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Thermochimica Acta 257 (1995) 21–37

thermochimica
acta

Group additivity values for standard heats of formation of gaseous chlorofluorocarbons and related species

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Received 20 August 1994; accepted 3 November 1994

Abstract

Group additivity values are presented which can be used to estimate standard heats of formation for a variety of gaseous fluorocarbons, chlorofluorocarbons, hydrofluorocarbons and hydrochlorofluorocarbons (molecules, radicals, diradicals and carbenes). Wherever these values cannot be obtained directly from standard heats of formation, they are estimated by requiring bond dissociation enthalpies to follow monotonic trends across homologous series of species. For cases where there is insufficient information to establish these trends, an alternative empirical procedure that stems from ab initio results is used. An estimate of the uncertainty in each group additivity value is provided.

Keywords: Chlorofluorocarbons; Heats of formation; Radicals; Carbenes

1. Introduction

A wide variety of gaseous, halogenated and partially halogenated hydrocarbons have important applications not only as commercial products (e.g., refrigerants, blowing agents and solvents [1]) but also as starting materials in the production of monomers (e.g., conversion of CF_2HCl to C_2F_4 [2,3] and of C_2F_4 to n-C_3F_6 [4]) which are subsequently used to manufacture polymers [5–7]. In recent years, many of the chemicals involved (e.g., chlorofluorocarbons (CFCs) and some FCs) have come under scrutiny because of environmental and toxicological concerns [8,9], and others (e.g., some HCFCs and HFCs) have received considerable attention as potentially less hazardous replacement materials [10–12]. An important aspect of these developments is the need to use new or modified chemical processes that have high yields and, hence, generate only small quantities of hazardous waste streams [13]. An integral part of such changes is a better understanding of the thermochemical behavior of the species

SSDI 0040-6031(94)02191-0

involved. Here, it is emphasized that "species" does not just refer to stable compounds but includes intermediates such as radicals [14] and carbenes [15] which could have a significant effect on the distribution of reaction products in chemical plants [11,16] and atmospheric processes [17,18].

At this time, quantitative information on the thermochemical properties of FCs, CFCs, HFCs, and HCFCs is quite limited, especially for intermediate species. Entropies and heat capacities can in principle be calculated using statistical mechanics if their structures and vibrational frequencies are known [19,20]. However, standard heats of formation $\Delta_f H^\ominus$ at 298.15 K, which are particularly important because they dictate the relative thermodynamic stability of the species, are more difficult to determine. Experiments and quantum mechanical calculations are currently being performed to obtain $\Delta_f H^\ominus$ values [21–25], but it will be a considerable time before reliable results are available for the many relevant FCs, CFCs, HFCs and HCFCs. Meanwhile, it is necessary to develop empirical procedures that will give approximate yet reasonable values for their standard heats of formation.

The most successful empirical method for estimating standard heats of formation of gaseous species is based on the additivity of group properties [19,26,27]. With this approach, $\Delta_f H^\ominus$ for a compound AB is obtained by summing the contributions from constituent groups (A and B) according to the relationship

$$\Delta_f H^\ominus(\mathrm{AB}) = \Delta_f H^\ominus(\mathrm{-A}) + \Delta_f H^\ominus(\mathrm{-B}) \qquad (1)$$

Additional terms would be needed on the right-hand side of Eq. (1) if the species contained more than two groups. Each term of the form $\Delta_f H^\ominus(\mathrm{-A})$ is referred to as a group additivity value (GAV). These GAVs can be established fairly readily if accurate $\Delta_f H^\ominus$ values are available. For example, one could set $\Delta_f H^\ominus(\mathrm{-A}) = 0.5\Delta_f H^\ominus(\mathrm{A_2})$ and then use $\Delta_f H^\ominus(\mathrm{-A})$, $\Delta_f H^\ominus(\mathrm{AB})$ and Eq. (1) to obtain $\Delta_f H^\ominus(\mathrm{-B})$. The values may need to be modified somewhat so that they also apply to other species containing group A or B. Overall, one would like to pick GAVs that minimize the errors in $\Delta_f H^\ominus$ incurred when the values are applied to a broad range of compounds [28–31]. The accuracy of the method depends on the number and accuracy of known $\Delta_f H^\ominus$ values available for fitting the GAVs and on the compromise involved in picking a GAV suitable for several species. For hydrocarbons, the procedure has yielded results for $\Delta_f H^\ominus$ with uncertainties generally $< 8\ \mathrm{kJ\,mol^{-1}}$ [27–31]. For halogenated and partially halogenated hydrocarbon species, however, the paucity of reliable $\Delta_f H^\ominus$ information and the nature of the compounds have made it more difficult to assign meaningful GAVs [30,31]. Consequently, the uncertainties in calculated values of $\Delta_f H^\ominus$ are larger (see below) and, in many cases (e.g., radicals, carbenes, and some molecules containing halogenated groups), GAVs have not yet been determined.

When insufficient information is available for establishing GAVs, one must usually resort to a simpler approach which sums average properties associated with each bond in a molecule [19,27]. Preliminary calculations for some FCs and CFCs using this method yielded $\Delta_f H^\ominus$ values with errors $> 75\ \mathrm{kJ\,mol^{-1}}$ for molecules and even larger errors for radicals [32]. The large errors associated with the bond additivity approach, coupled with its inability to distinguish isomers, indicate that it is unsuitable for CFCs and related species.

In this paper, GAVs are presented which can be used to estimate standard heats of formation for a variety of FCs, CFCs, HFCs and HCFCs (molecules, radicals, diradicals and carbenes). Wherever these GAVs cannot be obtained from $\Delta_f H^\ominus$ values directly, an adaptation of the group additivity method is used in which GAVs are estimated from trends in bond dissociation enthalpies. A similar approach has given reasonable results for species involved in production of $Al_xGa_{1-x}As$ from trimethylgallium or triethylgallium and arsine [33]. For cases in which there is insufficient information to establish trends in bond strengths, an alternative empirical procedure (which stems from ab initio results) is used.

2. Methodology

The standard heat of formation $\Delta_f H^\ominus(AB)$ can be written as

$$\Delta_f H^\ominus(AB) = \Delta_f H^\ominus(A) + \Delta_f H^\ominus(B) - D^\ominus[A-B] \qquad (2)$$

where $D^\ominus[A-B]$ is the dissociation enthalpy of the bond(s) linking group A and group B in AB and $\Delta_f H^\ominus(A)$ and $\Delta_f H^\ominus(B)$ are the standard heats of formation for species A and B, respectively. For organic species, it is convenient for each group X (where X is A or B) to contain only one carbon atom, as data are available for these standard heats of formation (see Table 1). Here it should be noted that X is a radical or carbene (depending on the starting species) and that $\Delta_f H^\ominus(X)$ is not the same quantity as the GAV $\Delta_f H^\ominus(-X)$.

The standard heat of formation $\Delta_f H^\ominus(AB)$ can be calculated from Eq. (2) if bond dissociation enthalpies of the type $D^\ominus[A-B]$ can be estimated. Conversely, $D^\ominus[A-B]$ can be determined from Eq. (2) if all three $\Delta_f H^\ominus$ values are known. Values of $D^\ominus[A-B]$ obtained in this way appear to vary monotonically across homologous series (see Figs. 1 and 2) and, in some cases, the trends are linear. Moreover, each $D^\ominus[A-B]$ value can be broken down into GAVs, i.e.

$$D^\ominus[A-B] = D^\ominus[-A] + D^\ominus[-B] \qquad (3)$$

In Fig. 2, the trends in $D^\ominus[A-B]$ are equivalent to trends in $D^\ominus[-A]$, as one group remains unchanged across the series. This result suggests that $D^\ominus[-A]$ can be expected to follow monotonic variations across homologous series. Note that, for partially fluorinated hydrocarbons, the variations in $D^\ominus[-A]$ across a series are much smaller than those in $\Delta_f H^\ominus(-A)$. Consequently, a stipulation that $D^\ominus[-A]$ should follow monotonic trends yields narrower bounds for an unknown value than if one required the $\Delta_f H^\ominus(-A)$ values themselves to vary monotonically. Therefore, we have chosen to use trends in $D^\ominus[A-B]$ and $D^\ominus[-A]$ to help specify the most suitable GAVs for $\Delta_f H^\ominus$ in Eq. (1) for cases where there are insufficient data on heats of formation to construct a complete table of $\Delta_f H^\ominus(-A)$ values directly.

