# Enthalpy of Formation of Phenyl Formate and Related Bond Dissociation Energies

By **Martin E. Anthoney, A. Selwood Carson,** and **Peter G. Laye,*** Department of Physical Chemistry, The University, Leeds LS2 9JT

The enthalpy of combustion of phenyl formate, $C_7H_6O_2$, has been determined as $-3\,343.4 \pm 2.8$ kJ mol$^{-1}$. This yields an enthalpy of formation of the liquid of $-268.6 \pm 2.9$ kJ mol$^{-1}$. The enthalpy of vaporisation, $\Delta H_{vap} = 52.9 \pm 1.0$ kJ mol$^{-1}$, has been derived from vapour pressure measurements. Values of bond dissociation energies involving phenyl formate are discussed.

THERMOCHEMICAL information on aromatic esters and related compounds is sparse and often inconsistent. For phenyl formate, which is the simplest aromatic ester, there appears to be no previous calorimetric work. We now report the enthalpy of formation of gaseous phenyl formate based on the enthalpy of combustion of the liquid and the enthalpy of vaporisation obtained from vapour pressure measurements. The enthalpy of formation has been used to derive the dissociation energies of bonds in phenyl formate and to link these with values previously reported for related compounds.[1,2]

## EXPERIMENTAL

*Materials.*—Phenyl formate (Cambrian Chemicals) was prepared by the reaction between phenol and acetic formic anhydride using pyridine as a catalyst. The n.m.r. spectrum showed that the compound was *ca.* 97 mol % pure. Small quantities of likely impurities were added to samples of the material and the n.m.r. spectra showed that only phenyl acetate and acetic acid were present in amounts $>0.1$ mol %. Fractional distillation *in vacuo* at 303 K did not change significantly the purity of the sample. Above 313 K phenyl formate slowly decomposed in the gas phase. The low m.p. of phenyl formate, $<173$ K, and the ease with which it undergoes hydrolysis made it difficult to purify the sample by other methods. Accordingly the amounts of phenyl acetate and acetic acid were measured by integrating the areas of the n.m.r. peaks using at least seven scans for each peak. The results obtained were phenyl acetate $1.8 \pm 0.2$ and acetic acid $1.0 \pm 0.2$ mol %.

*Calorimetry.*—The combustion calorimeter has been described previously,[3] but it has now been modified in several important respects. (1) The platinum resistance thermometer has been replaced by a quartz thermometer (Hewlett–Packard, model 2801A) which is connected to a printer. The temperature is recorded with a resolution of $10^{-4}$ K at intervals of 10 s. (2) The outer mercury seal on the jacket has been replaced by a rubber O ring which acts as a seal between flanges on the lid and the body of the jacket. (3) The diameter of the floating lid has been reduced sufficiently to allow the thermometer and electrical connections to be inserted through the top of the calorimeter rather than through the lid itself.

The calorimeter was calibrated by burning in it thermochemical grade benzoic acid (B.D.H.) with a certified energy of combustion of $-26.435$ kJ g$^{-1}$ (weighted *in vacuo*) under standard calorimetric conditions. A series of six experiments gave an energy equivalent of $13.854 \pm 0.002$ kJ K$^{-1}$ for the empty calorimetric system at 298.15 K.

Phenyl formate was burnt in sealed Melinex bags which prevented both hydrolysis and loss through vaporisation prior to ignition. The bags were filled and sealed inside a glove box through which dry nitrogen was passed. To avoid detonation the mass of the samples of phenyl formate was less than 0.8 g. A platinum crucible and a cotton fuse were used. Water (1 cm$^3$) was placed in the combustion

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[1] G. P. Adams, D. H. Fine, P. Gray, and P. G. Laye, *J. Chem. Soc.* (*B*), 1967, 720.

[2] A. S. Carson, D. H. Fine, P. Gray, and P. G. Laye, *J. Chem. Soc.* (*B*), 1971, 1611.

