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Quantitative Aspects of the Mechanism of Reactions Involving Hydrocarbons

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This review attempts to generalise a method of evaluating the contributions to the heat of formation of hydrocarbons and their halogen derivatives based on modern views on the structure of the carbon atom. This approach throws new light on the mechanism of a number of reactions, and on the nature of the activation energy of these processes. 88 references.

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1. INTRODUCTION

The mathematical difficulty of exact calculations based on quantum theory[1-6], the complexity of atomic structures, and the wide variety of organic compound have given rise to a great deal of pessimism on the prospect of obtaining exact information useful to experimental chemists, in spite of the advent of electronic computer techniques. However, there is little doubt (in view of the many experimentally observed correlations) that relatively simple methods of solving these problems must exist. The need for simple computational methods arises on the one hand because of the large number of such computations envisaged, and on the other hand from the fact that many of the problems are only of passing interest. For this reason, semi-empirical methods are being applied on an increasing scale in various branches of chemistry[7-13], including quantum chemistry[14-17]. Descriptive (though not strictly accurate) concepts are often more useful to the practical worker than complicated and fully developed physical models. For example, the electronegativity concept[18-22] has played an important role in the development of chemical thinking in spite of the many criticisms which have been levelled at it.

This article aims to review the ideas which enable the heats of formation of hydrocarbons and their halogen derivatives to be correlated with structural parameters[23-26]. The proposed semi-empirical method for calculating heats of formation differs from alternative approaches[7-9,27,28] in its basic principles, and it allows calculation of the heats of formation not only of hydrocarbon molecules but also of their gaseous radicals and their halogen derivatives of practically any structure. Thus, the method is of value in the quantitative discussion of reaction mechanisms[29-32].

2. CONTRIBUTIONS TO THE HEAT OF FORMATION OF HYDROCARBONS

We shall make the following assumptions: 1) the energy of a covalent bond between two atoms is a constant, depending only on the chemical nature of the atoms involved; 2) the energy evolved when electrons become hybridised is determined by the form of the hybridisation of the orbitals; 3) hydrogen (or halogen) atoms combined with carbon atoms develop a constant charge, and the charge on the carbon atom is equal and opposite to the sum of the charges on these atoms. If these assumptions are true, the heat of formation (ΔH) of any gas-phase molecule or radical C_nH_p is given by the expression

$$\Delta H_{C_nH_p} = n_1\Delta H_{C'} + (n-n_1)\,\Delta H_C + p\Delta H_H - pE_{C-H} - wE_{p^3} - fE_{sp^3} - gE_{sp^2} - hE_{sp} - sE_{C-C} - tE_{C=C} - uE_{C\equiv C} - m\sum_{i=1}^{n} a_i^2 \qquad (1)$$

where $\Delta H_{C'}$, ΔH_C, and ΔH_H are respectively the heats of formation of a bivalent and a quadrivalent carbon atom from graphite, and of a hydrogen atom from its molecule; n_1 and p are the numbers of bivalent carbon atoms and hydrogen atoms respectively; E_{C-H}, E_{C-C}, $E_{C=C}$, and $E_{C\equiv C}$ are the energies of the covalent C–H, C–C, C=C, and C≡C bonds; s, t, and u are the numbers of C–C, C=C, and C≡C bonds; E_{p^2}, E_{sp^3}, E_{sp^2} and E_{sp} are the energies involved in p^2, sp^3, sp^2, snd sp hybridisation of the electrons; w, f, g, and h are the number of carbon atoms in p^2, sp^3, sp^2, and sp states of orbital hybridisation; $\sum_{i=1}^{n}$ denotes summation over values of i from 1 to n; a is the number of hydrogen atoms on the i-th carbon atom; m is the energy of the electrostatic attraction between a hydrogen atom and a carbon atom with an equal and opposite charge.

The last term of Eqn. (1) relates exclusively to the electrostatic interaction of the carbon atoms with the hydrogen atoms directly attached to them.

Applying Eqn. (1) to the heats of formation of methane, ethane, ethylene, and acetylene, and using these values to calculate the enthalpy of formation of a hydrocarbon molecule without conjugated double bonds, for which $n - n_1 = f + g + h = s + t + u + 1$, we obtain

$$\Delta H_{C_nH_p} = s\Delta H_{C_2H_6} + (f-2s)\,\Delta H_{CH_4} + t\Delta H_{C_2H_4} + u\Delta H_{C_2H_2} + m(16f - 14s + 8t + 2u - \sum_{i=1}^{n} a_i^2). \qquad (2)$$

This equation makes no allowance for possible conjugation of double bonds, which produces additional stabilisation energy, or for bond strain resulting from distortion of the bonds from their normal directions [24].

