno ovisna odstupanja od skoro entalpijske termoneutralnosti.