Comparison of Various Isodesmic and Homodesmotic Reaction Heats with Values derived from Published *Ab initio* Molecular Orbital Calculations

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Ab initio theoretical reaction heats, evaluated by using total molecular energies from ten basis sets as reported in the literature, are compared with experiment for nine acyclic C_4 hydrocarbons, seven cyclic C_3 and C_4 hydrocarbons, and five benzenoid hydrocarbons. The closeness of the agreement is examined to assess the effect of the greater matching of structural features in the homodesmotic reactions, and correlated with the type of basis set employed. Extended basis sets are essential for good agreement, other than fortuitous, if one of the reactant or product species is markedly destabilized or stabilized with repect to the rest, as is the case with the small ring structures and the benzenoid hydrocarbons, respectively.

It has long been recognized that single-determinant molecular orbital theory, which neglects large effects arising from electron correlation, can give erroneous values for the heat of atomization of molecules.[1,2] For ordinary chemical reactions, however, in which the number of formal covalent bonds broken equals the number formed, thus conserving the number of electron pairs, better values should be obtained. Snyder and Basch,[2,3] using a moderate size Gaussian basis set, DZ, showed this to be the case for the complete hydrogenation of a group of simple unsaturated molecules containing two or three heavy atoms, the predicted values of the reaction heat coming within 125 kJ mol^{-1} of the experimental values. Hehre *et al.*[4] then proposed that the overall hydrogenation should be considered as a two-step reaction: step (*a*) consisting of bond separation in which all formal bonds between heavy (non-hydrogen) atoms are separated into the simplest (parent) molecules with the same type of bond, and step (*b*) full hydrogenation of the reaction products. Much better agreement with experiment was found for the step (*a*). Even the minimal basis set STO-3G is capable of estimating bond separation heats for molecules containing up to six heavy atoms, whereas the extended basis set 4—31G is required to estimate hydrogenation heats as accurately.[4] The better agreement for bond separation was attributed to the matching of the bonds in reactant and product species according to their formal type (single, double, or triple), resulting in a more complete cancellation of effects arising from electron correlation and use of a limited size basis set. Such reactions were termed *isodesmic*.

The above definition actually covers many different kinds of reaction in which other structural features in the reactants and products besides the number of formal bonds of each type are matched to a lesser or greater degree. We have focussed attention on a restricted subclass of such reactions in which (i) there are equal numbers of each type of carbon–carbon bond (C[4]–C[4], C[4]–C[3], C[3]–C[3], C[3]=C[3], *etc.*) † and (ii) there are equal numbers of each type of carbon atom (C[4], C[3], *etc.*) with zero, one, two, and three hydrogen atoms attached in reactants and products.[1] These reactions are particularly suitable for evaluating stabilization energies for cyclic conjugated hydrocarbons and acyl structures [5-8] and destabilization (strain) energies which are a characteristic property of the majority of saturated and non-conjugated ring systems.[9] This is because extraneous energy terms that otherwise arise from changes in the bonding state of the carbon atoms in the CC bonds and/or changes in CH bonding are kept to a minimum. To distinguish this special subclass of reactions we introduced the term *homodesmotic*, to emphasize the sameness in the character of the bonding over and above the equality in the number of bonds of each formal type, which is the sole criterion for an isodesmic reaction. As compared with other isodesmic reactions, homodesmotic reactions would be expected to minimize still further contributions to the reaction heat from electron correlation and other effects.

In this paper we extend the use of homodesmotic reactions to bring about the separation of structural elements in acyclic C_4 molecules to see whether, as might be expected, there is even better agreement between theoretical and experimental reaction heats than that found for isodesmic bond separation. Similar detailed comparisons are made for C_3 and C_4 cyclic molecules, amplifying the treatment of destabilization energies which we have given recently.[9] Isomerization reactions

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† The numbers in brackets indicate the total numbers of other atoms bonded to each carbon atom, *e.g.* the carbon atoms in $CH_3–CH_3$, $CH_2=CH_2$ and $CH\equiv CH$ are C[4], C[3], and C[2], respectively.

[1] L. Radom and J. A. Pople, *Internat. Rev. Sci., Phys. Chem.*, 1972, **1**, 71.

[2] L. C. Snyder, *J. Chem. Phys.*, 1967, **46**, 3602.

[3] L. C. Snyder and H. Basch, *J. Amer. Chem. Soc.*, 1969, **91**, 2189.

[4] W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 4796.

[5] P. George, M. Trachtman, C. W. Bock, and A. M. Brett, *Theor. Chim. Acta*, 1975, **38**, 121.

[6] P. George, M. Trachtman, C. W. Bock, and A. M. Brett, *J.C.S. Perkin II*, 1976, 1222.

[7] P. George, M. Trachtman, C. W. Bock, and A. M. Brett, *Tetrahedron*, 1976, **32**, 1357.

[8] P. George, M. Trachtman, C. W. Bock, and A. M. Brett, in preparation.

[9] P. George, M. Trachtman, C. W. Bock, and A. M. Brett, *Tetrahedron*, 1976, **32**, 317.

of benzene, naphthalene, and anthracene are studied, also reactions in which there is a rearrangement of the polycyclic benzenoid structure, and reactions in which benzene is broken up in stepwise reactions *via* C_3 and C_4 acyclic intermediates. In addition to the sort of isodesmic reaction exemplified by bond separation at one extreme and by homodesmotic reactions at the other, we have found it necessary to introduce further subdivisions in this broad class of reactions, recognizing *isodesmic reactions of the first kind* as those which fulfil condition (i) above but not condition (ii), and *isodesmic reactions of the second kind* as those which fulfil condition (ii) but not condition (i). Finally the factors underlying the extent to which agreement between theoretical and experimental reaction heats is to be expected are discussed for both aliphatic and aromatic molecules.

TABLE 1

Literature sources

Basis set	Geometry	References
STO–3G(A)	Standard	*a–f*
STO–3G(B)	Experimental	*f, g*
STO–3G(C)	Partially optimized	*f*
STO–3G(D)	Fully optimized	*h—j*
STO–4G(A)	Standard	*c*
LEMAO–6G(B)	Experimental	*g, k*
4–31G(B)	Experimental	*g, l*
4–31G(E)	Optimized STO–3G	*h—j*
6–31G(E)	Optimized STO–3G	*i, m*
6–31G *(E)	Optimized STO–3G	*j, n*
FSGO	Experimental	*o—q*
IBMOL	Experimental	*r—u*
FGGL	Experimental	*v—y*
LCGO	Experimental	*z*
[4*s*2*p*/2*s*]	Experimental	*aa—cc*
DZ	Experimental	*dd*

[a] Ref. 11. [b] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1969, **51**, 2657. [c] M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1969, **51**, 3927. [d] L. Radom, W. J. Hehre, and J. A. Pople, *J. Chem. Soc.* (*A*), 1971, 2299. [e] W. J. Hehre, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 1496. [f] Ref. 10. [g] Ref. 4. [h] W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1971, **93**, 808. [i] L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1971, **93**, 5339. [j] Ref. 16. [k] R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1970, **52**,, 5001. [l] R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724. [m] W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257. [n] P. C. Hariharan, and J. A. Pople, *Chem. Phys. Letters*, 1972, **16**, 217. [o] Ref. 17. [p] Ref. 18. [q] Ref. 19. [r] J. M. André, M. C. André, and G. Leroy, *Bull. Soc. chim. belges*, 1969, **78**, 539. [s] J. M. André, M. C. André, and G. Leroy, *Bull. Soc. chim. belges*, 1971, **80**, 265. [t] J. M. André, P. Degand, and G. Leroy, *Bull. Soc. chim. belges*, 1971, **80**, 585. [u] G. Berthier, A. Y. Meyer, and L. Praud, ' The Jerusalem Symposia on Quantum Chemistry and Biochemistry, III,' 1971, p. 1974. [v] R. J. Buenker, S. D. Peyerimhoff, and J. L. Whitten, *J. Chem. Phys.*, 1967, **46**, 2029. [w] R. J. Buenker, and S. D. Peyerimhoff, *J. Chem. Phys.*, 1968, **48**, 354. [x] R. J. Buenker, J. L. Whitten, and J. D. Petke, *J. Chem. Phys.*, 1968, **49**, 2261. [y] R. J. Buenker and S. D. Peyerimhoff, *Chem. Phys. Letters*, 1969, **3**, 337. [z] M. H. Palmer, and S. M. F. Kennedy, *J.C.S. Perkin II*, 1974, 1893. [aa] T. H. Dunning, W. J. Hunt, and W. A. Goddard, *Chem. Phys. Letters*, 1969, **4**, 147. [bb] T. H. Dunning, R. P. Hosteny, and I. Shavitt, *J. Amer. Chem. Soc.*, 1973, **95**, 5067. [cc] P. J. Hay and I. Shavitt, *J. Chem. Phys.*, 1974, **60**, 2865. [dd] L. C. Snyder and H. Basch, ' Molecular Wave Functions and Properties,' Wiley, New York, 1972.