The procedure used in this paper is as follows: (i) known $\Delta_f H^\ominus$ values (see Table 2) are used to establish as many GAVs for the heats of formation as possible by minimizing the errors in $\Delta_f H^\ominus$ values obtained by summation of GAVs according to Eq. (1); (ii) this incomplete set of $\Delta_f H^\ominus(-A)$ values is converted into $D^\ominus[-A]$ values

Table 1
Standard heats of formation at 298.15 K for intermediate species. The uncertainties in the average values are estimated from the variations in the values obtained from the literature (including any uncertainties cited for those values). For each species, the order of the references and the literature values correspond directly. Note that values of $\Delta H_f^\ominus$ for F, Cl and H atoms are given elsewhere [34, 35]

Species	$\Delta_f H^\ominus$/kJ mol^{-1}		References
	Average	Literature values	
$:\dot{C}F$	244.9 ± 19	248.5; 254.8; 233.4; 242.7	36–39
$:\dot{C}H$	595.1 ± 17	597.9; 594.1; 594.1; 594.1	38, 40–42
$:\dot{C}Cl$	433.9 ± 21	432.6; 435.1	38, 43
$:CF_2$	-194.2 ± 17	-213.8; -205.0; -190.0; -194.1; -172.0; -190.0	38, 43–47
$:CFH$	116.7 ± 17	136.8; 108.8; 104.6	38, 43, 48
$:CFCl$	6.0 ± 15	13.8; -8.4; 12.6	38, 43, 49
$:CHCl$	307.1 ± 11	317.1; 297.1	38, 43
$:CCl_2$	201.0 ± 42	163.2; 213.4; 226.4	43, 50, 51
$:CH_2$	385.4 ± 4	385.8, 384.9	52, 53
$^{\cdot}CF_3$	-470.3 ± 4	-465.3; -468.6; -470.3; -477.0	54–57
$^{\cdot}CF_2H$	-242.7 ± 4	-247.7; -238.9; -241.4	58–60
$^{\cdot}CF_2Cl$	-269.0 ± 8	-269.0	61
$^{\cdot}CFH_2$	-32.5 ± 8	-32.2; -32.6; -32.6	58–60
$^{\cdot}CFHCl$	-55.6 ± 4	-55.6	62
$^{\cdot}CFCl_2$	-92.9 ± 4	-87.9; -97.9	62, 63
$^{\cdot}CH_2Cl$	119.8 ± 8	119.7; 121.3; 118.4	62, 64, 65
$^{\cdot}CHCl_2$	103.6 ± 6	97.5; 109.6; 103.8	62, 65, 66
$^{\cdot}CCl_3$	77.3 ± 6	74.9; 75.3; 79.5; 79.5	62, 67–69
$^{\cdot}CH_3$	147.1 ± 7	145.6; 146.4; 148.1; 148.1	53, 62, 70, 71
$^{\cdot}CF_2CF_3$	-892.0 ± 11	-890.4; -894.5; -891.2	72–74
$^{\cdot}CFHCF_3$	-674.5 ± 13	-688.3; -680.7	75, 76
$^{\cdot}CH_2CF_3$	-520.7 ± 8	-524.3; -517.1	77, 78
$^{\cdot}CF_2CF_2H$	-663.0 ± 12	-660.2; -665.7	72, 76
$^{\cdot}CFHCF_2H$	-451.9	-451.9	75
$^{\cdot}CH_2CF_2H$	-277.4	-277.4	77
$^{\cdot}CF_2CFH_2$	-446.0 ± 8	-446.0	72
$^{\cdot}CFHCFH_2$	-235.6	-235.6	75
$^{\cdot}CH_2CFH_2$	-44.8	-44.8	77
$^{\cdot}CF_2CH_3$	-299.2 ± 11	-295.8; -302.5	79, 80
$^{\cdot}CFHCH_3$	-74.0 ± 11	-72.4; -71.5; -78.2	79, 81, 82
$^{\cdot}CH_2CH_3$	-118.8 ± 2	-118.8	82
$^{\cdot}CF_2CF_2Cl$	-686.2 ± 17	-686.2	83
$^{\cdot}CH_2CF_2Cl$	-310.9 ± 7	-310.9	84
$^{\cdot}C_3F_7$	-1299.1 ± 8	-1299.1	85

using the $\Delta_f H^\ominus(\mathrm{A})$ values listed in Table 1 and the relationship

$$D^\ominus[-\mathrm{A}] = \Delta_f H^\ominus(\mathrm{A}) - \Delta_f H^\ominus(-\mathrm{A}) \tag{4}$$

(iii) $D^\ominus[-\mathrm{A}]$ values that could not be obtained in step (ii) are estimated by imposing the requirement that they follow trends across all the relevant homologous series (e.g., see

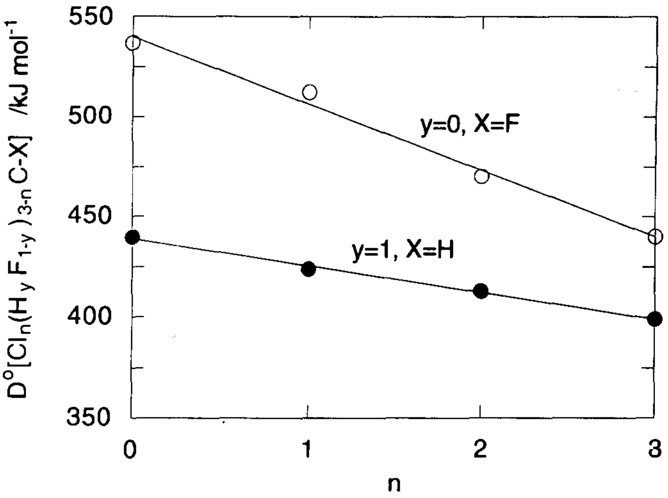

Fig. 1. Dependence of bond dissociation enthalpies $D^{\ominus}[\mathrm{Cl}_n\mathrm{F}_{3-n}\mathrm{C{-}F}]$ and $D^{\ominus}[\mathrm{Cl}_n\mathrm{H}_{3-n}\mathrm{C{-}H}]$ on the composition of saturated one-carbon compounds. The circles denote values determined from $\Delta_f H^{\ominus}$ information (see Table 1 and [75, 80, 86–90]) and Eq. (2). The lines are linear least-squares fits for each set of circles. Note that the C–H and C–F bonds become weaker as the chlorine content increases.

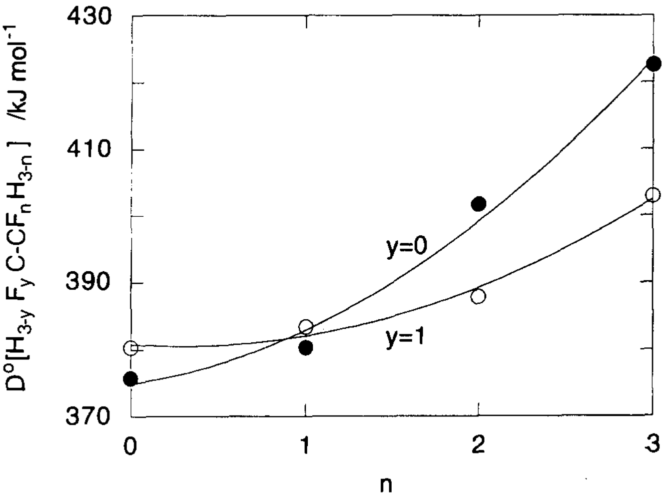

Fig. 2. Dependence of the bond dissociation enthalpy $D^{\ominus}[\mathrm{H}_{3-y}\mathrm{F}_y\mathrm{C{-}CF}_n\mathrm{H}_{3-n}]$ on the stoichiometry (y and n) of saturated two-carbon compounds. The circles denote values determined from $\Delta_f H^{\ominus}$ information (see Table 2 and [24, 86, 87]) and Eq. (2). The lines are polynomial least-squares fits for each set of circles. Note that the C–C bond becomes stronger as the fluorine content increases.

Fig. 3) and by assuming that these variations are linear if two $D^{\ominus}[-\mathrm{A}]$ values in a series of three are available; (iv) Eq. (4) is used to convert the estimated $D^{\ominus}[-\mathrm{A}]$ values into the corresponding $\Delta_f H^{\ominus}(-\mathrm{A})$ values; and (v) $\Delta_f H^{\ominus}(-\mathrm{A})$ values are substituted into Eq. (1) to yield standard heats of formation that were not previously known.