[3] A. S. Carson and B. R. Wilmshurst, *J. Chem. Thermodynamics*, 1971, **3**, 251.

bomb. The initial oxygen pressure was 30 atm. The samples were ignited at 298.15 K by passing an electric current through a fine platinum wire. The nitric acid which was formed from the small amount of nitrogen in the sealed bags and from nitrogen impurity in the oxygen was determined by titrating against aqueous sodium hydroxide.

*Vapour Pressure Measurements.*—Vapour pressure measurements were made in the temperature range 287—305 K using a precision, quartz-spiral, Bourdon gauge (Texas Instruments model 144-01). The optical system enabled pressures to be measured with a resolution of $10^{-3}$ Torr [Torr = (101.325/760) kPa]. The sample was thermostatted to within 0.01 K and the temperature was measured using an N.P.L. calibrated thermometer. The gauge head was maintained at a higher temperature (*ca.* 313 K) than that of the sample to eliminate condensation in the spiral. To prevent decomposition of phenyl formate in the gauge head, the liquid was isolated from the head whilst equilibrium was established. Readings were taken within 15 min of opening the liquid to the gauge. Between measurements the system was evacuated to check the zero position of the gauge. The performance of the apparatus was tested by determining the enthalpy of vaporisation of *m*-xylene. Although the vapour pressure of this compound is rather higher than that of phenyl formate, it is readily obtained pure and its enthalpy of vaporisation has been reasonably well established. The value obtained with the present apparatus was $\Delta H_{vap} = 42.75 \pm 0.34$ kJ mol$^{-1}$ which is in good agreement with the value $42.68 \pm 0.04$ kJ mol$^{-1}$ found by direct calorimetry[4] and $42.51 \pm 0.21$ kJ mol$^{-1}$ from other vapour pressure measurements.[5]

TABLE 1

Combustion of phenyl formate $C_7H_6O_2$

$M = 122.123$ g mol$^{-1}$ $\rho = 1.11$ g cm$^{-3}$ $\varepsilon = 13.854 \pm 0.002$ kJ K$^{-1}$

| $m$(sample) /g | $10^3 n$ (phenyl formate) /mol | $\Delta T$/K | $q_N$/kJ | $q_f$/kJ | $q_M$/kJ | $q_{PA}$/kJ | $q_{HA}$/kJ | $q_i$/kJ | $q_W$/kJ | $-\Delta U^\circ_c$† /kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.720 11 | 5.748 8 | 1.535 6 | 0.006 7 | 0.043 8 | 1.550 2 | 0.421 0 | 0.051 7 | 0.024 4 | 0.016 7 | 3 341.31 |
| 0.668 44 | 5.336 3 | 1.441 9 | 0.006 5 | 0.055 7 | 1.639 0 | 0.390 7 | 0.048 0 | 0.022 7 | 0.015 7 | 3 343.74 |
| 0.677 36 | 5.407 5 | 1.461 5 | 0.001 0 | 0.047 4 | 1.694 7 | 0.396 0 | 0.048 6 | 0.024 2 | 0.016 0 | 3 341.31 |
| 0.663 36 | 5.295 8 | 1.430 2 | 0.001 0 | 0.048 7 | 1.639 2 | 0.387 8 | 0.047 6 | 0.023 7 | 0.015 6 | 3 341.85 |
| 0.593 16 | 4.735 3 | 1.295 1 | 0.000 7 | 0.057 3 | 1.663 4 | 0.346 7 | 0.042 6 | 0.021 3 | 0.014 1 | 3 344.84 |
| 0.648 71 | 5.178 8 | 1.397 9 | 0.000 5 | 0.037 2 | 1.613 4 | 0.379 2 | 0.046 6 | 0.023 1 | 0.015 3 | 3 340.04 |

† $-\Delta U^\circ_c$/kJ mol$^{-1}$ = $n^{-1}(\varepsilon\Delta T - q_N - q_f - q_M - q_{PA} - q_{HA} + q_i - q_W)$. Mean $\Delta U^\circ_c = -3\,342.18 \pm 2.80$ kJ mol$^{-1}$ where the uncertainty is twice the standard deviation of the mean and includes the error in the calibration experiments and allowance for the uncertainty in estimating the amounts of phenyl acetate and acetic acid. $\Delta H^\circ_c = -3\,343.42 \pm 2.80$ kJ mol$^{-1}$.