Sources of Theoretical Data.—Table 1 lists the references from which we have obtained the majority of total molecular energies, the basis set used in the calculations, and the geometry employed. The capital letters in parentheses following some basis sets are used to distinguish amongst various geometrical configurations currently being used.* A and B denote the standard [11] and experimental geometries respectively, and are not dependent on any particular basis set, C signifies the standard geometry except that CCC angles in acyclic molecules have been optimized in the specified basis set, and D denotes the geometry obtained from complete optimization of all bond lengths and angles subject to certain symmetry constraints. Unlike A and B, geometries C and D clearly depend on the basis set in which the optimization is carried out. E indicates that the STO-3G optimized geometry was used, but that the total energies were evaluated in another basis set.

In some instances, we have supplemented the energy values from the literature using programs available through the Quantum Chemistry Program Exchange [*i.e.* STO-3G(B) s-*trans*,*trans*,s-*trans*-hexa-1,3,5-triene,[12,13] $E_t = -228.955\,46$ a.u., STO-3G(B) s-*trans*-buta-1,3-diene [14,15] $E_t = -153.016\,74$]. In other cases authors have kindly provided us with additional values as indicated in the acknowledgements. For all C_4 structures, the total molecular energies in the 6—31G* basis set have been estimated from the corresponding 4—31G values by using the increments given in reference 19 of Hehre and Pople.[16] However, not every basis set in Table 1 could be used for all the reactions we have investigated, since in some of them total molecular energies are available for only a limited number of molecules. The homodesmotic and isodesmic reactions discussed in this paper have been chosen to give as extensive a comparison as possible amongst reaction heats calculated by using different basis sets.

Experimental reaction heats have been calculated from the data given in the Appendix. All the values, both theoretical and experimental, listed in the Tables have been calculated initially to two decimal places, and then rounded off to the nearest tenth of a kJ mol^{-1}. In a few instances this leads to a small discrepancy when the difference between theoretical and experimental reaction heats is evaluated.

Comparison of Theoretical and Experimental Reaction

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* The geometries denoted by B, C, and D do not correspond to the usage of Radom and Pople [10] in which B denotes optimized CCC angle(s) for the minimum energy conformation and rigid rotation; C denotes optimized CCC angles for all conformations; and D denotes experimental geometry for the most stable conformation and rigid rotation.

[10] L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 4789.

[11] J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, 1967, **89**, 4253.

[12] M. Traetteberg, *Acta Chem. Scand.*, 1968, **22**, 628.

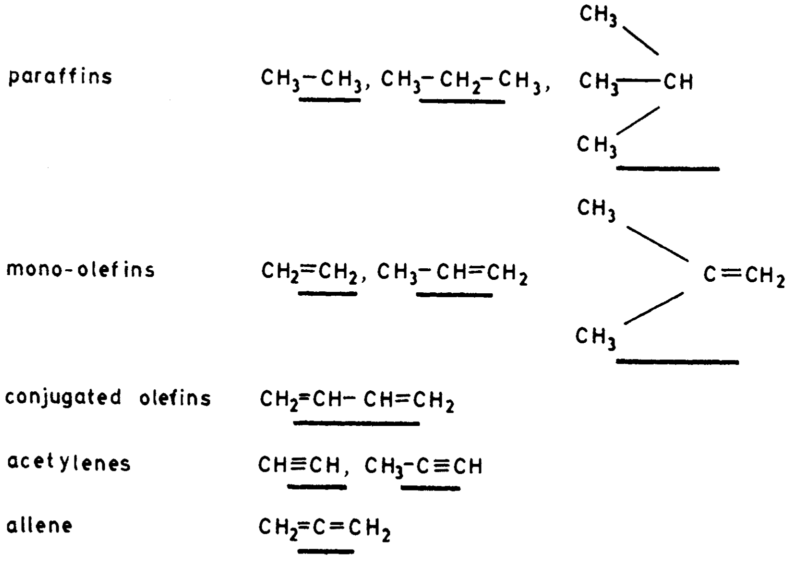
[13] W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, University of Indiana,

[14] K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Structure*, **1**, 463.

[15] A. Veillard, *Theor. Chim. Acta*, 1970, **18**, 21.

[16] W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, 1975, **97**, 6941.

Heats for Isodesmic Bond Separation and Homodesmotic Group Separation Reactions.—The isodesmic bond separation reaction for hydrocarbons, by definition,[4] requires just three molecules as the reference structures (ethane, ethylene, and acetylene). These furnish the single, double, and triple CC bonds respectively to match those in the reactants. In a similar way the criteria for a homodesmotic reaction also dictate the structural features required in the corresponding reference compounds. If these are the smallest molecules that possess the necessary groups of atoms bonded together, then, by analogy with isodesmic bond separation, we designate the reaction a *homodesmotic group separation.* Since the criteria for homodesmotic reactions are so much more restrictive than those for isodesmic reactions, the number of reference molecules needed is inevitably larger. For the hydrocarbon reactions under consideration in this paper the list comprises those given in Scheme 1. The unique structural element contained in each of these small molecules, which is matched with the corresponding structural element in the larger reactant molecule, has been underlined in each case. It is to be understood that the structural element comprises, in addition to the central carbon atom (C[4], C[3], or C[2] as the case may be) the next nearest neighbour atoms, C and/or H, and in the case of carbon, the nature of the formal bonding between the carbon atoms. Homodesmotic reactions of hydrocarbons thus match the local symmetry about each carbon atom in the reactants and products as completely as possible.



Scheme 1

C_4 Molecules.—Theoretical and experimental reaction heats for isodesmic bond separation (IBS) and homodesmotic group separation (HGS) reactions are compared in Tables 2 and 3 for a variety of acyclic and cyclic hydrocarbons respectively. All the HGS reactions involve larger molecules than the corresponding IBS reactions as a consequence of the stringent bond- and group-matching criteria for homodesmotic reactions. Nevertheless the agreement between theoretical and experimental values is better for the HGS reactions in the vast majority of cases (92%) in accord with expectation. In those few cases in which IBS results are better, this seems to be fortuitous, since there is no systematic correlation with the type of basis set employed.

However, in spite of the larger molecules needed in the HGS reactions, for acyclic structures the sum of the total molecular energies of reactant and product species is systematically slightly less, by 1—4 a.u., than that for the corresponding IBS reactions. This comes about simply because fewer molecules are required in the HGS reactions. On the other hand more molecules are required in the HGS reactions for ring structures and the sum of the total molecular energies is considerably greater, *ca.* 75, 115, and 155 a.u., depending upon the particular ring structure involved. The better agreement noted for HGS reactions in general cannot therefore be attributed to an accident of stoicheiometry.

The following points are also noted. (*a*) At the STO-3G level, no matter whether standard geometry, experimental geometry, or STO-3G optimized geometry is used, the agreement between theory and experiment is very much the same, differing by at most a few kJ mol^{-1}. Hence it appears that the choice of geometry is not a major factor in computing reaction heats at this level of theory, provided the same geometry is used consistently for all reactant and product species. This observation could be of some importance in carrying out calculations involving compounds whose structure has not yet been determined experimentally, or where complete geometry optimization is not practical.

(*b*) Table 3 shows that neither IBS nor HGS reactions of unsaturated ring compounds are treated as adequately by the minimal STO-3G or even the extended 4—31G or 6—31G basis sets, although there is satisfactory agree-

TABLE 2

ΔH° Values for (i) the isodesmic bond separation reaction, and (ii) the homodesmotic group separation reaction of n-butane, but-1-ene, *trans*-but-2-ene, but-1-yne, but-2-yne, and buta-1,2-diene