Table 2
Standard heats of formation at 298.15 K for halogenated and partially halogenated hydrocarbon molecules. The uncertainties in the average values are estimated from the variations in the values obtained from the literature (including any uncertainties cited for those values). For each species, the order of the references and the literature values correspond directly

Species	$\Delta_f H^\ominus$/kJ mol^{-1}		References
	Average	Literature values	
CF_3CF_3	-1359.2 ± 6	-1392.0; -1342.6; -1343.1	24, 56, 91
CF_3CF_2H	-1106.6 ± 8	-1114.6; -1108.3; -1105.0; -1104.6; -1100.4	24, 72, 92-95
CF_3CF_2Cl	-1111.7 ± 15	-1106.7; -1116.7	33, 92
CF_3CH_3	-754.3 ± 6	-754.0; -745.6	24, 95
CF_2HCF_2H	-878.9 ± 6	-879.1; -878.6	24, 72
CF_2HCFH_2	-663.0 ± 8	-667.8; -658.1	24, 72
CF_2ClCF_2Cl	-896.6 ± 2	-896.6	96
CF_2ClCH_3	-529.7 ± 5	-529.7	97
CFH_2CFH_2	-445.6	-445.6	24
CFH_2CH_3	-265.7 ± 11	-263.2; -268.2	98, 99
CCl_3CCl_3	-144.3 ± 11	-143.5; -148.1; -141.4	100-102
CCl_3CHCl_2	-143.8 ± 5	-145.2; -142.3	101, 102
CCl_3CH_3	-144.4 ± 3	-142.3; -146.4	103, 104
$CHCl_2CHCl_2$	-152.1 ± 6	-154.8; -149.4	101, 105
$CHCl_2CH_2Cl$	-147.5 ± 4	-146.9; -148.1	105, 106
$CHCl_2CH_3$	-123.5 ± 2	-123.8; -123.4; -123.4	105, 107, 108
CH_2ClCH_2Cl	-130.0 ± 5	-125.5; -132.2; -132.2	108-110
CH_2ClCH_3	-110.4 ± 4	-112.5; -106.7; -112.1	111-113
CH_3CH_3	-83.7 ± 5	-83.7; -83.7; -83.7	114-116
$CF_3CF_2CF_3$	-1758.8 ± 25	-1783.2; -1734.3	87, 117
$CF_3(CF_2)_5CF_3$	-3384.9 ± 4	-3384.9	118
$CH_3CH_2CH_3$	-104.2 ± 1	-104.6; -103.8	116, 119
$CH_2FCH_2CH_3$	-285.8 ± 2	-285.8	120
$CH_3CHClCH_3$	-184.0 ± 4	-144.8; -145.2; -138.5; -144.8	111, 113, 121, 122
$CH_2ClCHClCH_3$	-162.8 ± 3	-162.8; -162.8	108, 123
$CH_2(CH_2Cl)_2$	-159.4 ± 8	-159.4	110
$CHCl(CH_2Cl)_2$	-182.8 ± 2	-182.8	124
$CH_3CCl_2CH_3$	-173.2 ± 8	-173.2	124
CH_3CHFCH_3	-293.3 ± 2	-293.3	120
$C_3H_7CH_2Cl$	-154.4 ± 1	-154.4	110
$C_4H_9CH_2Cl$	-174.9 ± 2	-174.9	110
CF_2CF_2	-656.9 ± 5	-658.1; -655.6	99, 125
CF_2CFH	-490.4 ± 8	-490.4	126
CF_2CH_2	-340.6 ± 6	-343.9; -333.9; -343.9	99, 125, 126
CF_2CCl_2	-335.6 ± 4	-335.6	127
CF_2CHCl	-331.4 ± 6	-331.4	127
$CFHCFH$	-296.2	-296.2	99
$CFHCH_2$	-133.9	-133.9	99
CCl_2CCl_2	-11.8 ± 9	-12.6; -10.9	102, 128
CCl_2CHCl	-8.0 ± 10	-8.8; -7.1	128, 129
CCl_2CH_2	2.3 ± 2	2.1; 2.5	102, 130
$CHClCHCl$	5.5 ± 8	13.8; -2.9	99, 131

Table 2 (*continued*)

Species	$\Delta_f H^{\ominus}$/kJ mol^{-1}		References
	Average	Literature values	
$CHClCH_2$	33.7 ± 5	28.0; 38.1; 35.1	99, 112, 132
CH_2CH_2	52.7 ± 5	52.7; 52.7; 52.7	114, 115, 133
CF_2CFCF_3	−1114.2 ± 1	−1113.8; −1114.6	134, 135
CH_2CHCF_3	−614.2 ± 7	−614.2	136
CH_2CHCH_3	19.4 ± 1	18.8; 19.7; 19.7	115, 133, 137
$CF_2CFCFCF_2$	−938.1 ± 9	−938.1	138

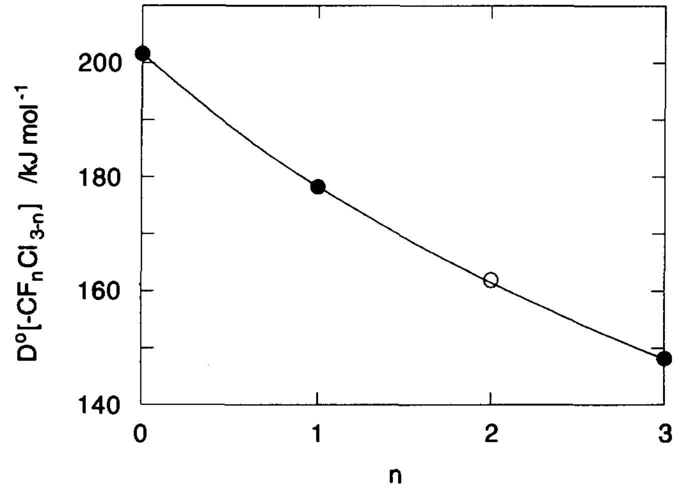

Fig. 3. Dependence of the group contribution $D^{\ominus}[CF_nCl_{3-n}]$ on the stoichiometric factor n. The line represents a polynomial least-squares fit through the three full circles, which are obtained from $\Delta_f H^{\ominus}$ values and Eq. (2). The open circle shows the value of $D^{\ominus}[-CFCl_2]$ estimated using the trend across the homologous series.

Steps (i)–(v) can in principle be applied to any type of species. However, in some cases, the necessary $D^{\ominus}[-A]$ values cannot be determined: either there is insufficient information available to establish meaningful trends (e.g., for carbenes and some radicals) or a group (e.g., $-\overset{|}{C}F-$ or $=CF-$) does not fall into an appropriate homologous series. Under these circumstances, an alternative approach is used to estimate the GAV. Specifically, ab initio calculations [139] have shown that the CF_3 substituent affects the geometry and singlet–triplet splitting energy ΔE_{s-t} in a manner similar to that of hydrogen, e.g., $\Delta E_{s-t}[:CFCF_3] \approx \Delta E_{s-t}[:CFH]$. On this basis, it is postulated that CF_3 and H influence the bond dissociation enthalpy in the same way, e.g.

$$D^{\ominus}[CF_3CX_nY_{2-n}-Z] \approx D^{\ominus}[HCX_nY_{2-n}-Z] \qquad (5)$$

where $0 \leq n \leq 2$ and X, Y and Z are F, Cl, H or a carbon-containing group. Similar relationships can be written for unsaturated compounds or radicals. The validity of Eq. (5) is illustrated in Table 3. Note that, as Z is the same on both sides of the equation, Eq. (5) also implies that $D^{\ominus}[\mathrm{CF_3CX_nY_{2-n}}\text{–}] \approx D^{\ominus}[\mathrm{HCX_nY_{2-n}}\text{–}]$. This relationship can be used to estimate GAVs such as $\Delta_f H^{\ominus}(\text{–CXY–})$, i.e., $\Delta_f H^{\ominus}(\text{–CXY–}) = \Delta_f H^{\ominus}(\mathrm{CF_3CXY}\text{–}) - D^{\ominus}[\mathrm{CF_3CXY}\text{–}] - \Delta_f H^{\ominus}(\mathrm{CF_3})$ and $D^{\ominus}[\mathrm{CF_3CXY}\text{–}] \approx D^{\ominus}[H\mathrm{CXY}\text{–}]$. The quantity $D^{\ominus}[\mathrm{HCXY}\text{–}]$ can be determined independently from $\Delta_f H^{\ominus}$ values and Eq. (4) or, if necessary, from trends in $D^{\ominus}[\mathrm{HCXY}\text{–}]$ (see step (iii) above).