For the special case of gaseous paraffin hydrocarbons with an unbranched chain (C_nH_{2n+2}), Eqn. (2) takes the simpler form

$$\Delta H_{C_nH_{2n+2}} = (n-1)\,\Delta H_{C_2H_6} + (2-n)\,\Delta H_{CH_4} + (2-n)\,2m\,. \qquad (3)$$

Table 1. Heats of formation of gaseous hydrocarbons under standard conditions.

Formula	Compound	ΔH, kcal mole^{-1}		$\Delta H_{calc} - \Delta H_{corr}$ kcal mole^{-1}
		corrected (Refs.9,28, 33,34)	calculated by Eqn.(2)	
1	2	3	4	5
C_4H_{10}	Butane	−30.15	−30.09	+0.06
C_7H_{16}	Heptane	−44.89	−44.88	+0.01
$C_{10}H_{22}$	Decane	−59.67	−59.67	0.00
$C_{13}H_{28}$	Tridecane	−74.45	−74.46	−0.01
$C_{16}H_{34}$	Hexadecane	−89.23	−89.24	−0.01
$C_{19}H_{40}$	Nonadecane	−104.00	−104.03	−0.03
C_4H_8	But-1-ene	−0.03	+0.06	+0.09
C_7H_{14}	Hept-1-ene	−14.89	−14.73	+0.16
$C_{10}H_{20}$	Dec-1-ene	−29.67	−29.52	+0.15
$C_{13}H_{26}$	Tridec-1-ene	−44.45	−44.30	+0.15
$C_{16}H_{32}$	Hexadec-1-ene	−59.23	−59.09	+0.14
$C_{19}H_{38}$	Nonadec-1-ene	−74.00	−73.88	+0.12
C_4H_6	But-1-yne	+39.48	+39.17	−0.32
C_7H_{12}	Hept-1-yne	+24.62	+24.38	−0.24
$C_{10}H_{18}$	Dec-1-yne	+9.85	+9.60	−0.25
$C_{13}H_{24}$	Tridec-1-yne	−4.93	−5.19	−0.26
$C_{16}H_{30}$	Hexadec-1-yne	−19.71	−19.98	−0.27
$C_{19}H_{36}$	Nonadec-1-yne	−34.49	−34.76	−0.27
C_6H_{14}	Hexane	−39.96	−39.95	+0.01
C_6H_{14}	2-Methylpentane	−41.66	−42.53	−0.87
C_6H_{14}	3-Methylpentane	−41.02	−42.53	−1.51
C_6H_{14}	2,3-Dimethylbutane	−42.49	−45.12	−2.63
C_6H_{14}	2,2-Dimethylbutane	−44.35	−47.70	−3.35
C_6H_{10}	Pent-1-ene	−5.00	−4.87	+0.13
C_5H_{10}	*Cis*-pent-2-ene	−6.71	−7.46	−0.75
C_5H_{10}	*Trans*-pent-2-ene	−7.59	−7.46	+0.13
C_5H_{10}	3-Methylbut-1-ene	−6.92	−7.46	−0.54
C_5H_{10}	2-Methylbut-2-ene	−10.17	−12.62	−2.45
C_5H_8	Pent-1-yne	+34.50	+34.24	−0.26
C_5H_8	Pent-2-yne	+30.80	+29.08	−1.72
C_5H_8	2-Methylbut-3-yne	+32.60	+31.66	−0.94
C_5H_8	1,4-Pentadiene	+25.20	+25.28	+0.08
C_6H_{10}	Cyclohexane*	−29.43	−29.57	−0.14
C_7H_{14}	Methylcyclohexane	−36.99	−37.08	−0.09
C_8H_{16}	Ethylcyclohexane	−41.05	−42.01	−0.96
C_8H_{16}	*Cis*-1,3-diemthylcyclohexane	−44.16	−44.60	−0.44
C_6H_{10}	Cyclohexene	−1.70	−2.01	−0.31
C_8H_8	Cyclooctatetraene**	+71.12	+70.84	−0.28

* The carbon atoms of the cyclohexane molecule are not coplanar [35,36]; as a result, the bonds are unstrained.
** The carbon atoms in the cyclooctatetraene molecule lie in different planes [35,38]. This may explain the absence of a conjugation effect.