Reaction	Experimental values (kJ mol^{-1})			Theoretical values (kJ mol^{-1})		$\Delta H^\circ_{\mathrm{CALC}} - (\Delta H^\circ_0)_{\mathrm{ZPE}}$
	ΔH°_{298}	ΔH°_0	$(\Delta H^\circ_0)_{\mathrm{ZPE}}$	Basis	$\Delta H^\circ_{\mathrm{CALC}}$	
n-Butane						
(i) $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 + 2CH_4 \longrightarrow 3CH_3{\cdot}CH_3$	$+22.6 \pm 2.9$	+26.4	+18.8	IBMOL	−1.3	−20.1
				6–31G*(E)	+2.5	−16.3
				STO–3G(D)	+2.9	−15.9
				STO–3G(A)	+3.8	−14.6
				STO–4G(A)	+4.2	−14.2
				4–31G(E)	+6.7	−12.1
				6–31G(E)	+7.1	−11.3
				STO–3G(C)	+7.5	−11.3
				DZ	+14.6	−3.8
(ii) $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 + CH_3{\cdot}CH_3 \longrightarrow 2CH_3{\cdot}CH_2{\cdot}CH_3$	$+3.8 \pm 2.5$	+5.9	+5.9	IBMOL	+58.6	+52.3
				4–31G(E)	−2.5	−8.4
				STO–3G(C)	−2.1	−7.9
				STO–3G(D)	−2.1	−7.9
				6–31G*(E)	−1.3	−7.5
				6–31G(E)	−1.3	−7.1
				STO–3G(A)	−0.4	−6.3
But-1-ene						
(i) $CH_3{\cdot}CH_2{\cdot}CH{=}CH_2 + 2CH_4 \longrightarrow 2CH_3CH_3 + CH_2{=}CH_2$	$+33.5 \pm 2.5$	+36.0	+29.7	IBMOL	−38.5	−67.8
				STO–3G(A)	−0.4	−30.1
				6–31G*(E)	+11.3	−18.4
				STO–3G(D)	+13.4	−16.3
				6–31G(E)	+17.6	−12.1
				4–31G(E)	+18.0	−11.7
				STO–3G(C)	+23.4	−6.3
(ii) $CH_3{\cdot}CH_2{\cdot}CH{=}CH_2 + CH_3{\cdot}CH_3 \longrightarrow CH_3{\cdot}CH_2{\cdot}CH_3 + CH_3{\cdot}CH{=}CH_2$	$+2.1 \pm 4.2$	+2.9	+2.5	STO–3G(A)	−20.5	−23.0
				STO–3G(D)	−7.5	−10.0
				6–31G*(E)	−6.7	−9.6
				6–31G(E)	−4.6	−7.5
				4–31G(E)	−4.2	−6.7
				STO–3G(C)	−0.8	−3.8
				IBMOL	+4.2	+1.7
trans-But-2-ene						
(i) $CH_3{\cdot}CH{=}CH{\cdot}CH_3 + 2CH_4 \longrightarrow 2CH_3{\cdot}CH_3 + CH_2{=}CH_2$	$+44.8 \pm 2.9$	+48.1	+41.0	IBMOL	−3.3	−44.5
				6–31G*(E)	+22.6	−18.8
				6–31G(E)	+28.5	−13.0
				4–31G(E)	+28.9	−12.6
				STO–3G(D)	+29.3	−11.7
				STO–3G(A)	+33.5	−7.5
				STO–3G(C)	+39.3	−2.1
(ii) $CH_3{\cdot}CH{=}CH{\cdot}CH_3 + CH_2{=}CH_2 \longrightarrow 2CH_3{\cdot}CH{=}CH_2$	$+1.3 \pm 2.5$	+2.1	0.0	IBMOL	+21.8	+21.8
				6–31G*(E)	−10.0	−10.0
				STO–3G(D)	−7.5	−7.5
				6–31G(E)	−7.5	−7.5
				4–31G(E)	−6.3	−6.3
				STO–3G(C)	−1.7	−1.7
				STO–3G(A)	−1.7	−1.7
But-1-yne [a]						
(i) $CH_3{\cdot}CH_2{\cdot}C{\equiv}CH + 2CH_4 \longrightarrow 2CH_3{\cdot}CH_3 + CH{\equiv}CH$	$+42.7 \pm 3.3$	+44.8	+38.0	STO–3G(D)	+27.6	−10.9
				6–31G(E)	+45.2	+6.7
				4–31G(E)	+42.7	+4.2
				STO–3G(A)	+36.0	−2.1
				6–31G*(E)	+36.8	−1.3
				STO–3G(C)	+37.7	−0.4
(ii) $CH_3{\cdot}CH_2{\cdot}C{\equiv}CH + CH_3{\cdot}CH_3 \longrightarrow CH_3{\cdot}CH_2{\cdot}CH_3 + CH_3{\cdot}C{\equiv}CH$	$+1.3 \pm 2.9$	+1.7	+1.3	STO–3G(D)	−10.0	−11.3
				6–31G(E)	+5.0	+3.8
				STO–3G(C)	−1.3	−2.5
				STO–3G(A)	+3.3	+2.1
				4–31G(E)	+2.1	+0.8
				6–31G*(E)	+1.3	0.0
But-2-yne [a]						
(i) $CH_3{\cdot}C{\equiv}C{\cdot}CH_3 + 2CH_4 \longrightarrow 2CH_3{\cdot}CH_3 + CH{\equiv}CH$	$+62.3 \pm 3.3$	+65.3	+58.2	6–31G(E)	+72.4	+13.8
				4–31G(E)	+69.9	+11.3
				STO–3G(A)	+67.4	+9.2
				STO–3G(C)	+67.4	+9.2
				6–31G*(E)	+64.0	+5.9
				STO–3G(D)	+57.3	+1.3

TABLE 2 (*Continued*)

Reaction	Experimental values (kJ mol^{-1})			Theoretical values (kJ mol^{-1})		$\Delta H^\circ_{CALC} - (\Delta H^\circ_0)_{ZPE}$
	ΔH°_{298}	ΔH°_0	$(\Delta H^\circ_0)_{ZPE}$	Basis	ΔH°_{CALC}	
(ii) $CH_3\cdot C\equiv C\cdot CH_3 + CH\equiv CH \longrightarrow 2CH_3\cdot C\equiv CH$	−1.3 ± 3.3	−0.4	−2.9	STO-3G(D)	−13.4	−10.5
				6-31G(E)	+0.4	+3.3
				4-31G(E)	−2.1	+1.3
				6-31G*(E)	−3.3	−0.4
				STO-3G(A)	−2.9	0.0
				STO-3G(C)	−2.9	0.0
Buta-1,2-diene [b]						
(i) $CH_3\cdot CH=C=CH_2 + 2CH_4 \longrightarrow CH_3\cdot CH_3 + 2CH_2=CH_2$	+7.1 ± 2.5	+8.8	+5.9	STO-3G(C)	+25.9	+20.1
				STO-4G(A)	+23.8	+18.0
				STO-3G(A)	+23.8	+18.0
				6-31G*(E)	−9.6	−15.5
				6-31G(E)	−5.9	−11.7
				4-31G(E)	−4.2	−10.5
(ii) $CH_3\cdot CH=C=CH_2 + CH_2=CH_2 \longrightarrow CH_2=C=CH_2 + CH_3\cdot CH=CH_2$	−2.9 ± 2.9	−2.5	−2.5	6-31G*(E)	−7.5	−5.0
				4-31G(E)	−7.1	−4.6
				6-31G(E)	−6.7	−4.2
				STO-3G(C)	−4.2	−1.7
				STO-3G(A)	−2.9	−0.4

[a] ZPE Values estimated; see Appendix. [b] ΔH°_f Values at 0 K and ZPE estimated; see Appendix.

TABLE 3

ΔH° Values for (i) the isodesmic bond separation reaction, and (ii) the homodesmotic group separation reaction of cyclopropane, cyclopropene, methylcyclopropane, methylenecyclopropane, cyclobutane, cyclobutene, and bicyclo[1.1.0]butane

Reaction	Experimental values			Theoretical values		$\Delta H^\circ_{CALC} - (\Delta H^\circ_0)_{ZPE}$
	ΔH°_{298}	ΔH°_0	$(\Delta H^\circ_0)_{ZPE}$	Basis	ΔH°_{CALC}	
Cyclopropane						
(i) $[CH_2]_3 + 3CH_4 \longrightarrow 3CH_3\cdot CH_3$	−82.8 ± 2.9	−77.0	−97.9	IBMOL	−271.1	−173.2
				STO-3G(B)	−202.1	−104.2
				STO-3G(D)	−188.3	−90.4
				4-31G(B)	−127.2	−29.3
				4-31G(E)	−115.9	−17.6
	−110.9 ± 3.8	−107.5	−117.2	6-31G(E)	−113.0	−15.1
				6-31G*(E)	−109.6	−11.3
				LEMAO-6G(B)	−109.6	−11.3
				DZ	−98.3	−0.4
(ii) $[CH_2]_3 + 3CH_3\cdot CH_3 \longrightarrow 3CH_3\cdot CH_2\cdot CH_3$	−169.9 ± 5.0	−162.8	−187.4	STO-3G(B)	−204.2	−87.0
				STO-3G(D)	−195.8	−78.7
				IBMOL	−181.6	−64.4
				4-31G(B)	−139.7	−22.6
				LEMAO-6G(B)	−131.8	−14.6
				4-31G(E)	−131.0	−13.8
				6-31G(E)	−125.5	−8.4
				6-31G*(E)	−115.5	+1.7
Cyclopropene						
(i) $C_3H_4 + 3CH_4 \longrightarrow 2CH_3\cdot CH_3 + CH_2=CH_2$	−222.6 ± 5.9	−218.8	−235.1	IBMOL	−315.5	−128.0
				STO-3G(B)	−276.6	−89.1
				STO-3G(D)	−274.5	−87.0
				4-31G(E)	−243.1	−55.6
				4-31G(B)	−242.7	−55.2
				6-31G(E)	−241.0	−53.6
				DZ	−234.3	−46.9
				LEMAO-6G(B)	−224.7	−37.2
				6-31G*(E)	−210.9	−23.4
(ii) $C_3H_4 + 2CH_3\cdot CH_3 + CH_2=CH_2 \longrightarrow CH_3\cdot CH_2\cdot CH_3 + 2CH_2=CH\cdot CH_3$				STO-3G(D)	−313.8	−78.7
				STO-3G(B)	−311.3	−76.1
				4-31G(E)	−282.4	−47.3
				4-31G(B)	−281.2	−46.0
				6-31G(E)	−281.2	−46.0
				LEMAO-6G(B)	−274.9	−39.7
				IBMOL	−260.2	−25.5
				6-31G*(E)	−245.2	−10.0
Methylcyclopropane						
(i) $C_4H_8 + 4CH_4 \longrightarrow 4CH_3\cdot CH_3$	−63.2 ± 4.6	−57.3 [a]	−78.7 [a]	IBMOL	−250.6	−197.1
				STO-3G(D)	−180.3	−102.1
				4-31G(E)	−107.9	−29.3
				6-31G(E)	−107.5	−28.9
				6-31G*(E)	−105.9	−27.6
(ii) $C_4H_8 + 3CH_3\cdot CH_3 \longrightarrow (CH_3)_3CH + 2CH_3\cdot CH_2\cdot CH_3$	−113.4 ± 4.6	−109.6 [a]	−119.7 [a]	IBMOL	−200.8	−81.2
				STO-3G(D)	−187.9	−68.2
				4-31G(E)	−125.5	−5.9
				6-31G(E)	−125.1	−5.4
				6-31G*(E)	−114.1	+5.4