RESULTS

The following symbols are used in expressing the experimental results: $\varepsilon$, energy equivalent of the empty calorimetric system at 298.15 K; $m$, mass; $M$, molar mass; $n$, number of moles; $\rho$, density; $\Delta T$, corrected temperature change; $q_N$, energy correction for nitric acid; $q_f$, energy correction for the cotton fuse; $q_M$, energy correction for the combustion of Melinex; $q_{PA}$, energy correction for the combustion of phenyl acetate; $q_{HA}$, energy correction for the combustion of acetic acid; $q_i$, heat capacity correction involved in reducing the combustion process to 298.15 K; $q_W$, the Washburn correction.

The corrections $q_i$ and $q_W$ were calculated according to ref. 6 and included contributions from the Melinex, phenyl acetate, and acetic acid. The formula of Melinex was assumed to be $C_{10}H_8O_4$. The corrections for the formation of nitric acid and the combustion of the cotton fuse were based on the values 57.8 kJ mol$^{-1}$ and 16.24 kJ g$^{-1}$ respectively.[6] The correction for Melinex was based on the value $\Delta U^\circ_c = -22.837$ kJ g$^{-1}$ which was measured previously for the same material as used in the present work.[7] The corrections for phenyl acetate and acetic acid were based on the values $\Delta U^\circ_c(CH_3CO_2Ph,l) = -3\,954.11$ and $\Delta U^\circ_c(CH_3CO_2H,l) = -874.38$ kJ mol$^{-1}$ which were calculated from the enthalpies of formation listed by Cox and Pilcher.[8] It has been assumed that the enthalpies of mixing of phenyl acetate and acetic acid with phenyl formate are small and will not significantly affect the enthalpy of combustion.

The results of six combustion experiments are shown in Table 1. Using the values[9] $\Delta H^\circ_f(CO_2,g) = -393.51 \pm 0.13$ and $\Delta H^\circ_f(H_2O,l) = -285.830 \pm 0.042$ kJ mol$^{-1}$ the standard enthalpy of formation is $\Delta H^\circ_f(C_7H_6O_2,l,298.15\ K) = -268.6 \pm 2.9$ kJ mol$^{-1}$.

The enthalpy of vaporisation of phenyl formate, $\Delta H_{vap} = 52.9 \pm 1.0$ kJ mol$^{-1}$, was derived from the vapour pressure measurements. The uncertainty includes an allowance for the effect of the impurities. Combining the enthalpy of vaporisation with the enthalpy of formation of the liquid we obtain $\Delta H^\circ_f(C_7H_6O_2,g,298.15\ K) = -215.7 \pm 3.1$ kJ mol$^{-1}$ = $-51.55 \pm 0.74$ kcal mol$^{-1}$ (1 cal = 4.184 J).

DISCUSSION

Although the enthalpy of formation of phenyl formate has not been reported previously there are values for formic acid[8] and methyl formate.[10] The data are reasonably self-consistent as judged on the basis of the group additivity scheme proposed by Benson and his co-workers.[11,12] If the present result is combined with

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[4] N. S. Osborne and D. C. Ginnings, *J. Res. Nat. Bur. Stand.*, 1947, **39**, 453.

[5] K. S. Pitzer and D. W. Scott, *J. Amer. Chem. Soc.*, 1943, **65**, 803.

[6] ' Experimental Thermochemistry,' ed. F. D. Rossini, Interscience, New York, 1956.