By inserting known values [9,28,33,34] of ΔH into Eqn. (3) it can be shown that $m = 1.291$ kcal mole^{-1}. Knowing m, Eqn. (2) can be used to calculate the enthalpies of formation of various gaseous hydrocarbons [23,24], saturated or unsaturated, aliphatic or cyclic. The precision of some of these calculations is illustrated in Table 1: evidently, there is a loss of precision when the carbon chain is branched. Eqn. (2) can be used to calculate approximate enthalpies of formation not only at the standard temperature [26]. It can be used also to evaluate [24] the effect of strain in cyclic molecules due to distortion of the bonds from their normal tetrahedral angles [35-37], and the energy of conjugated double bonds due to π-bond delocalisation [5,6,35-37].

3. QUANTITATIVE EXPRESSIONS FOR THE CONTRIBUTIONS TO THE HEATS OF FORMATION

It is experimentally known [27,34] that an expenditure of 80 kcal mole^{-1} is needed to abstract the hydrogen atom from a diatomic CH particle in which the carbon atom is bivalent and the electrons are not in any way hybridised. Since the electrostatic attraction energy between the C and H atoms in this case is m, it follows that the energy of the covalent C−H bond is $E_{C-H} = 78.71$ kcal mole^{-1}.

Also, applying Eqn. (1) to the experimental values for the heats of formation of methane, methyl, and allene (−17.889 kcal mole^{-1} [33,34], +31.5 kcal mole^{-1} [33,39], and +45.92 kcal mole^{-1} [33,34] respectively), we can easily show that

$$\Delta H_C - E_{sp^3} = 109.25 \text{ kcal mole}^{-1}\,, \qquad (4)$$

$$\Delta H_C - E_{sp^2} = 122.98 \text{ kcal mole}^{-1}\,, \qquad (5)$$

$$\Delta H_C - E_{sp} = 150.04 \text{ kcal mole}^{-1}\,. \qquad (6)$$

Since the heat of formation of a gaseous carbon atom in the ground state (C′) from graphite is $\Delta H_{C'} = 171.698$ kcal mole^{-1} [34], we obtain the value $E_{p^2} = 47.3$ kcal mole^{-1} [24] for the p^2-hybridisation energy by taking the heat of formation of methylene as 66 kcal mole^{-1} [27,40]. Using Eqns. (4)−(6) and the enthalpies of formation of ethane, ethylene, and acetylene we arrive at $E_{C-C} = 55.9$ kcal mole^{-1}, $E_{C=C} = 116.6$ kcal mole^{-1}, and $E_{C\equiv C} = 190.1$ kcal mole^{-1}. Eqns. (4)−(6) also show that the energy of sp^3-hybridisation of the orbitals of a quadrivalent carbon atom is greater than the energy of sp^2-hybridisation by 13.7 kcal and is greater than the energy of sp-hybridisation by 40.8 kcal.

Thus, since $n - n_1 = f + g + h$, all the quantities which appear in Eqn. (1) are known, and they can be used in principle for approximate calculations of the heats of formation of gaseous hydrocarbon molecules or radicals free from conjugation or strain effects. However, simpler and more accurate methods [7-9,27,28,34] are available for calculating the heat of formation of molecules, including our Eqn. (2). Hence, Eqn. (1) is most effectively used, in conjunction with Hess's law, to calculate the thermochemistry of reactions involving hydrocarbon radicals, and also to evaluate the heats of formation of the radicals.

4. HEATS OF SOME REACTIONS BETWEEN HYDROCARBON MOLECULES AND RADICALS

a. Hydrogen Atom Removal Reactions

All the carbon atoms in paraffin hydrocarbon molecules are in the sp^3 state of orbital hybridisation. When a combined hydrogen atom is removed, the carbon atom passes from the sp^3 to the sp^2 form of electron hybridisation, and at the same time the electrostatic contribution to the C−H bond energy of the carbon atom changes. The heat of this reaction (Q_1) is given by Eqn. (1) and Hess's law in the form

$$Q_1 = E_{C-H} + E_{sp^3} - E_{sp^2} + m\,(2a-1) \qquad (7)$$

where a is the number of hydrogen atoms bound to the original carbon atom [30].

Similarly, when a hydrogen atom is removed from an unsaturated molecule containing a double bond, the reacting

carbon atom passes from the sp^2 to the sp hybridisation form, and the heat of the reaction (Q_2) is given by

$$Q_2 = E_{C-H} + E_{sp^3} - E_{sp} + m(2a - 1) . \quad (8)$$

The heats of a number of reactions in which hydrogen atoms are removed from hydrocarbon molecules and radicals, calculated in this way, are listed in Table 2. Where experimental values exist, the agreement is satisfactory.

Table 2. Heats of hydrogen atom removal from hydrocarbon molecules and radicals.