TABLE 3 (*Continued*)

Reaction	Experimental values			Theoretical values		$\Delta H^\circ_{\mathrm{CALC}} - (\Delta H^\circ_0)_{\mathrm{ZPE}}$
	ΔH°_{298}	ΔH°_0	$(\Delta H^\circ_0)_{\mathrm{ZPE}}$	Basis	$\Delta H^\circ_{\mathrm{CALC}}$	
Methylenecyclopropane						
(i) $C_4H_6 + 4CH_4 \longrightarrow CH_2{=}CH_2 + 3CH_3{\cdot}CH_3$	−102.9 ± 5.0	−96.7[a]	−119.7[a]	STO-3G(D)	−193.7	−74.1
				6-31G(E)	−136.0	−16.3
				4-31G(E)	−135.6	−15.9
				6-31G*(E)	−131.0	−11.3
(ii) $C_4H_6 + 3CH_3{\cdot}CH_3 \longrightarrow (CH_3)_2C{=}CH_2 + 2CH_3{\cdot}CH_2{\cdot}CH_3$	−172.0 ± 5.0	−168.2[a]	−181.2[a]	STO-3G(D)	−227.2	−46.0
				6-31G*(E)	−158.6	+23.0
				6-31G(E)	−174.1	+7.1
				4-31G(E)	−174.5	+6.7
Cyclobutane						
(i) $[CH_2]_4 + 4CH_4 \longrightarrow 4CH_3{\cdot}CH_3$	−67.8 ± 3.8	−61.9	−85.4	STO-3G(D)	−113.8	−28.5
				6-31G*(E)	−102.9	−17.6
				4-31G(E)	−100.4	−15.1
				6-31G(E)	−100.0	−14.6
(ii) $[CH_2]_4 + 4CH_3{\cdot}CH_3 \longrightarrow 4CH_3{\cdot}CH_2{\cdot}CH_3$	−105.0 ± 5.0	−102.5	−110.9	STO-3G(D)	−123.4	−13.0
				4-31G(E)	−118.4	−7.5
				6-31G(E)	−116.7	−5.9
				6-31G*(E)	−110.9	0.0
Cyclobutene						
(i) $C_4H_6 + 4CH_4 \longrightarrow 3CH_3{\cdot}CH_3 + CH_2{=}CH_2$	−59.4 ± 4.6	−52.3[a]	−79.5[a]	IBMOL	−163.6	−84.1
				STO-3G(D)	−117.6	−38.1
				6-31G(E)	−113.4	−34.3
				4-31G(E)	−113.0	−33.5
				6-31G*(E)	−98.3	−19.2
(ii) $C_4H_6 + CH_2{=}CH_2 + 3CH_3{\cdot}CH_3 \longrightarrow 2CH_3{\cdot}CH_2{\cdot}CH_3 + 2CH_3{\cdot}CH{=}CH_2$	−121.8 ± 5.9	−118.4[a]	−133.1[a]	IBMOL	−78.7	+54.4
				STO-3G(D)	−159.4	−25.9
				6-31G(E)	−157.7	−24.3
				4-31G(E)	−156.9	−23.8
				6-31G*(E)	−134.7	−1.7
Bicyclo[1.1.0]butane						
(i) $C_4H_6 + 6CH_4 \longrightarrow 5CH_3{\cdot}CH_3$	−191.6 ± 5.9	−179.5[a]	−222.2[a]	STO-3G(D)	−440.6	−218.4
				4-31G(E)	−306.7	−84.5
				6-31G(E)	−306.3	−84.5
				DZ	−282.8	−60.7
				6-31G*(E)	−266.9	−44.8
(ii) $C_4H_6 + 5CH_3{\cdot}CH_3 \longrightarrow 2(CH_3)_3CH + 2CH_3{\cdot}CH_2{\cdot}CH_3$	−272.8 ± 5.4	−266.1[a]	−285.3[a]	STO-3G(D)	−449.8	−164.8
				6-31G(E)	−333.0	−47.7
				4-31G(E)	−332.6	−47.3
				6-31G*(E)	−279.5	+5.4

[a] Estimated values; see Appendix.

ment in the case of acyclic olefins (and acetylenes) and the corresponding saturated ring structures. The results for methylenecyclopropane, with its exocyclic double bond, are significant in this connection. The agreement with experiment is better in this case, which indicates that it is not solely a question of a C[3] carbon atom in the ring, but a pair of C[3] carbon atoms, with the concomitant formation of the double bond. As the total molecular energies become available, it will be of interest to see whether cyclopentene and cyclohexene show the same behaviour. Since the conventional ring strain energy is much less in these larger molecules, better agreement might be anticipated. The inclusion of polarization functions on the carbon atoms in the 6—31G* basis set improves the agreement between theory and experiment in the isodesmic bond separation reactions for cyclopropene and cyclobutene, but the convergence is clearly slow.

C_6 *and Larger Molecules.*—Since few total molecular energies have been calculated for these larger molecules any comparison of reaction heats is unavoidably limited in scope. Furthermore, for the benzenoid hydrocarbons, not only is the energy of s-*trans*-buta-1,3-diene needed for the HGS reactions * but also the energy for reference structures containing a quaternary C[3] carbon atom, *i.e.* isobutene [$(CH_3)_2C{=}CH_2$]. Values for either or both of these compounds have not yet been calculated in many of the basis sets. The comparison of theoretical and experimental reaction heats in Table 4 has therefore been amplified by including 90°-buta-1,3-diene and s-*trans,trans*,s-*trans*-hexa-1,3,5-triene as reference compounds in some instances, and, in addition, by including values for isodesmic fission reactions of the first kind.

Out of the seven cases where a comparison between IBS and HGS values can be made, the agreement between theory and experiment is better for the HGS reactions only for the acyclic s-*trans,trans*,s-*trans*-hexa-1,3,5-triene. For the remaining cases, benzene and styrene, the agreement is better for the IBS reactions: but the discrepancies are much larger for both IBS and HGS reactions of these aromatic compounds than for any of the C_4 compounds in Tables 2 and 3. Moreover in five of the six cases only the minimal STO-3G basis set is involved. With the present results the sign of

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* The homodesmotic reaction involving s-*trans*-buta-1,3-diene, the group separation reaction defined above, is the reaction employed in our previous papers to evaluate stabilization energies, HSE.[5–7]

TABLE 4

ΔH° Values for (i) the isodesmic bond separation reaction, (ii) an isodesmic fission reaction, (iii) the homodesmotic group separation reaction, and (iv) a homodesmotic fission reaction of s-*trans*,*trans*,s-*trans*-hexa-1,3,5-triene, benzene, styrene, naphthalene, and anthracene