It has been noted previously [19, 141] that Eq. (1), the basis of the original group additivity method, should not be used for (a) two-carbon species (i.e., molecules, radicals, carbenes, or diradicals) with only H atoms on one carbon and only F or Cl atoms on the other or (b) ring compounds. Therefore, for case (a), Eq. (1) has been modified empirically with a correction factor E_{corr}, viz.

$$\Delta_f H^{\ominus}(\mathrm{AB}) = \Delta_f H^{\ominus}(\text{–A}) + \Delta_f H^{\ominus}(\text{–B}) - E_{\mathrm{corr}} \tag{6}$$

which, in accordance with Eq. (4), gives

$$D^{\ominus}[\mathrm{AB}] = D^{\ominus}[\text{–A}] + D^{\ominus}[\text{–B}] + E_{\mathrm{corr}} \tag{7}$$

The extra term in Eqs. (6) and (7) is an estimate of polarization effects [30] or redistribution energy [127]. Note that estimation of $\Delta_f H^{\ominus}$ for $\mathrm{CF_3CH_2CF_3}$ would use Eq. (6) rather than Eq. (1) because, in keeping with Eq. (5), $D^{\ominus}[\mathrm{CF_3\text{–}CH_2CF_3}] \equiv D^{\ominus}[\mathrm{CH_3\text{–}CF_3}]$. In contrast, estimation of $\Delta_f H^{\ominus}$ for $\mathrm{CH_3CF_2CH_3}$ would not require E_{corr}. For case (b), Eq. (1) has been rewritten as

$$\Delta_f H^{\ominus}\left(\overset{\mathrm{B}}{\overset{/\ \backslash}{\mathrm{A\text{–}C}}}\right) = \Delta_f H^{\ominus}(\text{–A–}) + \Delta_f H^{\ominus}(\text{–B–}) + \Delta_f H^{\ominus}(\text{–C–}) + \mathrm{E_{strain}} \tag{8}$$

Table 3

Comparison of bond dissociation enthalpies $D^{\ominus}[\mathrm{A\text{–}B}]$ calculated by two different methods: (a) Eq. (2) and averages of published $\Delta_f H^{\ominus}$ values are used to estimate $D^{\ominus}[\mathrm{A'\text{–}B}]$ for a species A'B (with the $\mathrm{CF_3}$ group(s) in A replaced by a hydrogen atom(s)) and then Eq. (5) is applied; (b) Eq. (2) is applied directly using averages of published $\Delta_f H^{\ominus}$ values

Groups or atoms A–B	$D^{\ominus}[\mathrm{A\text{–}B}]/\mathrm{kJ\,mol^{-1}}$	
	Method (a)	Method (b)
$\mathrm{(CF_3)_2C{=}CF_2}$	525.9	512.1
$\mathrm{CF_3CH_2\text{–}CF_3}$	426.8	422.6
$\mathrm{CF_3CF_2\text{–}CF_3}$	395.4	397.1
$\mathrm{CF_3CF_2\text{–}F}$	527.2	531.4
$\mathrm{CF_3CF_2\text{–}H}$	419.2	430.1
$\mathrm{CF_3CF_2CF_2\text{–}H}$	438.5	435.6[a]
$\mathrm{CF_3CF_2\text{–}\dot{C}F_2}$	223.4	213.3

[a] Eq. (2) was not required, as a value for the bond dissociation energy was available in the literature [140].

for a three-membered ring, and similar relationships apply for larger rings. The strain energy E_{strain} in Eq. (8) can be obtained from known standard heats of formation for cyclic CFCs. If $\Delta_f H^{\ominus}$ for a cyclic species is not known, E_{strain} is estimated by interpolation from known values with different ring sizes or extents of fluorine substitution.

3. Results and discussion

The GAVs calculated for CFCs and related molecules are presented in Table 4. Most of these GAVs are obtained directly from Eq. (1) using the average values of $\Delta_f H^{\ominus}$ listed in Table 2. For almost all these examples, the results are close to those reported previously [19,29–31]. One exception is the value for $\Delta_f H^{\ominus}(\text{-CF}_2\text{H})$. Here, one can calculate values of $D^{\ominus}[\text{-A}]$ for saturated compounds using Eq. (4) (e.g., see Table 5) and then check to see whether or not the results follow monotonic trends across homologous series. Specifically, the value of -437.2 kJ mol^{-1} for $\Delta_f H^{\ominus}(\text{-CF}_2\text{H})$ yields $D^{\ominus}[\text{-CF}_2\text{H}] = 194.5$ kJ mol^{-1}, which meets expectations for the two trends $[\text{-CF}_{3-y}\text{H}_y; 0 \le y \le 3]$ and $[\text{-CHF}_{2-y}\text{Cl}_y;\ 0 \le y \le 2]$. In contrast, the value of -488.7 kJ mol^{-1} [30] yields $D^{\ominus}[\text{-CF}_2\text{H}] = 246.0$ kJ mol^{-1}, which would not satisfy either trend even when uncertainties are taken into consideration. This result suggests that trends in $D^{\ominus}[\text{-A}]$ values could be helpful in checking GAVs for $\Delta_f H^{\ominus}$ that are obtained from Eq. (1).

Table 4 also lists $\Delta_f H^{\ominus}(\text{-A})$ values that were obtained by imposing trends in $D^{\ominus}[\text{-A}]$. In most cases, these values are close to previously reported estimates [29–31]. An exception is $\Delta_f H^{\ominus}(\text{-CFHCl})$, where our result differs by 34.3 kJ mol^{-1} from one of the earlier values. Again, if trends in $D^{\ominus}[\text{-A}]$ values are considered, a value of 215.9 kJ mol^{-1} for $D^{\ominus}[\text{-CFHCl}]$ (based on $\Delta_f H^{\ominus} = -271.5$ kJ mol^{-1} [30]) seems too high in the context of the three series $[\text{-CClF}_{2-y}\text{H}_y; 0 \le y \le 2]$, $[\text{CHF}_{2-y}\text{Cl}_y; 0 \le y \le 2]$ and $[\text{CFCl}_{2-y}\text{H}_y; 0 \le y \le 2]$ (see Table 5). Similarly, a value of $\Delta_f\text{H}^{\ominus}(\text{-CFCl}_2) = -322.6$ kJ mol^{-1} [31] seems too high, as it would give a large maximum along two series of $D^{\ominus}[\text{-A}]$ values in Table 5. Another significant difference between our values in Table 4 and one of the recently reported estimates [30] is for $\Delta_f H^{\ominus}(\text{-CF}_2\text{-})$. Our result is an average obtained using two sets of $\Delta_f H^{\ominus}$ values: (i) $\Delta_f\text{H}^{\ominus}(\text{C}_3\text{F}_8) - 2\Delta_f\text{H}^{\ominus}(\text{-CF}_3) = -1758.8 + 2 \times 672.0 = -414.8$ kJ mol^{-1}, and (ii) $[\Delta_f\text{H}^{\ominus}(\text{C}_7\text{F}_{16}) - 2\Delta_f\text{H}^{\ominus}(\text{-CF}_3)]/5 = [-3384.9 + 2 \times 672.0]/5 = -408.2$ kJ mol^{-1}.