No.	Reaction	State of carbon atom: initial V	initial H	final V	final H	Q, kcal mole^{-1}: calc.	exper. (Ref.41)
	Removal of H from molecules						
1	$CH_4 \rightarrow CH_3 + H$	4	sp^3	4	sp^3	101.5	103±2
2	$-CH_3 \rightarrow -CH_2 + H$	4	sp^3	4	sp^2	98.9	97±1
3	$>CH_2 \rightarrow >CH + H$	4	sp^3	4	sp^2	96.3	94±2
4	$>CH \rightarrow >C + H$	4	sp^3	4	sp^2	93.7	89±2
5	$=CH_2 \rightarrow =CH + H$	4	sp^2	4	sp	109.6	104
6	$\equiv CH \rightarrow \equiv C + H$	4	sp^2	4	sp	107.0	—
	Removal of H from radicals						
7	$CH_3 \rightarrow CH_2 + H$	4	sp^2	4	sp	112.2	—
8	$CH_3 \rightarrow CH_2 + H$	4	sp^2	2	p^2	86.6	85±7
9	$-CH_2 \rightarrow -CH + H$	4	sp^2	4	sp	109.6	—
10	$-CH_2 \rightarrow -CH + H$	4	sp^2	2	p^2	84.0	—
11	$>CH \rightarrow >C + H$	4	sp	4	sp	107.0	—
12	$>CH \rightarrow >C + H$	4	sp^2	2	p^2	81.4	—
13	$=CH \rightarrow =C + H$	4	sp	2	—	101.7	—
14	$CH_2 \rightarrow CH + H$	2	p^2	2	—	129.9	128±6
15	$-CH \rightarrow -C + H$	2	p^2	2	—	127.3	—

Note. V = valency, H = hybridisation.

Tatevskii has pointed out[42] that the distinction between molecules and radicals is to some extent arbitrary. Therefore, the following reasoning may be justified. Reactions 7, 9, and 11 (Table 2) give rise to "hot" particles, containing an excess of energy as compared with the bivalent state of the carbon atom with p^2 hybridisation (reactions 8, 10, and 12 of Table 2). However, since the rate of collisions between gas-phase particles can be as high as 10^{28} per second[43,44] [sic!, 10^{10} at one atm. is more reasonable, (Ed. of Translation)], the excess of energy is quickly dissipated[45], and these "hot" particles have no practical existence.

b. Hydrogen Atom Exchange Reactions Involving Radicals

Using Eqn. (1) and Hess's law, we obtain the following expression for the heat (Q_3) of hydrogen atom exchange reactions involving radicals, in which the reacting carbon atoms are in the sp^3 hybridisation and the sp^2 hybridisation in the initial molecule and radical respectively (Table 3, reactions 1–4, 7–9, 12, 13, 16):

$$Q_3 = 2m(a - a_1 - 1) \quad (9)$$

where a and a_1 are the numbers of hydrogen atoms on the reacting carbon atoms of the original molecule and radical respectively.

When the reacting carbon atoms in the radical and the molecule have the same (sp^3) hybridisation, as in reactions 5, 6, 10, 11, 15, 17, 18 of Table 3, the heat of the reaction (Q_4) is given by

$$Q_4 = 2E_{sp^3} - E_{sp^3} - E_{sp} + 2m(a - a_1 - 1) \quad (10)$$

Table 3. Heats of radical reactions involving hydrogen exchange and biradical formation.