Reaction	Experimental values (kJ mol^{-1})			Theoretical values (kJ mol^{-1})		ΔH°_{CALC} − $(\Delta H^\circ_0)_{ZPE}$
	ΔH°_{298}	ΔH°_0	$(\Delta H^\circ_0)_{ZPE}$	Basis	ΔH°_{CALC}	
(A) Aliphatic						
s-*trans*,*trans*,s-*trans*-Hexa-1,3,5-triene						
(i) $C_6H_8 + 3CH_4 \longrightarrow 2CH_3{\cdot}CH_3 + 3CH_2{=}CH_2$	+120.9 ± 5.0	+125.9	+111.7	FSGO	−545.2	−656.9
				STO–3G(B)	+85.4	−26.4
(iii) $C_6H_8 + CH_2{=}CH_2 \longrightarrow 2CH_2{=}CH{\cdot}CH{=}CH_2$	+1.3 ± 3.3	+1.7	−1.3	STO–3G(B)	−15.1	−13.8
(B) Aromatic						
Benzene						
(i) $C_6H_6 + 6CH_4 \longrightarrow 3CH_3{\cdot}CH_3 + 3CH_2{=}CH_2$	+268.6 ± 5.0	+275.3	+255.6	FSGO	−962.3	−1 218.4
				LEMAO–6G(B)	+328.4	+72.8
				STO–3G(A)	+315.5	−59.8
				STO–4G(A)	+312.1	+56.5
				STO–3G(B)	+301.2	+45.2
				LCGO	+276.1	+20.5
				4–31G(B)	+272.8	+16.7
				IBMOL	+267.8	+12.1
(iii) $C_6H_6 + 3CH_2{=}CH_2 \longrightarrow 3(\text{s-}trans\text{-})CH_2{=}CH{\cdot}CH{=}CH_2$	+88.7 ± 3.3	+89.1	+86.6	FGGL	+166.1	+79.5
				STO–3G(A)	+156.9	+69.9
				STO–4G(A)	+156.1	+69.5
				STO–3G(B)	+150.6	+64.0
				STO–3G(C)	+141.4	+54.8
				[4*s*2*p*/2*s*] [c]	+136.0	+49.4
				4–31G(B)	+112.1	+25.5
(iii) $C_6H_6 + 3CH_2{=}CH_2 \longrightarrow 3(90^\circ)CH_2{=}CH{\cdot}CH{=}CH_2$ [a]	+178.7 ± 12.6	+178.7	+176.6	STO–3G(A)	+240.2	+63.6
				STO–3G(C)	+225.9	+49.4
				LCGO	+212.5	+36.0
(iii) $C_6H_6 + \frac{3}{2}CH_2{=}CH_2 \longrightarrow \frac{3}{2}CH_2{=}CH{\cdot}CH{=}CH{\cdot}CH{=}CH_2$	+87.0 ± 3.8	+86.2	+88.3	FSGO	−144.8	−233.0
				STO–3G(B)	+172.8	+84.5
Styrene [b]						
(i) $C_6H_5{\cdot}CH{=}CH_2 + 8CH_4 \longrightarrow 4CH_3{\cdot}CH_3 + 4CH_2{=}CH_2$	+320.9 ± 7.1	+330.5	+304.6	STO–3G(A)	+358.6	+54.0
(ii) $C_6H_5{\cdot}CH{=}CH_2 + 4CH_2{=}CH_2 \longrightarrow 4CH_2{=}CH{\cdot}CH{=}CH_2$	+80.8 ± 5.4	+82.0	+79.1	STO–3G(A)	+146.9	+68.2
(ii) $C_6H_5{\cdot}CH{=}CH_2 + 4CH_2{=}CH_2 \longrightarrow 4(90^\circ)CH_2{=}CH{\cdot}CH{=}CH_2$	+200.8 ± 17.2	+201.7	+199.2	STO–3G(A)	+258.2	+59.4
				LCGO	+208.4	+9.6
(iii) $C_6H_5{\cdot}CH{=}CH_2 + 3CH_2{=}CH_2 + 2CH_3{\cdot}CH{=}CH_2 \longrightarrow 4CH_2{=}CH{\cdot}CH{=}CH_2 + (CH_3)_2C{=}CH_2$	+745.5 ± 6.7	+74.5	+74.5	STO–3G(A)	+146.4	+71.5
Naphthalene						
(i) $C_{10}H_8 + 12CH_4 \longrightarrow 6CH_3{\cdot}CH_3 + 5CH_2{=}CH_2$	+499.6 ± 9.6	+517.1	+472.0	FSGO	−2 082.8	−2 554.8
				LCGO	+484.5	+15.9
(ii) $C_{10}H_8 + 7CH_2{=}CH_2 \longrightarrow 6(\text{s-}trans)CH_2{=}CH{\cdot}CH{=}CH_2$	+140.2 ± 7.9	+144.3	+133.9	FGGL	+277.8	+143.9
(ii) $C_{10}H_8 + 7CH_2{=}CH_2 \longrightarrow 6(90^\circ)CH_2{=}CH{\cdot}CH{=}CH_2$ [a]	+319.7 ± 25.5	+313.4	+313.4	LCGO	+356.9	+43.5
(ii) $C_{10}H_8 + 4CH_2{=}CH_2 \longrightarrow 3CH_2{=}CH{\cdot}CH{=}CH{\cdot}CH{=}CH_2$	+136.8 ± 7.9	−138.9	+137.2	FSGO	−447.7	−584.9
Anthracene						
(i) $C_{14}H_{10} + 18CH_4 \longrightarrow 9CH_3{\cdot}CH_3 + 7CH_2{=}CH_2$	+718.8 ± 17.2	+746.0	+673.6	FSGO	−3 329.6	−4 003.7
(ii) $C_{14}H_{10} + \frac{13}{2}CH_2{=}CH_2 \longrightarrow \frac{9}{2}CH_2{=}CH{\cdot}CH{=}CH{\cdot}CH{=}CH_2$	174.5 ± 15.1	178.7	185.8	FSGO	−876.5	−1 062.3

[a] $H^\circ_{298} - H^\circ_0$ and ZPE for 90°-buta-1,3-diene taken to be the same as for s-*trans*-buta-1,3-diene. [b] ΔH°_f at 0 K and ZPE estimated; see Appendix. [c] The ethylene energy used was from the [4*s*3*p*/2*s*] basis set.

$[\Delta H^\circ_{CALC} - (\Delta H^\circ_0)_{ZPE}]$ is probably of greater significance than whether the agreement is better for one or the other of the two reactions, a point which will be taken up later in the discussion.*

The better agreement that can be expected as a consequence of the cancellation of extraneous energy terms is nevertheless demonstrated by the results for benzene, naphthalene, and anthracene using total molecular energies calculated by Christoffersen's molecular fragment method.[17,18] In the absence of the energy for s-*trans*-1,3-butadiene, s-*trans*,*trans*,s-*trans*-hexa-1,3,5-triene has been utilized in corresponding

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* The symbol $(\Delta H^\circ_0)_{ZPE}$ denotes the reaction heat at 0 K calculated from experimental ΔH°_f data at 298 K and $(H^\circ_{298} - H^\circ_0)$ values further corrected for the zero-point vibrational energies of reactants and products.

[17] R. E. Christoffersen, D. W. Genson, and G. M. Maggiora, *J. Chem. Phys.*, 1971, **54**, 239.

[18] R. E. Christoffersen, *J. Amer. Chem. Soc.*, 1971, **93**, 4104.

isodesmic fission reactions of the first kind. Although this basis set, FSGO, is quite restricted,[17] it has been shown to provide a satisfactory description of many aspects of molecular structure. But the total molecular energies are much less negative than the Hartree–Fock limit by *ca.* 15%, so less good agreement between theory and experiment is to be anticipated. Even so, the isodesmic fission reaction heats for benzene, naphthalene, and anthracene are more accurate than the IBS reaction heats by a factor of *ca.* 5 in each case. The agreement in the case of the isodesmic fission of the first kind for benzene (to within 210 kJ mol^{-1}, as compared with 125 kJ mol^{-1} for the STO-3G basis set) is surprising, in view of the fact that the total molecular energy is no less than 30 a.u., *i.e. ca.* 80 000 kJ mol^{-1}, more positive.

TABLE 5

ΔH° Values for some homodesmotic and isodesmic reactions of benzene, naphthalene, and anthracene

	Experimental values (kJ mol^{-1})			Theoretical values (kJ mol^{-1})		
Reaction	ΔH°_{298}	ΔH°_0	$(\Delta H^\circ_0)_{ZPE}$	Basis	ΔH°_{CALC}	$\Delta H^\circ_{CALC} - (\Delta H^\circ_0)_{ZPE}$
(i) Homodesmotic isomerization						
naphthalene ⟶ azulene	$+156.9 \pm 5.0$		$+156.9$ [a]	FGSO	$+377.8$	$+221.3$
				FGGL	$+210.0$	$+53.6$
phenanthrene ⟶ anthracene	$+23.8 \pm 9.2$		$+23.8$ [a]	FGSO	$+9.6$	-14.2
(ii) Isodesmic isomerization						
benzene ⟶ fulvene	$+102.5 \pm 7.5$		$+102.5$ [a]	FGSO	$+308.8$	$+206.7$
				IBMOL	$+144.8$	$+42.7$
(iii) Homodesmotic reorganization						
benzene + anthracene ⟶ 2 naphthalene	-12.2 ± 5.0	-13.0	-14.6	FGSO	-126.8	-112.1
(iv) Isodesmic fission						
naphthalene + ethylene ⟶ 2 benzene	-37.2 ± 2.5	-35.1	-39.3	FGSO	-157.7	-118.4
				LCGO	-67.4	-28.0
				FGGL	-54.8	-15.1
anthracene + 2 ethylene ⟶ 3 benzene	-86.6 ± 7.1	-80.3	-93.3	FGSO	-442.2	-348.9

[a] $(\Delta H^\circ_0)_{ZPE}$ taken as identical with ΔH°_{298}; see Appendix for an estimation of the uncertainty.