For unsaturated CFCs and related compounds containing two carbon atoms, all the GAVs except $\Delta_f H^{\ominus}(=\text{CFCl})$ can be determined from $\Delta_f H^{\ominus}$ values and Eq. (1). The value for the $=$CFCl group is obtained from $D^{\ominus}[=\text{CFCl}]$, which is taken to be 168.6 kJ mol^{-1} by linear interpolation between $D^{\ominus}[=\text{CF}_2] = 134.3$ and $D^{\ominus}[=\text{CCl}_2] = 202.9$ kJ mol^{-1}. Note that a value of -235.1 kJ mol^{-1} [31] for $\Delta_f H^{\ominus}(=\text{CFCl})$ would not give a monotonic trend for $D^{\ominus}[=\text{CF}_n\text{Cl}_{2-n}]$ with $0 \le n \le 2$. The GAV for $=\text{CCl}_2$ is a compromise obtained using values for $\Delta_f H^{\ominus}(\text{CXY}{=}\text{CCl}_2)$ where X and Y are H, F or Cl and, hence, $\Delta_f H^{\ominus}(\text{CH}_2{=}\text{CCl}_2)$ obtained from Table 4 is ≈ 10 kJ mol^{-1} too negative. This discrepancy can be attributed, at least in part, to the use of a single value for E_{corr}. Higher-order models [97] that account for variations in charge distributions [142]

Table 4

Group additivity values for standard heats of formation (at 298.15 K) of halogenated and partially halogenated hydrocarbon molecules. Each group shows the single and/or double bonds that it forms with carbon atom(s) in adjacent group(s). If a number is given in column M, it indicates that the GAV is chosen to minimize the errors for the M reported heats of formation (see Table 2) in which it can participate according to Eq. (1). Note that, for certain compounds (as described in the text), $\Delta_f H^\ominus$ should be calculated using Eq. (6) rather than Eq. (1). A value of 31.4 kJ mol^{-1} for $E_{\rm corr}$ in Eq. (6) was found by fitting results for CH_3–CX_3 and CH_2=CX_2 where X is Cl and F. The uncertainties listed reflect (i) the impact of variations in $\Delta_f H^\ominus$ values reported for a given compound and (ii) the averaging procedure inherent in the group additivity approach. If a letter is given in column M, it indicates that the GAV is calculated using Eq. (4) and the information in Table 1. The methods used to estimate $D^\ominus$[–A] in Eq. (4) are: A, trends across sets of homologous series; B, Eq. (5). In these cases, the uncertainties listed are overall estimates based on the approximations involved

Group (–A)	$\Delta_f H^\ominus$(–A)/kJ mol^{-1}					M
	Previous work				This work	
	[19]	[29]	[30]	[31]		
–CF_3	−673.6	−672.4	−662.7	−673.6	−672.0 ± 6	8
–CF_2H	−428.0	−457.3	−488.7	−454.8	−437.2 ± 6	3
–CF_2Cl	−444.8	−449.4	−461.5	−462.8	−445.6 ± 8	3
–CFH_2	−215.5	−216.7	−222.6	−220.9	−223.8 ± 8	4
–CFHCl	–	−238.9	−271.5	−271.1	−237.2 ± 13	A
–$CFCl_2$	–	−257.7	−259.4	−322.6	−255.6 ± 13	A
–CCl_3	−86.6	−79.9	−75.3	−82.0	−70.7 ± 6	3
–$CHCl_2$	−79.0	−79.1	−74.9	−79.1	−76.6 ± 13	4
–CH_2Cl	−69.0	−65.3	−69.9	−69.5	−65.7 ± 4	8
–CH_3	−42.7	−42.3	−41.8	−42.3	−42.7 ± 2	15
=CF_2	−324.3	−329.3	−327.2	−329.7	−328.4 ± 4	7
=CFCl	–	−163.2	–	−235.1	−162.8 ± 21	A
=CFH	−157.3	−157.3	−146.9	−165.3	−156.5 ± 8	3
=CCl_2	−7.5	−6.3	−7.1	−11.3	−2.1 ± 6	4
=CHCl	−5.0	8.8	2.5	4.2	0.8 ± 4	4
=CH_2	26.4	26.4	26.4	26.4	26.4 ± 4	7
–CF_2–	−414.2	−406.3	−439.3	−411.3	−411.5 ± 6	2
–CFH–	−205.0	−202.5	−209.2	−204.6	−207.9 ± 4	1
–CFCl–	–	−225.9	–	–	−221.8 ± 17	B
–CHCl–	−61.9	−53.6	−61.1	−55.6	−55.2 ± 4	3
–CCl_2–	−92.0	−81.6	−89.5	−79.5	−87.9 ± 4	1
–CH_2–	−20.5	−20.5	−20.9	−20.5	−21.8 ± 2	5
$-\overset{\vert}{C}F-$	−202.9	−181.6	−202.9	−202.9	−193.3 ± 20	B
=CF–	–	–	−136.0	–	−131.8 ± 8	2
=CH–	36.0	–	36.0	36.4	36.0 ± 2	2
=CCl–	–	–	–	5.0	2.1 ± 20	B

may give a more accurate value of $\Delta_f H^\ominus$ for this compound. For cyclic CFC compounds, $\Delta_f H^\ominus$ values should be obtained using Eq. (8). Here, one can use the values for $\Delta_f H^\ominus$(–A–) specified in Table 4 together with strain energies $E_{\rm strain}$ estimated by comparison with data for cyclic hydrocarbons (see Table 6).

Table 5
Values of $D^{\ominus}[-A]$ in kJ mol^{-1} for saturated CFCs and related compounds that contain two carbon atoms. The uncertainties listed are the sum of those for the corresponding $\Delta_f H^{\ominus}$ values given in Tables 1 and 4. For $-CFCl_2$ and $-CFHCl$, the group values are estimated by requiring $D^{\ominus}[-A]$ to follow trends across all the homologous series (rows, columns and diagonals) in which that group participates; the corresponding uncertainties include an estimate for the additional effect of interpolating based on trends. Note that determination of $D^{\ominus}[CH_3-CCl_yF_{3-y}]$ $(0 \le y \le 3)$ from the values listed requires use of Eq. (7) rather than Eq. (3)

$-CF_3$	201.7 ± 6						
$-CF_2Cl$	176.6 ± 5	$-CF_2H$	194.5 ± 8				
$-CFCl_2$	162.7 ± 8	$-CFHCl$	181.6 ± 8	$-CFH_2$	191.3 ± 8		
$-CCl_3$	148.0 ± 8	$-CHCl_2$	180.2 ± 8	$-CH_2Cl$	185.5 ± 9	$-CH_3$	189.8 ± 4

Table 6
Strain energies E_{strain} in kJ mol^{-1} for cyclic compounds of the type c-C_nX_{2n} estimated using Eq. (8), $\Delta_f H^{\ominus}$ values at 298.15 K (references listed), and GAVs from Table 4. The uncertainties listed represent the variations in the corresponding $\Delta_f H^{\ominus}$ values (including any uncertainties cited for those values). However, the actual uncertainties in E_{strain} are expected to be larger because the GAVs are not known precisely. The one E_{strain} value shown without references is estimated by interpolation of E_{strain} for other c-C_nF_{2n} species. As a first approximation, values of E_{strain} for species of the type c-$C_nF_xH_{2n-x}$ can be estimated by linear interpolation, e.g., for c-C_3F_5H one would obtain 258.2 – (258.2 – 115.5)/6 = 234.4 kJ mol^{-1}

n	c-C_nH_{2n}		c-C_nF_{2n}	
	E_{strain}	References	E_{strain}	References
3	115.5 ± 1	143, 144	258.2	148
4	109.6 ± 1	145	105.9 ± 4	135, 149
5	26.4 ± 2	146	105.0	
6	0.0 ± 1	147	103.8 ± 8	150

Some data for heats $\Delta_r H$ of reactions were not used to establish the GAVs in Table 4 because $\Delta_f H^{\ominus}$ values for more than one of the species in the reaction were unknown. Nevertheless, data of this type can be used to test the validity of the GAVs. For example, $\Delta_r H$ for chlorination of CF_2CFCl calculated using $\Delta_r H = \Delta_f H^{\ominus}(-CF_2Cl) + \Delta_f H^{\ominus}(-CFCl_2) - \Delta_f H^{\ominus}(=CF_2) - \Delta_f H^{\ominus}(=CFCl)$ is -210.0 kJ mol^{-1}, which agrees fairly well with the experimental value of -204.2 ± 2.1 kJ mol^{-1} [151]. Also, $\Delta_r H$ for the disproportionation step $2CF_3CXCFCl = CF_3CXCF_2 + CF_3CXCCl_2$ is found to be -4.9 kJ mol^{-1}, which is reasonably close to the experimental values of -10.5 ± 1.6 and -11.1 ± 0.6 kJ mol^{-1} when X is Cl and F, respectively [152]. The calculated value of $\Delta_r H = -4.9$ kJ mol^{-1} also applies to the reaction $CF_3CFCFCl + CF_3CClCFCl = CF_3CFCF_2 + CF_3CClCCl_2$, which is in good agreement with the measured result of -5.8 ± 0.6 kJ mol^{-1} [152].