No.	Reaction	Q, kcal mole^{-1}
	H atom exchange reactions (Ref.31)	
1	$CH_3 + CH_4 \rightarrow CH_4 + CH_3$	0
2	$CH_3 + CH_3- \rightarrow CH_4 + CH_2-$	−2.6
3	$CH_3 + CH_2< \rightarrow CH_4 + CH<$	−5.2
4	$CH_3 + CH< \rightarrow CH_4 + C<$	−7.7
5	$CH_3 + CH_2= \rightarrow CH_4 + CH=$	+8.1
6	$CH_3 + CH\equiv \rightarrow CH_4 + C\equiv$	+5.6
7	$-CH_2 + CH_3- \rightarrow -CH_3 + CH_2-$	0
8	$-CH_2 + CH_2< \rightarrow -CH_3 + CH<$	−2.6
9	$-CH_2 + CH< \rightarrow -CH_3 + C<$	−5.2
10	$-CH_2 + CH_2= \rightarrow -CH_3 + CH=$	+10.7
11	$-CH_2 + CH\equiv \rightarrow -CH_3 + C\equiv$	+8.1
12	$>CH + CH_2< \rightarrow >CH_2 + CH<$	0
13	$>CH + CH< \rightarrow >CH_2 + C<$	−2.6
14	$>CH + CH_2= \rightarrow >CH_2 + CH=$	+13.3
15	$>CH + CH\equiv \rightarrow >CH_2 + C\equiv$	+10.7
16	$>C + CH< \rightarrow >CH + C<$	0
17	$>C + CH_2= \rightarrow >CH + CH=$	+15.9
18	$>C + CH\equiv \rightarrow >CH + C\equiv$	+13.3
19	$H + CH_4 \rightarrow H_2 + CH_3$	−2.7
20	$H + CH_3- \rightarrow H_2 + CH_2-$	−5.3
21	$H + CH_2< \rightarrow H_2 + CH<$	−7.8
22	$H + CH< \rightarrow H_2 + C<$	−10.4
23	$H + CH_2= \rightarrow H_2 + CH=$	+5.4
24	$H + CH\equiv \rightarrow H_2 + C\equiv$	+2.8
	Biradical formation reactions (Refs.30,32)	
25	$CH_4 \rightarrow H_2 + CH_2$	83.9
26	$-CH_3 \rightarrow H_2 + -CH$	78.7
27	$>CH_2 \rightarrow H_2 + >C$	73.5
28	$CH_3CH_3 \rightarrow CH_4 + CH_2$	68.4
29	$CH_3CH_2- \rightarrow CH_3 + CH_2$	71.0
30	$CH_3CH< \rightarrow CH_2< + CH_2$	73.6
31	$CH_3C< \rightarrow CH< + CH_2$	76.2
32	$-CH_2CH_3 \rightarrow CH_4 + -CH$	65.8
33	$>CHCH_3 \rightarrow CH_4 + >C$	63.2
34	$CH_3=CH_2 \rightarrow CH_3-CH$	45.9
35	$CH_2=CH- \rightarrow CH_3-C-$	43.3
36	$-CH=CH_2 \rightarrow -CH_2-CH$	48.5
37	$>C=CH_2 \rightarrow >CH-CH$	51.1
38	$CH\equiv CH \rightarrow CH_2=C$	65.5

When a hydrogen atom reacts with a molecule in which the reacting carbon atom is held by saturated σ bonds (reactions 19–22 of Table 3), the heat change (Q_5) is

$$Q_5 = E_{C-H} - 2\Delta H_H + E_{sp^3} - E_{sp^2} + m(2a - 1) \quad (11)$$

c. Biradical Formation Reactions

Table 3 includes the heats of some biradical formation reactions, which may be involved in the intermediate steps of a number of processes[46-52]. The active carbon atom in the biradical is assumed to be in the bivalent ground state with p^2 hybridisation of the orbitals. The heat (Q_6) of formation of such a biradical by the removal of a hydrogen molecule from the saturated hydrocarbon (reactions 25–27 of Table 3) is given by the expression

$$Q_6 = \Delta H_{C'} - E_{p^2} - \Delta H_C + E_{sp^3} - 2\Delta H_H + 2E_{C-H} + 4m(a-1). \quad (12)$$

The heats of the other reactions listed in Table 3 may be obtained in a similar way. The ability to calculate the heats of even hypothetical reactions is a useful feature of Eqn. (1), since it enables us to select the correct mechanism of various processes.

5. HALOGEN DERIVATIVES OF HYDROCARBONS

The ideas discussed above can be extended to halogen derivatives of hydrocarbons[25,29]. In this case, the contributions to the heat of formation of the gaseous halogenated hydrocarbon molecules and radicals of composition $C_nH_pX_v$ are given by the expression

$$\Delta H_{C_nH_pX_v} = n_1\Delta H_{C'} + (n-n_1)\,\Delta H_C + p\Delta H_H + v\Delta H_X - pE_{C-H} - vE_{C-X} - wE_{p^2} - fE_{sp^3} - gE_{sp^3} - hE_{sp} - sE_{C-C} - tE_{C=C} - uE_{C\equiv C} - m\sum_{i=1}^{n}(a+dk)\left(a+dk\frac{l_{CH}}{l_{CX}}\right), \quad (13)$$

where E_{C-X} is the energy of the covalent C–X bond, d is the number of halogen atoms on the i-th carbon atom, k is the proportionality coefficient[25] between the charge on the halogen atom and the charge on the hydrogen atom, l_{CH} and l_{CX} are the mean lengths of the CH and CX bonds.

Table 4. Characteristics of hydrogen and halogen atoms in hydrocarbons and their derivatives.