Comparison of Theoretical and Experimental Reaction Heats for Isomerization, Reorganization, and Break-up Reactions of Benzene, Naphthalene, and Anthracene.—In view of the minimal structural changes that occur, the best agreement between theoretical and experimental reaction heats would be expected for homodesmotic isomerizations. Excellent agreement is obtained for the phenanthrene–anthracene reaction, even though energies from the limited FGSO basis set are used[19] (see Table 5). Agreement is not so good, however, for the naphthalene–azulene reaction, not only when FGSO energies are used but also when FGGL energies, which are similar in magnitude to those of the 4—31G basis set, are employed. But although both isomerizations are homodesmotic, in the former case both reactants and products are benzenoid, each characterized by a considerable stabilization energy, whereas, in the latter, although naphthalene is benzenoid, azulene is not, and has a much lower stabilization energy.[5] The possible significance of this structural distinction, which is beyond those involved in the homodesmotic criteria, will be taken up in the later discussion.

A corresponding change occurs in the benzene–fulvene isomerization, although in this case the reaction is not homodesmotic but an isodesmic reaction of the first kind. Comparison of theory and experiment shows just the same features as the naphthalene–azulene reaction, namely a sizeable positive difference. Experimental values are not yet available for the other two benzene isomers of this type, dimethylenecyclobutene and trimethylenecyclopropane.

The other 'valence' isomers of benzene (Dewar benzene, benzvalene, and prismane) differ in structure to such an extent that the isomerization reactions are no longer isodesmic. Reactions of this kind, which may be designated *anisodesmic*, will be treated in a forthcoming publication. In fact many isomerizations involve very deep-seated structural changes, especially those in which the molecules contain few heavy atoms. Even with the paraffins, where all the CC bonds are of the same formal type, at least a C_6 structure is needed to give an homodesmotic isomerization, *i.e.* 2-methylpentane ⟶ 3-methylpentane.

An equally interesting reaction of benzenoid hydrocarbons which is homodesmotic and has all the attributes of the homodesmotic isomerization, is a reorganization of the polycyclic structure, as exemplified by benzene + anthracene ⟶ 2 naphthalene. Agreement using the FGSO basis set is to within 110 kJ mol^{-1}, a marked improvement upon the differences for the other reactions using this basis set listed in Table 4. Yet the sum of the total molecular energies of the reactants or products in this case is well over 100 a.u. (*ca.* 262 000 kJ mol^{-1}) less negative than the Hartree–Fock limit. This kind of homodesmotic reaction is, of course, characterized by reactant and product species being exclusively aromatic.

A closely related reaction is the fission of the polycyclic benzenoid hydrocarbon yielding benzene, with the inclusion of the requisite number of ethylene molecules to complete the stoicheiometry. This type of reaction is another isodesmic fission reaction of the first kind. As can be seen in Table 5, the more extended basis sets LCGO and FGGL give excellent agreement for

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[19] R. E. Christoffersen, *Internat. J. Quantum Chem.*, 1973, Symp. **7**, 169.

the naphthalene reaction. Although reactants and products are not exclusively aromatic in reactions of this type the majority of the carbon atoms are present in aromatic structures.

TABLE 6

ΔH° Values for the isodesmic bond separation reaction of benzene broken down into four reaction pathways: (i) *via* propene, (ii) *via trans*-but-2-ene, (iii) *via* s-*trans*-buta-1,3-diene, and (iv) *via* buta-1,2-diene

	Experimental values (kJ mol^{-1})			Theoretical values (kJ mol^{-1})		
Reaction	ΔH°_{298}	ΔH°_0	$(\Delta H^\circ_0)_{ZPE}$	Basis	ΔH°_{CALC}	$\Delta H^\circ_{CALC} - (\Delta H^\circ_0)_{ZPE}$
(i) *via* Propene						
$C_6H_6 + 3CH_3{\cdot}CH_3 + 3CH_2{=}CH_2 \longrightarrow 6CH_2{=}CH{\cdot}CH_3$	+137.2 ± 7.5	+138.1	+132.2	IBMOL	+343.5	+211.3
				STO–3G(A)	+207.1	+74.9
				LEMAO–6G(B)	+201.3	+69.0
				STO–3G(B)	+199.6	+67.4
				STO–3G(C)	+192.9	+60.7
				STO–4G(A)	+191.2	+59.0
				4–31G(B)	+169.9	+37.7
$CH_2{=}CH{\cdot}CH_3 + CH_4 \longrightarrow CH_3{\cdot}CH_3 + CH_2{=}CH_2$	+21.8 ± 2.1	+23.0	+20.5	6–31G*(E)	+16.3	−4.2
				STO–3G(B)	+17.2	−3.8
				4–31G(B)	+17.2	−3.3
				STO–3G(A)	+17.6	−2.9
				STO–3G(D)	+17.6	−2.9
				6–31G(E)	+18.0	−2.9
				4–31G(E)	+19.7	−0.8
				STO—4G(A)	+20.1	−0.4
				STO–3G(C)	+20.5	+0.0
				LEMAO–6G(E)	+21.3	+0.4
				IBMOL	−12.6	+33.1
(ii) *via trans*-But-2-ene						
$C_6H_6 + 3CH_3{\cdot}CH_3 \longrightarrow 3CH_3{\cdot}CH{=}CH{\cdot}CH_3$	+133.5 ± 4.2	+131.0	+132.2	IBMOL	+278.2	+146.0
				STO–3G(A)	+214.6	+82.4
				STO–3G(C)	+197.5	+65.3
$CH_3{\cdot}CH{=}CH{\cdot}CH_3 + 2CH_4 \longrightarrow 2CH_3{\cdot}CH_3 + CH_2{=}CH_2$	+44.8 ± 2.9	+48.1	+41.0	IBMOL	−3.3	−44.8
				6–31G*(E)	+22.6	−18.8
				6–31G(E)	+28.5	−13.0
				4–31G(E)	+28.9	−12.6
				STO–3G(D)	+29.3	−11.7
				STO–3G(A)	+33.5	−7.5
				STO–3G(C)	+39.3	−2.1
(iii) *via* s-*trans*-Buta-1,3-diene						
$C_6H_6 + 3CH_2{=}CH_2 \longrightarrow 3CH_2{=}CH{\cdot}CH{=}CH_2$	+88.7 ± 3.8	+89.1	+86.6	FGGL	+166.1	+79.5
				STO–3G(A)	+156.9	+69.9
				STO–4G(A)	+150.6	+64.0
				STO–3G(C)	+141.4	+54.8
				[4*s*2*p*/2*s*] [b]	+136.0	+49.4
				4–31G(B)	+112.1	+25.5
$CH_2{=}CH{\cdot}CH{=}CH_2 + 2CH_4 \longrightarrow CH_3{\cdot}CH_3 + 2CH_2{=}CH_2$	+59.8 ± 2.5	+62.3	+56.5	6–31G*(E)	+46.9	−9.6
				6–31G(E)	+48.5	−7.9
				4–31G(E)	+49.8	−6.7
				STO–3G(B)	+50.2	−6.3
				STO–4G(A)	+51.9	−4.2
				4–31G(B)	+53.6	−2.9
				STO–3G(A)	+54.0	−2.5
				STO–3G(C)	+58.2	+2.1
(iv) *via* Buta-1,2-diene [a]						
$C_6H_6 + 3CH_2{=}CH_2 \longrightarrow 3CH_3{\cdot}CH{=}C{=}CH_2$	+247.7 ± 3.8	+248.5	+237.7	STO–3G(A)	+243.5	+5.9
				STO–4G(A)	+240.2	+2.5
				STO–3G(C)	+237.2	−0.4
$CH_3{\cdot}CH{=}C{=}CH_2 + 2CH_4 \longrightarrow CH_3{\cdot}CH_3 + 2CH_2{=}CH_2$	+7.1 ± 2.5	+8.8	+5.9	STO–3G(C)	+25.9	+20.1
				STO–4G(A)	+23.8	+18.0
				STO–3G(A)	+23.8	+18.0
				6–31G*(E)	−9.6	−15.5
				6–31G(E)	−5.9	−11.7
				4–31G(E)	−4.2	−10.5

[a] ΔH°_f at 0 K and ZPE estimated; see Appendix. [b] See footnote *c*, Table 4.

Against the background of these results involving some of the largest molecules for which *ab initio* total molecular energies have yet been calculated, those for the IBS and HGS reactions of benzene in Table 4 provide an instructive contrast. In these reactions there is no retention of aromatic structure, the products being exclusively acyclic and aliphatic. Hehre and Pople[4,16] have drawn attention to the excellent agreement obtained for the IBS reaction to within 13 kJ mol^{-1} at the 4—31G level. But, as the results in Table 4 show, the agreement is as good if not better with the IBMOL energies, which are appreciably more positive than those at the 4—31G level, while with the LEMAO-6G basis set, which gives energies even more negative than those at the 4—31G level, the agreement is considerably worse. This somewhat haphazard behaviour suggests that opposing factors may be contributing to the closeness of the agreement between theory and experiment.