[7] R. S. Butler, A. S. Carson, P. G. Laye, and W. V. Steele, *J. Chem. Thermodynamics*, 1971, **3**, 277.

[8] J. D. Cox and G. Pilcher, ' Thermochemistry of Organic and Organometallic Compounds,' Academic Press, London, 1970.

[9] CODATA key values for thermodynamics, *J. Chem. Thermodynamics*, 1971, **3**, 1.

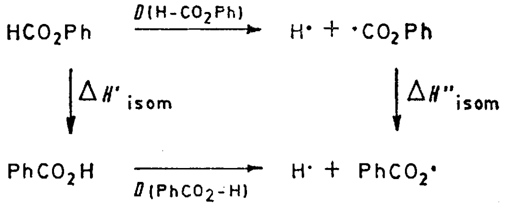
[10] H. K. Hall and J. H. Baldt, *J. Amer. Chem. Soc.*, 1971, **93**, 140.

[11] 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.*, 1969, **69**, 279.

[12] H. K. Eigenmann, D. M. Golden, and S. W. Benson, *J. Phys. Chem.*, 1973, **77**, 1687.

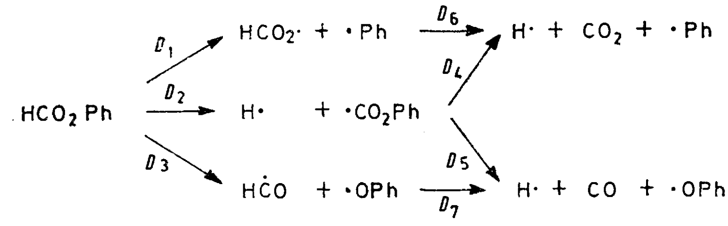
the enthalpies of formation of formic acid and methyl formate a value of 31.5 kcal mol$^{-1}$ is obtained for the group parameter for formates, $E$[CO — (O)(H)]. This value will then reproduce all the experimental data to $\pm 1$ kcal mol$^{-1}$.

*Thermochemical Relationships.*—Phenyl formate is isomeric with benzoic acid and the two may be related by the hypothetical reaction scheme shown in Scheme 1. $\Delta H''_{\text{isom}}$ is known to be small (*ca.* $-1$ kcal mol$^{-1}$) from the enthalpies of formation of the benzoate and phenoxycarbonyl radicals. Thus the enthalpy of isomerisation of phenyl formate, $\Delta H'_{\text{isom}} = -19.1 \pm 0.7$ kcal mol$^{-1}$, is a measure of the difference between the strength of the O–H bond in benzoic acid and the weaker C(O)–H bond in phenyl formate.



SCHEME 1 Isomerisation of phenyl formate

*Dissociation Energies.*—The dissociation energies of bonds in phenyl formate are inter-related to one another and to those in other aromatic esters.[1,2] The dissociation scheme for phenyl formate is shown in Scheme 2. Three new dissociation energies $D_1$—$D_3$ can be calculated from the enthalpy of formation of phenyl formate. The values are given in Table 2 together with values for the corresponding bonds in related compounds.



SCHEME 2 Dissociation scheme for phenyl formate

*Phenoxy-Carbonyl Bond.*—This bond is generally the weakest in phenyl esters and this is true for phenyl formate. The dissociation energy ($D_3 = 73 \pm 4$ kcal mol$^{-1}$) is close to that for the corresponding bond in phenyl acetate ($75 \pm 4$ kcal mol$^{-1}$), but markedly less than that for the alkoxycarbonyl bond in methyl formate ($96 \pm 3$ kcal mol$^{-1}$). This difference reflects the increased stability of the phenoxyl radical compared with the methoxyl radical.