Radicals, carbenes, and diradicals are expected to be relevant species in chemical processes involving CFCs and related compounds because a wide variety of elementary reactions can take place [16, 17, 23]. The thermochemical properties of these species are important because they influence species concentrations in addition to reaction rate constants [32]. Up until now, traditional group contribution theory has not been used to estimate their standard heats of formation, at least in part because of the lack of data for such species. However, with Eqs. (3)–(5) and the assumption that $D^\ominus[-A]$ values follow monotonic trends across homologous series, many initial estimates of $\Delta_f H^\ominus$ can be obtained (see Table 7). Here it is emphasized that the values listed are (i) usually not as accurate as those for molecules and (ii) subject to improvement as more data become available. For a given group, it is necessary to have a separate GAV for radicals (slightly more negative than for molecules) in order to avoid systematic errors in $\Delta_f H^\ominus$ values.

Standard heats of formation for CFC carbenes are available for only a few species (see Table 1). Average values of $\Delta_f H^\ominus$ for other carbenes are estimated using Eqs. (2) and (5), as illustrated in Table 8. Subsequently, GAVs for carbenes are obtained assuming that the GAV for the radical CF_3 is applicable.

Values of $\Delta_f H^\ominus$ for diradicals can be obtained by addition of two GAVs for radicals from Table 7, e.g.

$$\Delta_f H^\ominus(^\bullet CF_2)_3{}^\bullet) = 2\Delta_f H^\ominus(-\dot{C}F_2) + \Delta_f H^\ominus(-CF_2-) = -847.1\ \mathrm{kJ\,mol^{-1}}$$

However, the results should be regarded as preliminary because a thermochemical data base for carbenes in the HCFC family has not yet been established. It is interesting to note that the relationship

$$D^\ominus[^\bullet(CZ_2)_n\text{–}X] \approx D^\ominus[Y(CZ_2)_n\text{–}X] \qquad (9)$$

which has been proposed for $n \geq 3$ and X=Y=Z=H [153], yields $\Delta_f H^\ominus$ values for diradicals that are in fairly good agreement with those obtained using the GAVs, i.e., for

Table 7

Group additivity values for standard heats of formation (at 298.15 K) of radicals, carbenes, and diradicals. The meanings of the symbols and the uncertainties are as specified in Table 4. Note that, for species which require Eq. (6) rather than Eq. (1), a value of 31.4 kJ mol^{-1} for E_{corr} was found by fitting the $\Delta_f H^\ominus$ values for CF_3–CH_2 and CH_3–CF_2. Methods used for the calculations (see column M): A, Eq. (4) and trends in $D^\ominus[-CF_{3-x-y}H_xCl_y]$ for $0 \leq x \leq 2$ and $0 \leq y \leq 2$; B/n, average value obtained using Eqs. (4) and (5) for n species; C/n, average value obtained using Eq. (4), Eq. (5), and trends in $D^\ominus[-CF_{3-x-y}H_xCl_y]$ ($0 \leq x \leq 2$; $0 \leq y \leq 2$) for n species

(-A)	$\Delta_f H^\ominus$(-A)/kJ mol^{-1}	M	(-A)	$\Delta_f H^\ominus$(-A)/kJ mol^{-1}	M
$-CF_3$	−672.0 ± 4	3	$-\dot{C}F_2$	−220.0 ± 8	5
$-CF_2H$	−440.2 ± 4	3	$-\dot{C}FCl$	−40.2 ± 18	B/3
$-CF_2Cl$	−466.1 ± 8	2	$-\dot{C}FH$	−12.6 ± 8	4
$-CFH_2$	−225.9 ± 4	3	$-\dot{C}Cl_2$	103.8 ± 20	B/1
$-CFHCl$	−250.2 ± 13.	A	$-\dot{C}HCl$	127.6 ± 11	B/1
$-CFCl_2$	−286.6 ± 13	A	$-\dot{C}H_2$	177.0 ± 8	5
$-CH_3$	−51.5 ± 4	3	$-\ddot{C}F$	146.9 ± 20	B/3
$-CF_2-$	−407.1 ± 8	1	$-\ddot{C}H$	397.5 ± 15	B/2
$-CFH-$	−207.9 ± 15	B/6	$-\ddot{C}Cl$	318.8 ± 20	B/2
$-CFCl-$	−234.7 ± 20	C/6			
$-CH_2-$	−17.2 ± 20	C/6			
$-CHCl-$	−68.6 ± 20	C/6			
$-CCl_2-$	−93.3 ± 20	C/6			

Table 8
Routes used to obtain the average value of -525.0 ± 25 kJ mol^{-1} for $\Delta_f H^{\ominus}(:CFCF_3)$. Species X in Eq. (5) is F for all three routes. The uncertainties listed are estimates based on: (i) the validity of Eq. (5); (ii) uncertainties in $\Delta_f H^{\ominus}$ of starting species; (iii) uncertainties in $D^{\ominus}[A-B]$ values (from Table 1, Table 4, and Eq. (4)). An analogous procedure is used to find $\Delta_f H^{\ominus}(:CHCF_3)$ and $\Delta_f H^{\ominus}(:CClCF_3)$. These values are then used to estimate $\Delta_f H^{\ominus}(:CX-)$ (X is H, F, and Cl, see Table 7)

Species AB in Eq. (2)	Species Y in Eq. (5)	$\Delta H^{\ominus}_{f,298}(:CFCF_3)$/kJ mol^{-1}
CF_2CFCF_3	$=CF_2$	-507.1 ± 15
CF_2CF_3	-F	-532.6 ± 15
$CFHCF_3$	-H	-535.1 ± 15

a group of nine diradicals of the type $^{\bullet}CF_2CFX\dot{C}YZ$ (where X, Y and Z are F, Cl or H), $\Delta_f H^{\ominus}$ values obtained using Eqs. (2) and (9) were only 1–7% more negative than those calculated from Table 7 [32].

4. Conclusions

Group contribution theory can be applied to FCs, CFCs, HFCs, and HCFCs, although it usually leads to larger uncertainties in standard heats of formation than those reported for hydrocarbons. In cases where standard heats of formation have not been reported, group additivity values can be estimated by requiring bond dissociation enthalpies to follow monotonic trends across homologous series of species. The concept of trends in bond strengths can also be used to check the appropriateness of group additivity values estimated from standard heats of formation alone. If there is insufficient information to establish the trends in bond strengths directly, one can estimate bond dissociation enthalpies by assuming that a CF_3 group is equivalent to a hydrogen atom. These methods can be used for radicals, diradicals and carbenes even though the group additivity values for these species are slightly different from those required for molecules. The accuracy of the group additivity values, especially for reactive intermediates, can be improved as more extensive and reliable standard heats of formation become available.

Acknowledgements

This research project was supported by E.I. du Pont de Nemours & Co. Inc. The continued interest of Dr. James A. Trainham is greatly appreciated.

References

[1] O. Badr, S.D. Probert and P.W. O'Callaghan, Appl. Energy, 37 (1990) 247.
[2] E. Broyer, A.Y. Bekker and A.B. Ritter, Ind. Eng. Chem. Res., 27 (1988) 208.