To examine this possibility in greater detail, the IBS reaction for benzene has been broken down into two steps, thereby diminishing the influence in each of the rather drastic structural changes that characterize the overall reactions (see Table 6). In the first, a C_3 or C_4 acyclic intermediate is formed, and in the second this smaller less complicated structure is made to undergo the IBS reaction. Examination of the structural changes which occur in the first step reveals that the propene and *trans*-but-2-ene reactions are examples of an isodesmic fission reaction of the second kind. The reaction giving buta-1,2-diene, on the other hand, comes into the same category of poorly matched reactions as the overall IBS reaction.

The most striking feature about the propene, *trans*-but-2-ene and s-*trans*-buta-1,3-diene reactions is the relatively poor agreement for the first step, in contrast to the excellent agreement with all but the IBMOL basis set for the second. The differences $[\Delta H^{\circ}_{\mathrm{CALC}} - (\Delta H^{\circ}_{0})_{\mathrm{ZPE}}]$ are for the majority of basis sets positive for the first reaction, but negative for the second. The extent of the agreement for the final step closely parallels the agreement obtained for the overall IBS reaction of the benzene. The far better agreement for the IBS reactions of propene and s-*trans*-buta-1,3-diene is but a replication of that already noted for *trans*-but-2-ene and the other C_3 and C_4 structures in Tables 2 and 3.

The stepwise breakdown of the overall IBS reaction for benzene nevertheless shows that the excellent agreement obtained at the extended 4—31G level is also, at least in part, the result of compensating factors, since the agreement is again not so good for the breakdown into C_3 or C_4 intermediates as it is for the overall IBS reaction. For propene and *trans*-but-2-ene the agreement is to within 37.7 and 25.5 kJ mol^{-1} for the first step, as compared with *ca.* 15 kJ mol^{-1} for the overall reaction. Even though the agreement is really good for the IBS reactions of the C_3 and C_4 intermediates, the differences $[\Delta H^{\circ}_{\mathrm{CALC}} - (\Delta H^{\circ}_{0})_{\mathrm{ZPE}}]$ are opposite in sign for the breakdown of these aliphatic intermediates, and so, with the stoicheiometric coefficients taken into account, substantial compensation occurs.

The exceptionally good agreement noted with the IBMOL basis set can be seen to arise through fortuitous rather than systematic compensation. The differences are much larger and opposite in sign, *i.e.* +33.0 and −44.8 kJ mol^{-1} for the IBS reactions of the simpler propene and *trans*-but-2-ene, respectively, as compared with the small negative values obtained with almost all the other basis sets.

Discussion.—With the exception of the three isomerization reactions benzene ⟶ fulvene, naphthalene ⟶ azulene, and phenanthrene ⟶ anthracene, the other fifty-three reactions of twenty different compounds dealt with in this paper follow the same general pattern, large molecule(s) + small molecule(s) ⟶ other smaller molecules. These reactions, in turn, fall into four groups: (*a*) those in which both reactants and products are simple chain molecules (Table 2): (*b*) those in which the large reactant molecule has a ring structure and is destabilized (Table 3): (*c*) those in which the large molecule is aromatic and thereby stabilized but not the products (Tables 4 and 5): and (*d*) those in which there is either complete or extensive retention of the benzenoid structure, and both reactant and product species are stabilized (Table 6). With this broad classification in mind, we now compare the agreement between theoretical and experimental reaction heats from the point of view of the basis set employed. For brevity we use the symbol $\delta\Delta H^{\circ}$ to denote the difference $[\Delta H^{\circ}_{\mathrm{CALC}} - (\Delta H^{\circ}_{0})_{\mathrm{ZPE}}]$.

(i) For reactions of type (*a*) the agreement does not appear to depend significantly on the particular choice of basis set. In the main $\delta\Delta H^{0}$ ranges from 4 to 17 kJ mol^{-1} for the IBS reactions and from 4 to 9 kJ mol^{-1} for the HGS reactions. Moreover, the minimal basis sets IBMOL and STO-3G often give as good if not better agreement than the more extended basis sets 4—31G and DZ, even those including polarization functions, 6—31G*. This behaviour is similar to that noted by Veillard [15] for calculations of the height of the barrier to rotation in ethane (staggered CH_3CH_3 ⟶ eclipsed CH_3CH_3), a conformational change which by necessity is an homodesmotic reaction. Veillard proposes that the less sophisticated calculations benefit from a slight cancellation of errors arising through the simultaneous neglect of polarization functions and geometry optimization, and we suggest that this is also the reason for the good agreement in the case of type (*a*) reactions.

(ii) By contrast, for the reactions of both types (*b*) and (*c*) more extended basis sets are needed to give as good agreement. Furthermore for type (*b*) there is a close parallelism between the results for the IBS and HGS reactions. When agreement is poor for the IBS reactions it is also poor for the HGS reactions, although usually to a lesser extent. Since all but the large molecules in these reactions are the small chain molecules with which good agreement was found in type (*a*) reactions, these observations suggest that larger basis sets are necessary to give molecular energies of comparable accuracy for the aliphatic and aromatic ring structures.

(iii) It does not appear, however, to be solely a question of ring structure that leads to poor agreement for type (*b*) reactions with the minimal basis sets, but rather one of ring size. Few molecular energies are available for aliphatic molecules larger than C_4, but for cyclopentane the agreement using STO-3G (C) is as good as that for type (*a*) reactions in general, $\delta\Delta H^{\circ}$ having the values −18.0 and −5.4 kJ mol^{-1} for IBS and HGS reactions respectively. Moreover these values compare favourably with $\delta\Delta H^{\circ} = -11.7$ kJ mol^{-1} for the IBS reaction of neopentane with the more extended DZ basis set.[20] Cyclopentane, as is well known, is destabilized to a considerably lesser extent than the C_3 and C_4 ring structures. For example in the case of C_3, C_4, and C_5 cycloparaffins the homodesmotic destabilization energies are 110.9, 105.0, and 18.8 kJ mol^{-1},

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[20] L. C. Snyder, personal communication.

respectively, and for the corresponding mono-olefins 222.6, 121.8, and 18.8 kJ mol^{-1}, respectively.[9] The less good agreement is thus found with ring structures that are subject to greater 'ring strain', *i.e.* greater destabilization.

(iv) It is surprising to find $\delta\Delta H^\circ$ having such large positive values when the minimal basis sets are used for benzene and benzenoid hydrocarbon reactions in Table 5, reactions which are all of type (*c*). Since equation (i)

$$\delta\Delta H^\circ = \Sigma E(\text{products}) - \Sigma E(\text{reactants}) - (\Delta H^\circ_0)_{\text{ZPE}} \quad \text{(i)}$$

applies provided that the energies of the small molecules are consistent values, which seems to be substantiated by the good agreement found for the type (*a*) reactions, then a positive value for $\delta\Delta H^\circ$ implies a relatively more negative total energy for benzene as compared with the energies of the small molecules that take part in the various reactions. This same feature, $\delta\Delta H^\circ$ positive, is still present, although not so pronounced, in the results obtained by using the more extended basis sets. It could well be that cancellation of some kind, although different in detail from that inferred by Veillard in connection with the calculation of barrier heights for ethane, is involved in the calculation procedure for aromatic atructures.

(v) In this context the better agreement noted for the reactions of type (*d*), in which there is either complete or extensive retention of benzenoid structure, as compared with that for type (*c*), in which the benzenoid structure is destroyed, gains added significance. With reactants and products exclusively benzenoid, the possibility of cancellation occurring between factors tending to give anomalous values for aromatic molecules would presumably be optimized.