X	k	E_{C-X}, kcal mole^{-1}	l_{C-X}, Å (Ref.34)
H	1	78.71	1.09
F	−0.54	98.52	1.35
Cl	+0.27	63.89	1.75
Br	+0.43	50.47	1.93
I	+0.68	34.06	2.12

For the case of gaseous halogenated hydrocarbons of composition $C_nH_pX_v$ without conjugated double bonds, Eqn. (14) can be obtained from Eqn. (13) by transformations similar to those used in the derivation of Eqn. (2):

$$\Delta H_{C_nH_pX_v} = s\Delta H_{C_nH_4} + (f-2s)\,\Delta H_{CH_4} + t\Delta H_{C_nH_4} + u\Delta H_{C_nH_2} + v(\Delta H_X - \Delta H_H + E_{C-H} - E_{C-X}) + m\left[16f - 14s + 8t + 2u - \sum_{i=1}^{n}(a+dk)\left(a+dk\frac{l_{CH}}{l_{CX}}\right)\right]. \quad (14)$$

The quantities E_{C-X} and k are evaluated[25] by substituting into Eqn. (14) the known values of $\Delta H C_nH_pX_v$ [33,34] listed in Table 4.

The following expression for the heat (Q_7) of removal of a halogen atom from halogenated alkanes (reactions 1–10 of Table 5) is readily obtained by using Hess's law and Eqn. (13):

$$Q_7 = E_{C-X} + E_{sp^3} - E_{sp^2} + m\left[ak\left(1+\frac{l_{CH}}{l_{CX}}\right) + (2d-1)\,k^2\frac{l_{CH}}{l_{CX}}\right]. \quad (15)$$

The heat of formation of biradicals from halogenated methane molecules by dehydrohalogenation (reactions 15, 17, 19 of Table 5) is given by the equation

$$Q_8 = \Delta H_{C'} - E_{p^2} - \Delta H_C + E_{sp^3} + \Delta H_{HX} - \Delta H_H - \Delta H_X + E_{C-H} + E_{C-X} - m\left[2a - 1 + (a+d-1)\,k\left(1+\frac{l_{CH}}{l_{CX}}\right) + (2d-1)\,k^2\frac{l_{CH}}{l_{CX}}\right] \quad (16)$$

where ΔH_{HX} is the heat of formation of a molecule of HX from its elements.

Table 5. Heats of formation of radicals from halogenated hydrocarbons.

No.	Reaction	X = F		X = Cl		X = Br		X = I	
		calc.	publ.	calc.	publ.	calc.	publ.	calc.	publ.
1	$CH_3X \rightarrow CH_3+X$	108.8	107[53]	79.4	78[53]	67.0	66.6[53]	52.1	52.6±±2.3[41]
2	$CH_2X_2 \rightarrow CH_2X+X$	110.6	109.6[52]	78.9	77.9[53]	66.3	65.5[53]	51.4	—
3	$CHX_3 \rightarrow CHX_2+X$	112.5	114.6[53]	78.5	78.3[53]	65.7	66.1[53]	50.6	—
4	$CX_4 \rightarrow CX_3+X$	114.4	116[53]	78.0	78.2[53]	65.1	66.6[53]	49.9	—
5	$-CH_2X \rightarrow -CH_2'+X$	110.0	—	78.8	83±7[54]; 77[55]	66.1	65.0[54]	50.8	51[41]
6	$-CHX_2 \rightarrow -CHX+X$	111.9	—	78.4	—	65.5	--	50.0	—
7	$-CX_3 \rightarrow -CX_2+X$	113.8	114[53]	77.9	—	64.9	--	49.3	—
8	$>CHX \rightarrow >CH+X$	111.3	—	78.2	73.3±2.3[41]	65.2	59[56]	49.4	52; 46[41]
9	$>CX_2 \rightarrow >CX+X$	113.2	109[53]	77.8	—	64.6	--	48.7	—
10	$>CX \rightarrow >C+X$	112.6	107[53]	77.7	75[55]	64.3	--	48.1	47[41]
11	$=CHX \rightarrow =CH+X$	124.6	—	91.6	85.5[54]	78.5	73.4[54]	62.8	66.5±2[41]
12	$=CX_2 \rightarrow =CX+X$	126.5	—	91.1	—	77.9	63±2[41]	62.0	—
13	$=CX \rightarrow =C+X$	125.9	—	91.0	—	77.7	--	61.4	—
14	$CH_3X \rightarrow H_2+CHX$	76.2	—	79.8	—	80.4	--	81.4	—
15	$CH_3X \rightarrow HX+CH_2$	60.8	—	62.8	—	66.1	--	63.7	—
16	$CH_2X_2 \rightarrow H_2+CX_2$	68.5	65.8*	75.8	—	77.0	--	78.9	—
17	$CH_2X_2 \rightarrow HX+CHX$	58.8	—	60.3	—	63.7	--	65.3	—
18	$CH_2X_2 \rightarrow X_2+CH_2$	171.8	—	87.3	—	66.7	--	38.8	—
19	$CHX_3 \rightarrow HX+CX_2$	56.8	58.4[58]	57.9	—	61.4	--	63.4	—
20	$CHX_3 \rightarrow X_2+CHX$	175.5	—	86.4	—	65.5	--	37.4	—
21	$CX_4 \rightarrow X_2+CX_2$	179.2	180.3*	85.5	—	64.3	--	36.0	—