[3] S.K. Sheremet'ev, G.V. Volkov, V.G. Barabanov, I.G. Zenkevich and K.A. V'yunov, J. Gen. Chem. USSR. (Engl. Transl.), 59 (1989) 559.
[4] N.N. Buravtsev, A.S. Grigor'ev and Y.A. Kolbanovskii, Kinet. Catal., 26 (1985) 1.
[5] F. Rodriguez, Principles of Polymer Systems, 3rd edn., Hemisphere, New York, 1989, Chap. 13.
[6] M.A. Golub, T. Wydeven and R.D. Cormia, J. Polym. Sci. Part A: Polym. Chem., 30 (1992) 2683.
[7] G.K. Kostov, St.V. Kotov, G.D. Ivanov and D. Todorova, J. Appl. Polym. Sci., 47 (1993) 735.
[8] A. Newman, Environ. Sci. Technol., 28 (1994) 35A.
[9] K. Verschueren, Handbook of Environmental Data on Organic Chemicals, Van Nostrand Reinhold, New York, 1977, p. 519.
[10] T.P. Nelson and S.L. Wevill, Alternative Formulations and Packaging to Reduce Use of Chlorofluorocarbons (CFCs), Noyes Data Corp., Park Ridge, NJ, 1990.
[11] L.E. Manzer and V.N.M. Rao, Adv. Catal., 39 (1993) 329.
[12] P. Zurer, Chem. Eng. News, 71 (1993) 12.
[13] L.E. Manzer, Catal. Today, 18 (1993) 199.
[14] L. Kaplan, in M. Jones and R.A. Moss (Eds.), Reactive Intermediates, Vol. 1, Wiley, New York, 1978, p. 163.
[15] W. Kirmse, Carbene Chemistry, Academic Press, New York, 1971.
[16] A.F. Ainagos, Kinet. Catal., 32 (1991) 720.
[17] R.A. Taccone, A. Olleta and O. Salinovich, Int. J. Chem. Kinet., 25 (1993) 353.
[18] R.F. Warren and A.R. Ravishankara, Int. J. Chem. Kinet., 25 (1993) 833.
[19] S.W. Benson, Thermochemical Kinetics, 2nd edn., Wiley, New York, 1976.
[20] G.J. Janz, Thermodynamic Properties of Organic Compounds, Academic Press, New York, 1958.
[21] D.A. Dixon, T. Fukunaga and B.E. Smart, J. Am. Chem. Soc., 108 (1986) 1585.
[22] T.S. Papina, V.P. Kolesov and Yu.G. Golovanova, Russ. J. Phys. Chem. (Engl. Transl.), 61 (1987) 1168.
[23] R.A. Taccone, O. Salinovich and E.H. Staricco, Int. J. Chem. Kinet., 21 (1989) 331.
[24] J.M. Martell and R.J. Boyd, J. Phys. Chem., 96 (1992) 6287.
[25] S.J. Paddison, Y. Chen and E. Tschuikow-Roux, Can. J. Chem., 72 (1994) 561.
[26] K.J. Laidler, Can. J. Chem., 34 (1956) 626.
[27] S.W. Benson and J.H. Buss, J. Chem. Phys., 29 (1958) 546.
[28] S.W. Benson, F.R. Cruickshank, D.M. Golden, G.R. Haugen, H.E. O'Neal, A.S. Rodgers, R. Shaw and R. Walsh, Chem. Rev., 69 (1969) 279.
[29] V.G. Kauschka and L. Kolditz, Z. Chem., 16 (1976) 377.
[30] N. Cohen and S.W. Benson, Chem. Rev., 93 (1993) 2419.
[31] E.S. Domalski and E.D. Hearing, J. Phys. Chem. Ref. Data, 22 (1993) 805.
[32] Z. Zhang, Ph.D. Dissertation, University of Houston, 1994.
[33] M. Tirtowidjojo and R. Pollard, J. Cryst. Growth, 77 (1986) 200.
[34] M.W. Chase, J.L. Curnutt, A.T. Hu, H. Prophet, A.N. Syverud and L.C. Walker, J. Phys. Chem. Ref. Data, 14, Suppl. 1, 1985.
[35] R.C. Weast, CRC Handbook of Chemistry and Physics, 68th edn., CRC Press, Boca Raton, FL, 1987.
[36] M. Farber, M.A. Frisch and H.C. Ko, Trans. Faraday Soc., 65 (1969) 3202.
[37] T.L. Porter, D.E. Mann and N. Acquista, J. Mol. Spectrosc., 16 (1965) 228.
[38] C.F. Rodriquez and A.C. Hopkinson, J. Phys. Chem., 97 (1993) 849.
[39] D.L. Hildenbrand, Chem. Phys. Lett., 32 (1975) 523.
[40] G. Herzberg, Spectra of Diatomic Molecules, Van Nostrand Reinhold, New York, 1950.
[41] M. Linevsky, J. Chem. Phys., 47 (1967) 3485.
[42] R.G. Brewer and F.L. Kester, J. Chem. Phys., 40 (1964) 812.
[43] S.G. Lias, Z. Karpas and J.F. Liebman, J. Am. Chem. Soc., 107 (1985) 6089.
[44] A.P. Modica and J.E. LaGraff, J. Chem. Phys., 43 (1965) 3383.
[45] E.N. Okafo and E. Whittle, J. Chem. Soc. Faraday Trans. 1, 70 (1974) 1366.
[46] K.F. Zmbov, O.M. Uy and J.L. Margrave, J. Am. Chem. Soc., 90 (1968) 5090.
[47] A.P. Modica and J.E. LaGraff, J. Chem. Phys., 44 (1966) 3375.
[48] T.N. Tang, T. Smail and F.S. Rowland, J. Am. Chem. Soc., 91 (1969) 2130.
[49] E. Illenberger, H.-U. Scheunemann and H. Baumgartel, Chem. Phys., 37 (1979) 21.

[50] D.W. Kohn, E.S.J. Robles, C.F. Logan and P. Chen, J. Phys. Chem., 97 (1993) 4936.
[51] B.A. Levi, R.W. Taft and W.J. Hehre, J. Am. Chem. Soc., 99 (1977) 8454.
[52] H. Prophet, J. Chem. Phys., 38 (1963) 2345.
[53] W.A. Chupka and C. Lifshitz, J. Chem. Phys., 48 (1968) 2337.
[54] J.E. Bassett and E.J. Whittle, J. Chem. Soc. Faraday Trans. 1, 68 (1972) 492.
[55] E. Tschuikow-Roux and S. Paddison, Int. J. Chem. Kinet., 19 (1987) 15.
[56] J.W. Coomber and E. Whittle, Trans. Faraday Soc., 63 (1967) 1394.
[57] R.H. Martin, F.W. Lampe and R.W. Taft, J. Am. Chem. Soc., 88 (1966) 1353.
[58] H.A. Skinner, Adv. Organomet. Chem., 2 (1965) 49.
[59] J.M. Pickard and A.S. Rodgers, Int. J. Chem. Kinet., 15 (1983) 569.
[60] J.A. Kerr and D.M. Timlin, Int. J. Chem. Kinet., 3 (1971) 427.
[61] L.M. Leyland, J.R. Majer and J.C. Robb, Trans. Faraday Soc., 66 (1970) 898.
[62] B.T. Luke, G.H. Loew and A.D. McLean, J. Am. Chem. Soc., 109 (1987) 1307.
[63] R. Foon and K.B. Tait, J. Chem. Soc. Faraday Trans. 1, 68 (1972) 104.
[64] J.J. DeCorpo, D.A. Bafus and J.L. Franklin, J. Chem. Thermodyn., 3 (1971) 125.
[65] S.J.W. Price, A.F. Trotman-Dickenson, Trans. Faraday Soc., 54 (1958) 1630.
[66] M. Weissman and S.W. Benson, J. Phys. Chem., 87 (1983) 243.
[67] J.W. Hudgens, R.D. Johnson III, R.S. Timonen, J.A. Seetula and D. Gutman, J. Phys. Chem., 95 (1991) 4400.
[68] G.D. Mendenhall, D.M. Golden and S.W. Benson, J. Phys. Chem., 77 (1973) 2707.
[69] S.W. Benson, J. Chem. Phys., 43 (1965) 2044.
[70] M.H. Baghal-Vayjooee, A.J. Colussi and S.W. Benson, J. Am. Chem. Soc., 100 (1978) 3214.
[71] M.H. Baghal-Vayjooee, A.J. Colussi and S.W. Benson, Int. J. Chem. Kinet., 11 (1979) 147.
[72] Y. Chen, A. Rauk and E. Tschuikow-Roux, J. Chem. Phys., 95 (1991) 2774.
[73] B.S. Evans and E. Whittle, Int. J. Chem. Kinet., 13 (1981) 59.
[74] E.-C. Wu and A.S. Rodgers, J. Am. Chem. Soc., 98 (1976) 6112.
[75] Y. Chen, A. Rauk and E. Tschuikow-Roux, J. Chem. Phys., 94 (1991) 7299.
[76] J.P. Martin and G. Paraskevopoulos, Can. J. Chem., 61 (1983) 861.
[77] Y. Chen, A. Rauk and E. Tschuikow-Roux, J. Chem. Phys., 93 (1990) 6620.
[78] E.-C. Wu and A.S. Rodgers, J. Phys. Chem., 78 (1974) 2315.
[79] Y. Chen, A. Rauk and E. Tschuikow-Roux, J. Chem. Phys., 93 (1990) 1187.
[80] J.M. Pickard and A.S. Rodgers, J. Am. Chem. Soc., 99 (1977) 691.
[81] E. Tschuikow-Roux and D.R. Salomon, J. Phys. Chem., 91 (1987) 699.
[82] M. Brouard, P.D. Lightfoot and M.J. Pilling, J. Phys. Chem., 90 (1986) 445.
[83] R. Foon and K.B. Tait, J. Chem. Soc. Faraday Trans. 1, 68 (1972) 1121.
[84] S.J. Paddison, Y. Chen and E. Tschuikow-Roux, Can. J. Chem., 72 (1994) 561.
[85] A.S. Rodgers, Am. Chem. Soc. Symp. Ser., 66 (1978) 296.
[86] B.E. Smart, in S. Patai and Z. Rappoport (Eds.), The Chemistry of Functional Groups, Suppl. D, Wiley, New York, 1983, p. 603.
[87] J.B. Pedley, R.D. Naylor and S.P. Kirby, Thermochemical Data of Organic Compounds, 2nd edn., Chapman and Hall, London, 1986.
[88] K.W. Egger and A.T. Cooks, Helv. Chim. Acta, 56 (1973) 1516.
[89] L.C. Walker, G.C. Sinke, D.J. Perettie and G.J. Janz, J. Am. Chem. Soc., 92 (1970) 4525.
[90] A. Lord, C.A. Goy and H.O. Pritchard, J. Phys. Chem., 71 (1967) 2705.
[91] G.C. Sinke, J. Phys. Chem., 70 (1966) 1326.
[92] J.W. Coomber and E. Whittle, Trans. Faraday Soc., 63 (1967) 2656.
[93] J.C. Amphlett and E. Whittle, Trans. Faraday Soc., 64 (1968) 2130.
[94] G.S. Buckley, W.G.F. Ford and A.S. Rodgers, Thermochim. Acta, 49 (1981) 199.
[95] V.P. Kolesov, A.M. Martynov and S.M. Skuratov, Russ. J. Phys. Chem. (Engl. Transl.), 39 (1965) 223.
[96] J.R. Lacher, J.J. McKinley, C. Walden, K. Lea and J.D. Park, J. Am. Chem. Soc., 71 (1949) 1334.
[97] G.S. Buckley and A.S. Rodgers, J. Phys. Chem., 87 (1983) 126.
[98] D.A. Dixon and B.E. Smart, J. Am. Chem. Soc., 108 (1986) 7172.
[99] Y. Zhang, J. Mol. Struct., 207 (1990) 217.