*Phenoxycarbonyl–Hydrogen Bond.*—Within the limits of experimental error the dissociation energy of this bond ($D_2 = 88 \pm 5$ kcal mol$^{-1}$) is the same as the corresponding dissociation energy in methyl formate ($89 \pm 5$ kcal mol$^{-1}$). The values calculated for the dissociation energies of the bonds $\cdot\text{CO}_2$–Ph and $\cdot$CO–OPh are $D_4 = 0 \pm 5$ and $D_5 = 2 \pm 6$ kcal mol$^{-1}$ respectively. The similarity between these dissociation energies can be contrasted with the situation in the methoxycarbonyl radical where $D(\cdot\text{CO}_2 - \text{Me}) = -12 \pm 5$ and $D(\cdot\text{CO–OMe}) = 24 \pm 5$ kcal mol$^{-1}$. Consistent with the thermochemistry is the observation[13] that the methoxycarbonyl radical decomposes quantitatively to a methyl radical and carbon dioxide. For the phenoxycarbonyl radical there is also the possibility of decomposition to carbon monoxide although at present there is no direct experimental information.

TABLE 2

Dissociation energies in phenyl formate and related compounds (in kcal mol$^{-1}$)

| R$^1$ | R$^2$ | $D(\text{R}^1\text{CO}_2\text{–R}^2)$ | $D(\text{R}^1\text{–CO}_2\text{R}^2)$ | $D(\text{R}^1\text{CO–OR}^2)$ |
|---|---|---|---|---|
| H | Ph | $95 \pm 5$ ($D_1$) | $88 \pm 5$ ($D_2$) | $73 \pm 4$ ($D_3$) |
| H | Me | $85 \pm 5$ | $89 \pm 5$ | $96 \pm 3$ |
| Me | Ph | $100 \pm 5$ | $85 \pm 5$ | $75 \pm 4$ |

*Phenyl–Formate Bond.*—It is more difficult to break this bond ($D_1 = 95 \pm 5$ kcal mol$^{-1}$) than the methyl–formate bond ($85 \pm 5$ kcal mol$^{-1}$). The large uncertainties may be discounted as far as this conclusion is concerned since they arise almost entirely from the enthalpy of formation of the $\text{HCO}_2\cdot$radical, which is common to both processes. However, the energy required to dissociate the phenyl–formate bond is similar to that for the phenyl–acetate bond ($100 \pm 5$ kcal mol$^{-1}$).

*Decomposition of Phenyl Formate.*—Although the decomposition of phenyl formate has not been studied extensively, room temperature photolysis,[14] pyrolysis[15] at 823 K, and distillation experiments,[16] indicate that phenol and carbon monoxide are the major products. In the case of room temperature photolysis the presence of polymeric material has also been reported. We have observed a brown polymeric material to be deposited from the vapour in decomposition experiments at 323 K. These experiments also confirmed the formation of phenol and carbon monoxide and the absence of carbon dioxide. This is surprising since of the two reactions (1) and (2) the first is more favourable from the thermo-

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[13] P. Gray and J. C. J. Thynne, *Nature*, 1961, **191**, 1357.

[14] W. M. Horspool and P. L. Pauson, *J. Chem. Soc.*, 1965, 5162.

[15] H. M. MacKinnon and P. D. Ritchie, *J. Chem. Soc.*, 1957, 2564.

[16] F. Adickes, W. Brunnert, and O. Lücker, *J. prakt. Chem.*, 1931, **130**, 163.

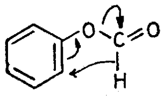
chemical point of view because although the entropy change for both reactions will be similar, the first is

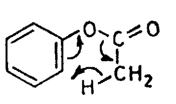
$$\mathrm{HCO_2Ph\ (g) \longrightarrow PhH\ (g) + CO_2\ (g)} \qquad (1)$$
$$\Delta H = -22.7 \pm 0.8\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{HCO_2Ph\ (g) \longrightarrow PhOH\ (g) + CO\ (g)} \qquad (2)$$
$$\Delta H = 2.1 \pm 0.8\ \mathrm{kcal\ mol^{-1}}$$

favoured by the enthalpy change. The implication is that the first reaction is kinetically very unfavourable.