TABLE 7

Compound	ΔH°_f(298 K) [a]/ kJ mol^{-1}	ΔH°_f(0 K) [b]/ kJ mol^{-1}	Zero-point vibrational energy (kJ mol^{-1})
Methane	-74.85 ± 0.29	-66.90	113.34 [e(1)]
Ethane	-84.69 ± 0.50	-69.12	189.33 [e(1)]
Ethylene	$+52.09 \pm 0.42$	$+60.58$	129.20 [e(1)]
Acetylene	$+227.36 \pm 0.79$	$+227.94$	67.70 [e(1)]
Propane	-103.89 ± 0.59	-81.55	261.46 [e(1)]
Propene	$+20.42 \pm 0.67$	$+35.44$	202.84 [e(2)]
Propyne	$+185.73 \pm 0.89$	$+192.84$	141.42 [e(1)]
Allene	$+190.92 \pm 1.13$	$+199.58$	144.47 [e(2)]
Butane (staggered)	-127.03 ± 0.67	-99.91	334.39 [e(1)]
But-1-ene	-0.84 ± 0.54	$+20.04$	274.68 [f(1)]
trans-But-2-ene	-12.51 ± 0.75	$+8.03$	274.22 [f(2)]
2-Methylpropene	-17.82 ± 0.63	$+3.18$	273.72 [f(2)]
s-*trans*-Buta-1,3-diene	$+109.24 \pm 0.63$	$+123.68$	215.22 [e(1)]
Buta-1,2-diene	$+162.26 \pm 0.59$	$+176.94$ [c]	218.15 [g]
But-1-yne	$+165.23 \pm 0.88$	$+178.87$	213.17 [h]
But-2-yne	$+145.23 \pm 0.84$	$+158.28$	212.71 [h]
Neopentane	-168.49 ± 1.05	-133.47	399.40 [f(3)]
Hexa-1,3,5-triene	$+165.31 \pm 1.67$	$+185.06$ [d]	298.40 [e(3)]
Cyclopropane	$+53.26 \pm 0.59$	$+70.21$	206.77 [e(1)]
Cyclopropene	$+276.98 \pm 2.51$	$+285.68$	143.01 [e(4)]
Cyclobutane	$+28.37 \pm 0.59$	$+52.97$	280.50 [e(1)]
Cyclopentane	-77.15 ± 0.84	-44.60	356.73 [e(5)]
Benzene	$+82.89 \pm 0.54$	$+100.37$	255.81 [e(1)]
Styrene	$+147.70 \pm 1.05$	$+170.50$ [c]	341.16 [g]
Naphthalene	$+150.83 \pm 1.05$	$+173.80$ [d]	376.56 [e(6)]
Anthracene	$+230.96 \pm 4.60$	$+260.29$ [d]	495.89 [e(7)]

[a] Values taken from Cox and Pilcher,[21] except that for s-*trans*,*trans*,s-*trans*-hexa-1,3,5-triene which has been calculated to be $+39.51 \pm 1.67$ kJ mol^{-1} from the heat of hydrogenation of -79.43 ± 0.22 kcal mol^{-1} reported by Turner *et al.*,[22] assuming that the solution heats of the hexatriene and n-hexane in acetic acid are identical. Despite this assumption, which might introduce an error of *ca.* 1 kcal, this ΔH°_f value is probably more reliable than that of $+34.34 \pm 3.0$ kcal mol^{-1} based on the combustion data of Kreysig *et al.*,[23] since the value of the enthalpy of evaporation employed in their calculation, 61.4 cal g^{-1} $\equiv$ 4.91 kcal mol^{-1},[24] appears unrealistically low for a C_6 hydrocarbon. Empirical equations for ΔH°_v based on the boiling point [21] gives values of *ca.* 8.3 kcal mol^{-1} and thus ΔH°_f of *ca.* 37.7, much more in keeping with the value obtained from the hydrogenation data. [b] Values calculated by using the increments [ΔH°_f (298 K) $-$ ΔH°_f (0 K)] given by Rossini *et al.*,[25] or API Research Project No. 44,[26] except for the compounds specified in footnotes *c* and *d*. [c] ΔH°_f Value for buta-1,2-diene at 0 K estimated by adding the mean of the increments $\Delta H^\circ_{298} - \Delta H^\circ_0$ for (propene minus ethylene) and for (propyne minus acetylene) to that for allene. [d] $H^\circ_{298} - H^\circ_0$ Value calculated by using the standard thermodynamic equations [27] and the fundamental vibrational frequencies listed in footnote e(3), (6), and (7). [e] Calculated by using the assignment of fundamental vibrational frequencies given by (1) Shimanouchi,[28] (2) Herzberg,[29] (3) Popov and Kogan,[30] (4) Eggers *et al.*,[31] Miller and Inskeep,[32] (6) Zhirnov,[33] and (7) Krainov.[34] [f] Following Cottrell,[35] and adding an arbitrary 200 wavenumbers for each torsional oscillation, values have been calculated from the assignment of fundamental frequencies given by (1) Aston *et al.*,[36] (2) Kilpatrick and Pitzer,[37] and (3) Pitzer and Kilpatrick.[38] [g] A value for buta-1,2-diene has been estimated by adding the mean of the increments (propene minus ethylene) and (propyne minus acetylene) to that for allene, and a value for styrene by adding the increment (but-1-ene minus ethane) to that for benzene. [h] Values for but-1-yne and but-2-yne have been evaluated by adding the increments (but-1-ene minus ethylene) and (but-2-ene minus ethylene), respectively, to that for acetylene.

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[21] J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, New York, 1970.

[22] R. B. Turner, B. J. Mallon, M. Tichy, W. von E. Doering, W. R. Roth, and G. Schroder, *J. Amer. Chem. Soc.*, 1973, **95**, 8605.

[23] Von D. Kreysig, R. Friebe, H. Aparowsky, and J. Schirmer, *J. prakt. Chem.*, 1968, **37**, 329.

[24] G. F. Woods and L. H. Schwartzman, *J. Amer. Chem. Soc.*, 1948, **70**, 3394.

[25] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimental, 'Selected Values of Properties of Hydrocarbons and Related Compounds,' Carnegie Press, Pittsburgh, 1953.

[26] 'Selected Values of Properties of Hydrocarbons and Related Compounds,' American Petroleum Institute Research Project No. **44**, Thermodynamics Research Center, Texas A and M University, 1975.

[27] G. J. Janz, 'Estimation of Thermodynamic Properties of Organic Compounds,' Academic Press, New York, 1968.

[28] T. Shimanouchi, 'Tables of Molecular Vibrational Frequencies,' NSRDS-NBS 6, 11, 17, U.S. Government Printing Office, Washington, D.C.

[29] G. Herzberg, 'Electronic Spectra of Polyatomic Molecules,' Van Nostrand, Princeton, 1965.

[30] E. M. Popov and G. A. Kogan, *Optics and Spectroscopy*, 1964, **16**, 532.

[31] D. F. Eggers, J. W. Schultz, K. B. Wiberg, E. L. Wagner, L. M. Jackson, and R. L. Erskine, *J. Chem. Phys.*, 1967, **47**, 946.

[32] F. A. Miller and R. G. Inskeep, *J. Chem. Phys.*, 1958, **18**, 1519.

[33] N. I. Zhirnov, *Optics and Spectroscopy*, 1960, **9**, 385.

[34] E. P. Krainov, *Optics and Spectroscopy*, 1964, **16**, 532.

[35] T. L. Cottrell, *J. Chem. Soc.*, 1948, 1448.

[36] J. G. Aston, G. Szasz, H. W. Wooley, and F. G. Brickwedde, *J. Chem. Phys.*, 1946, **14**, 67.

[37] J. E. Kilpatrick and K. S. Pitzer, *J. Res. Nat. Bur. Stand.*, 1947, **38**, 191.

[38] K. S. Pitzer and J. E. Kilpatrick, *Chem. Rev.*, 1946, **39**, 435.

(vi) We conclude that the closeness of agreement between theory and experiment depends not only on the matching of structural features in accord with the requirements of isodesmic and homodesmotic reactions, but also as to whether reactant or product species are markedly stabilized or destabilized with respect to each other.

APPENDIX

Experimental reaction heats have been calculated from the data listed in Table 7. Values of ΔH°_0 and $(\Delta H^\circ_0)_{ZPE}$ for the IBS and HGS reactions of methylcyclopropane, methylenecyclopropane, cyclobutene, and bicyclo[1.1.0]butane have been estimated by using the increments $[\Delta H^\circ_{298} - \Delta H^\circ_0]$ and $[\Delta H^\circ_0 - (\Delta H^\circ_0)_{ZPE}]$ from the reactions for similar ring compounds, *viz.* methylcyclopropane minus the cyclopropane values, methylenecyclopropane minus the mean of the cyclopropane and cyclopropene values, bicyclo[1.1.0]butane minus twice the cyclopropane values, and cyclobutene minus the cyclobutane value plus the net increments (cyclopropene minus cyclopropane).

Values of ΔH°_f at 298 K for methylcyclopropane, methylenecyclopropane, cyclobutene, bicyclo[1.1.0]butane, azulene, and phenanthrene have been taken from reference 21, and the value for fulvene was calculated from that for dimethylfulvene.[7] For the isomerization reactions in Table 5 it has been assumed that $(\Delta H^\circ_0)_{ZPE}$ is identical with ΔH°_{298}. Calculations for the isodesmic isomerization, cyclobutene ⟶ methylenecyclopropane, based on the above estimates, suggest that $(\Delta H^\circ_0)_{ZPE}$ may be less positive that ΔH°_{298} by *ca.* 2.1 kJ mol^{-1} This can be taken as a measure of the uncertainty for the benzene ⟶ fulvene isomerization in which a similar exocyclic double bond is formed. For the homodesmotic isomerizations naphthalene ⟶ azulene and phenanthrene ⟶ anthracene the uncertainty is probably smaller since there is even less change in structure.

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