[100] J. Puyo, D. Balesdent, M. Niclause and M. Dzierzynski, C. R. Acad. Sci., 256 (1963) 3471.
[101] F.W. Kirkbride, J. Appl. Chem., 6 (1956) 11.
[102] L. Smith, L. Bjellerup, S. Krook and H. Westermark, Acta Chem. Scand., 7 (1953) 65.
[103] M. Mansson, E. Ringner and S. Sunner, J. Chem. Thermodyn., 3 (1971) 547.
[104] A.T. Hu, G.C. Sinke and M.J. Mintz, J. Chem. Thermodyn., 4 (1972) 239.
[105] J. Laynez and I. Wadso, Acta Chem. Scand., 26 (1972) 3148.
[106] K.D. Williamson and R.H. Harrison, J. Chem. Phys., 26 (1957) 1409.
[107] J.C.M. Li and K.S. Pitzer, J. Am. Chem. Soc., 78 (1956) 1077.
[108] J.R. Lacher, A. Amador and J.D. Park, Trans. Faraday Soc., 63 (1967) 1608.
[109] G.C. Sinke and D.R. Stull, J. Phys. Chem., 62 (1958) 397.
[110] I. Wadso, Acta Chem. Scand., 22 (1968) 2438.
[111] K.E. Howlett, J. Chem. Soc., (1955) 1784.
[112] J.R. Lacher, E. Emery, E. Bohmfalk and J.D. Park, J. Phys. Chem., 60 (1956) 492.
[113] R.A. Fletcher and G. Pilcher, Trans. Faraday Soc., 67 (1971) 3191.
[114] G.B. Kistiakowsky, H. Romeyn, J.R. Ruhoff, H.A. Smith and W.E. Vaughan, J. Am. Chem. Soc., 57 (1935) 65.
[115] G.B. Kistiakowsky and A.G. Nickle, Discuss. Faraday Soc., 10 (1951) 175.
[116] D.A. Pittam and G. Pilcher, J. Chem. Soc. Faraday Trans. 1, 68 (1972) 2224.
[117] G.S. Buckley, Ph.D. Dissertation, Texas A & M University, 1982.
[118] G.D. Oliver and J.W. Grisard, J. Am. Chem. Soc., 73 (1951) 1688.
[119] F.D. Rossini, J. Res. Natl. Bur. Stand., 12 (1934) 735.
[120] J.R. Lacher, A. Kianpour and J.D. Park, J. Phys. Chem., 60 (1956) 1454.
[121] J.V. Davies, J.R. Lacher and J.D. Park, Trans. Faraday Soc., 61 (1965) 2413.
[122] I. Noren and S. Sunner, J. Chem. Thermodyn., 2 (1970) 597.
[123] R.R. Dreisbach and R.A. Martin, Ind. Eng. Chem., 41 (1949) 2875.
[124] J.D. Cox and G. Pilcher, Thermochemistry of Organic and Orgametallic Compounds, Academic Press, New York, 1970.
[125] C.A. Neugebauer and J.L. Margrave, J. Phys. Chem., 60 (1956) 1318.
[126] V.P. Kolesov, A.M. Martynov, S.M. Shtekher and S.M. Skuratov, Russ. J. Phys. Chem. (Engl. Transl.), 36 (1962) 1118.
[127] J.R. Lacher and H.A. Skinner, J. Chem. Soc. A, (1968) 1034.
[128] J.H. Mathews, J. Am. Chem. Soc., 48 (1926) 562.
[129] H.J. McDonald, J. Phys. Chem., 48 (1944) 47.
[130] D.L. Hildenbrand, R.A. McDonald, W.R. Kramer and D.R. Stull, J. Chem. Phys., 30 (1959) 930.
[131] A.M. Rozhnov, S.V. Levanova, G.A. Dvornikova and S.L. Sadovnikova, Russ. J. Appl. Chem. (Engl. Transl.), 47 (1974) 667.
[132] J.R. Lacher, H.B. Gottlieb and J.D. Park, Trans. Faraday Soc., 58 (1962) 2348.
[133] F.D. Rossini and J.W. Knowlton, J. Res. Natl. Bur. Stand., 19 (1937) 249.
[134] D.A. Dixon, T. Fukunaga and B.E. Smart, J. Am. Chem. Soc., 108 (1986) 4027.
[135] H.C. Duus, Ind. Eng. Chem., 47 (1955) 1445.
[136] V.P. Kolesov, A.M. Martynov and S.M. Skuratov, Russ. J. Phys. Chem. (Engl. Transl.), 41 (1967) 482.
[137] K.B. Wiberg and R.A. Fenoglio, J. Am. Chem. Soc., 90 (1968) 3395.
[138] E.W. Schlag and W.B. Peatman, J. Am. Chem. Soc., 86 (1964) 1676.
[139] D.A. Dixon, J. Phys. Chem., 90 (1986) 54.
[140] B.S. Evans, I. Weeks and E. Whittle, J. Chem. Soc. Faraday Trans. 1, 79 (1983) 1471.
[141] J.F. Liebman, W.R. Dolbier, Jr. and A. Greenberg, J. Phys. Chem., 90 (1986) 394.
[142] H.S. Wu and S.I. Sandler, Ind. Eng. Chem. Res., 30 (1991) 881.
[143] J.W. Knowlton and F.D. Rossini, J. Res. Natl. Bur. Stand., 43 (1949) 113.
[144] A. Greenberg, J.F. Liebman, W.R. Dolbier, Jr. and K.S. Medinger, Tetrahedron, 39 (1983) 1533.
[145] G.W. Rathjens and W.D. Gwinn, J. Am. Chem. Soc., 75 (1953) 5629.
[146] J.P. McCullough, P.E. Pennington, J.C. Smith, I.A. Hossenlopp and G. Waddington, J. Am. Chem. Soc., 81 (1959) 5880.
[147] N.S. Osborne and D.C. Ginnings, J. Res. Natl. Bur. Stand., 39 (1947) 453.

[148] D.S. Bomse, D.W. Berman and J.L. Beauchamp, J. Am. Chem. Soc., 103 (1981) 3967.
[149] H.E. O'Neal and S.W. Benson, J. Phys. Chem., 72 (1968) 1866.
[150] S.J.W. Price and H.J. Sapiano, Can. J. Chem., 57 (1979) 685.
[151] J.R. Lacher, J.M. McKinley, C.M. Snow, L. Michel, G. Nelson and J.D. Park, J. Am. Chem. Soc., 71 (1949) 1330.
[152] D.R. Coulson, J. Fluorine Chem., 50 (1990) 77.
[153] R.G. Bergman, in J.K. Kochi (Ed.), Free Radicals, Vol. 1, Wiley, New York, 1973, p. 191.