Decomposition studies of other formates present a confused picture in which it seems that both intramolecular[17,18] and radical mechanisms[19] may be relevant. A concerted mechanism for phenyl formate (1) is thermally allowed by the Woodward–Hoffmann rules.[20] This mechanism is isoelectronic with that originally proposed[21] for the thermolysis of phenyl acetate (2). Subsequent experiments with deuterium-labelled samples disproved the concerted mechanism for phenyl acetate and led to a radical mechanism being proposed[22] instead. A radical mechanism has also been suggested[21] for the vapour phase photolysis of phenyl acetate in which phenol, carbon monoxide, and a polymeric material are amongst the products. Both radical mechanisms involve dissociation of the phenoxy–carbonyl bond which is equally feasible for phenyl formate where the bond dissociation energy is very similar.


(1)


(2)

*Enthalpies of Formation of Radicals.*—These are listed in Table 3. Several values are different from those proposed previously as a result of more recent experimental work. In the case of the formate radical no previous value was available.

*Benzoate radical*, $\mathrm{PhCO_2\cdot}$. The value for the enthalpy of formation of the benzoate radical is derived from a new determination of the enthalpy of formation of dibenzoyl peroxide and the dissociation energy $D$ ($\mathrm{PhCO_2{-}OCOPh}$) = 31 kcal mol$^{-1}$.[23] The uncertainty quoted ($\pm$ 5 kcal mol$^{-1}$) allows for possible error in the dissociation energy, which was derived from solution experiments.

*Formyl radical*, H$\dot{\mathrm{C}}$O. Values for the formyl radical have been derived *via* three routes. The first is based on the enthalpy of formation of formaldehyde,[24] measured by flame calorimetry, and the H–CHO dissociation energy which is now reasonably well established by both photoionisation[25] and kinetic studies.[26] The second is from the enthalpy of formation of glyoxal[24] and the CHO–CHO bond dissociation energy.[27] The last is from electron impact studies[28] on methyl formate, ethyl formate, and acrolein. There is good agreement between the values obtained by the three routes and the quoted uncertainty ($\pm$ 2 kcal mol$^{-1}$) covers the individual values.

TABLE 3

Enthalpies of formation of radicals

| | $\Delta H^\circ_f$(g)/kcal mol$^{-1}$ | Reference |
|---|---|---|
| $\mathrm{\cdot CO_2Ph}$ | $-16 \pm 5$ | This paper |
| $\mathrm{\cdot CO_2Me}$ | $-48 \pm 5$ | This paper |
| $\mathrm{PhCO_2\cdot}$ | $-17 \pm 5$ | 23 |
| $\mathrm{MeCO_2\cdot}$ | $-45 \pm 4$ | 30 |
| $\mathrm{HCO_2\cdot}$ | $-34 \pm 5$ | This paper |
| Ph$\dot{\mathrm{C}}$O | $19 \pm 5$ | 2 |
| H$\dot{\mathrm{C}}$O | $9 \pm 2$ | This paper |
| PhO· | $12 \pm 3$ | *a, b* |
| MeO· | $2 \pm 2$ | 29 |
| Ph· | $77.7 \pm 2$ | *c* |

[a] D. H. Fine and J. B. Westmore, *Chem. Comm.*, 1969, 273. [b] L. R. Mahony and M. A. DaRooge, *J. Amer. Chem. Soc.*, 1970, **92**, 2187. [c] G. A. Chamberlain and E. Whittle, *Trans. Faraday Soc.*, 1971, **67**, 2077.