* Values used in the calculations: ΔH_{CF_2} = −39.7 kcal mole^{-1} [57], $\Delta H_{CH_2F_2}$ = −105.5 kcal mole^{-1} [33], ΔH_{CF_4} = −220.0 kcal mole^{-1} [27].

The heats of the other reactions listed in Table 5 can be obtained by means of expressions derived in a similar way.

It is evident from Table 5 that the biradical mechanism, involving removal of a molecule of hydrogen fluoride, is energetically more favourable than the formation of monoradicals by removal of a fluorine atom in the thermal decomposition of fluorinated methane derivatives. The biradical mechanism was confirmed experimentally in the pyrolysis of methyl fluoride[59] and trifluoromethane[58,60]. A similar mechanism also applies to the decomposition of chloroalkanes with removal of an HCl

molecule[61-64]. Furthermore, the heats of formation of mono- and biradicals from bromo derivatives are very similar, suggesting that the two processes can occur in parallel[65,66], whereas with the iodo derivatives the mechanism involving breaking a C–I bond or the removal of an I_2 molecule is energetically more favourable. The decomposition of methyl or ethyl iodide is a well known method of producing alkyl monoradicals[67,68].

6. DISCUSSION OF SOME REACTIONS IN THE LIGHT OF THE PROPOSED APPROACH

A knowledge of the contributions to the heat of formation of hydrocarbons allows us to re-examine the mechanism of a number of reactions, and also to speculate on the nature of the activation energy attending various processes[30-32].

Table 6. Activation energies of some radical reactions involving hydrogen atom exchange*.

No.	Reaction	E, kcal mole^{-1} calc.	E, kcal mole^{-1} publ.	References
		Eqn.(17)		
1	$CH_3+CH_4\rightarrow CH_4+CH_3$	13.7	11.2–14.3	39, 43, 69–72
2	$CH_3+H_3C-\rightarrow CH_4+H_2C-$	11.1	9.3–10.4	39, 70–72
3	$CH_3+H_2C<\rightarrow CH_4+CH<$	8.5	8.0–8.7	39, 70–72
4	$CH_3+HC<\rightarrow CH_4+C<$	6.0	6.9–7.9	39, 70–72
5	$-CH_2+CH_4\rightarrow -CH_3+CH_3$	16.3	15.0–18	70,73
6	$-CH_2+H_3C-\rightarrow -CH_3+H_2C-$	13.7	13.9–16.9	70
7	$-CH_2+H_2C<\rightarrow -CH_3+CH<$	11.1	12.7–15.4	70
8	$-CH_2+HC<\rightarrow -CH_3+C<$	8.5	8.9–14.2	70,74
9	$>CH+CH_4\rightarrow >CH_2+CH_3$	18.9	18.7–20.2	70
10	$>C<+CH_4\rightarrow >CH+CH_3$	21.4	22.7	70
11	$H+CH_4\rightarrow H_2+CH_3$	11.0	10.6±1.0	75
12	$H+H_3C-\rightarrow H_2+H_2C-$	8.4	9.5±2.0	75
13	$H+H_2C<\rightarrow H_2+HC<$	5.8	7.2±2.0	75
14	$H+HC<\rightarrow H_2+C<$	3.2	6.7±2.0	75
15	$H+H_2\rightarrow H_2+H$	—	6.2±1 7.5±1 7.3	39 43 76
		Eqn.(17a)		
16	$CH_3+H_2\rightarrow CH_4+H$	10.0	10.0	71,72
17	$-CH_2+H_2\rightarrow -CH_3+H$	12.6	13.3 12.2	72 73
18	$>CH+H_2\rightarrow >CH_2+H$	15.2	—	
19	$>C<+H_2\rightarrow >CH+H$	17.8	—	

* Q values are listed in Table 3.

Thus, we can assume that in hydrogen atom exchange radical reactions, in which the reacting carbon atom of the original molecule is in the sp^3 hybridisation and that of the original radical is in the sp^2 hybridisation, the necessary condition is conversion of the sp^3 hybridisation of the carbon atom of the molecule into the sp^2 form, which requires an expenditure of 13.7 kcal mole^{-1} of energy. But since the heat of the reaction is altered by the interaction of the molecule and the radical, the activation energy barrier (E) which the system must overcome is given by the sum of 13.7 kcal mole^{-1} and the heat of the reaction, i.e.

$$E = 13{,}7 + Q \ . \qquad (17)$$

If the activated state of the hydrocarbon molecules for reactions 11–14 of Table 6 is similar to that for reactions 1–10, the activation energy can be calculated in a similar way from formula (17).

Leaving aside the nature of the active state of the hydrogen molecule, it is reasonable to assume that the same state is involved in reactions 16–19 of Table 6 as in the reaction between a hydrogen molecule and a hydrogen atom, for which the activation (or excitation) energy of the hydrogen molecule is approximately[39,43,76] 7.3 kcal mole^{-1}. Hence, the activation energy of reactions 16 to 19 can be obtained from the expression

$$E \approx 7.3 + Q \qquad (17a)$$

Reactions 2, 3, 4 of Table 6 differ from 5, 9, 10, and reactions 11–14 differ from 16–19, in being the reverse of the other process. The intermediate state of the system must be different in the two cases, as the difference between the activation energies for the forward and the reverse reaction is not equal to the heat of the reaction[31].

It is interesting to compare the activation energies for the cracking reactions of various saturated hydrocarbons with the heats of formation of the hydrocarbons from their biradicals. Thus, a biradical is formed from a methane molecule by reaction 25 of Table 3 with a heat absorption of 83.9 kcal mole^{-1}, and the activation energy for the cracking of methane is variously given[77,78] as 79–90 kcal mole^{-1}. On cracking ethane, biradicals are formed by reactions 26 and 28 (Table 3) with absorption of 78.7 and 68.4 kcal mole^{-1} respectively. The experimental values of the activation energy for this process lie in the range 68.7–79.5 kcal mole^{-1} [78,79]. In the pyrolysis of trifluoromethane the activation energy corresponds to the heat of formation of the biradical CF_2 [58]. It is a plausible assumption that a biradical is formed by reaction 34 of Table 3, with a heat of 45.9 kcal mole^{-1}, as an intermediate in the gas-phase hydrogenation of ethylene. This value is close to the experimentally observed[80,81] activation energy of the process (43–44.8 kcal mole^{-1}).

Unless the numerical agreement between these quantities is fortuitous, it suggests some definite conclusions as to the origin of the activation energy of these reactions, and in particular it suggests the widespread occurrence of a biradical mechanism. A comparison of the properties of mono- and biradicals leads to the same conclusion. Thus, monoradicals can recombine only as a result of mutual collisions, not by collisions with molecules[39,43,72]. Biradicals can be studied both in addition reactions and following internal electronic rearrangements to give a double bond[82-84]. Recombination of monoradicals occurs with a negligibly small activation energy[39,43,72]. Presumably, the same is true of biradicals[82,83,85]. There is evidence[46,86,87] that chain reactions account for a very small fraction of the total number of alkane molecules decomposed in cracking reactions: this confirms the likelihood of a biradical mechanism in reactions of this type.

In conclusion, we shall consider specifically the reactions

$$CH{\equiv}CH \rightarrow CH{\equiv}C + H \qquad (18)$$

and

$$CH{\equiv}CH \rightarrow C{\equiv}C + 2\,H \ . \qquad (19)$$

Reaction (18) requires the expenditure of ~121 kcal mole^{-1} [39,88], and reaction (19) requires 246 kcal mole^{-1} [40]. Since the reacting quadrivalent carbon atom is converted from sp hybridisation to a valency state without any hybridisation of the orbitals, we can use the heats of these reactions to calculate the energy evolved as a result of sp hybridisation. The mean value of E_{sp} is ~42 kcal mole^{-1} (41 kcal mole^{-1} by reaction (18) and 43 kcal mole^{-1} by reaction (19)). Hence, according to Eqn. (6), the heat of formation of a quadrivalent carbon atom from graphite is approximately $\Delta H_C = 192$ kcal g-atom^{-1}. But since the heat of formation of gaseous carbon in the ground state is 171.7 kcal g-atom^{-1}, it follows that the transition of a $2s$ electron to a $2p$ orbital requires ~20 kcal g-atom^{-1}. Using the above value of ΔH_C and Eqns. (4) and (5), the energy evolved during sp^3 and sp^2 hybridisation can be calculated: $E_{sp^3} = 83$ kcal g-atom^{-1} and $E_{sp^2} = 69$ kcal g-atom^{-1}. Thus, the ideas discussed in this review allow quantitative evaluation of a number of important parameters in the chemistry of hydrocarbons.

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