*Methoxycarbonyl radical*, $\mathrm{\cdot CO_2Me}$. Two values exist for the enthalpy of formation of the methoxycarbonyl radical. Gray and Thynne estimated[13] $-52$ kcal mol$^{-1}$ based on a comparison of $D(\mathrm{CH_3{-}COCH_3})$ in acetone and $D(\mathrm{CH_3{-}CO_2CH_3})$ in methyl acetate. Solly and Benson proposed[29] $-40$ kcal mol$^{-1}$ from kinetic studies of the reaction between iodine and methyl formate. This becomes $-43$ kcal mol$^{-1}$ when the more recent value is used for the enthalpy of formation of methyl formate.[10] The kinetic result probably represents an upper limit. We have adopted a mean value, $-48 \pm 5$ kcal mol$^{-1}$, where the uncertainty covers both results.

*Phenoxycarbonyl radical*, $\mathrm{\cdot CO_2Ph}$. The enthalpy of formation of the phenoxycarbonyl radical was previously estimated[2] using Gray and Thynne's value for $\Delta H^\circ_f(\mathrm{\cdot CO_2Me})$. New values for $\Delta H^\circ_f(\mathrm{\cdot CO_2Me})$ and other thermochemical quantities change $\Delta H^\circ_f(\mathrm{\cdot CO_2Ph})$ to $-16 \pm 5$ kcal mol$^{-1}$.

*Formate radical*, $\mathrm{HCO_2\cdot}$. The enthalpy of formation of the formate radical has been estimated from the enthalpy difference $\Delta H^\circ_f(\mathrm{RCO_2\cdot}) - \Delta H^\circ_f(\mathrm{RCO_2H,g})$ *ca.* 57 kcal mol$^{-1}$ established for R = Me and Et.[8,30] For R = H the enthalpy of formation of gaseous formic acid,[8] $\Delta H^\circ_f(\mathrm{HCO_2H,g}) = -90.57$ and so $\Delta H^\circ_f(\mathrm{HCO_2\cdot}) = -34$

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[17] D. V. S. Jain and B. S. Murwaha, *Indian J. Chem.*, 1969, **7**, 901.

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[19] M. J. Yee Quee and J. C. J. Thynne, *Trans. Faraday Soc.*, 1967, **63**, 1656.

[20] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, London, 1970.

[21] J. W. Meyer and G. S. Hammond, *J. Amer. Chem. Soc.*, 1972, **94**, 2219.

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[23] A. S. Carson, P. G. Laye, and H. Morris, *J. Chem. Thermodynamics*, 1975, **7**, 993.

[24] R. A. Fletcher and G. Pilcher, *Trans. Faraday Soc.*, 1970, **66**, 794.

[25] P. Warneck, *Z. Naturforsch.*, 1971, **26a**, 2047.

[26] R. Walsh and S. W. Benson, *J. Amer. Chem. Soc.*, 1966, **88**, 4570.

[27] D. B. Hartley, *Chem. Comm.*, 1967, 1281.

[28] M. A. Haney and J. L. Franklin, *Trans. Faraday Soc.*, 1969, **65**, 1794.

[29] R. K. Solly and S. W. Benson, *Internat. J. Chem. Kinetics*, 1969, **1**, 427.

[30] J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465.

kcal mol$^{-1}$. The procedure may also be used to calculate the enthalpy of formation of the formyl radical using the difference $\Delta H^\circ_f(\mathrm{R\dot{C}O}) - \Delta H^\circ_f(\mathrm{RCHO,g})$ *ca.* 36 kcal mol$^{-1}$. The result $\Delta H^\circ_f(\mathrm{H\dot{C}O}) = 10$ kcal mol$^{-1}$ is in close agreement with the value 9 kcal mol$^{-1}$ which is proposed above. A similar calculation for the methoxyl radical based on $\Delta H^\circ_f(\mathrm{RCH_2O\cdot}) - \Delta H^\circ_f(\mathrm{RCH_2OH,g})$ *ca.* 50 kcal mol$^{-1}$ gives the result $\Delta H^\circ_f(\mathrm{MeO\cdot}) = 2$ kcal mol$^{-1}$, in agreement with the literature value [30] $2 \pm 2$ kcal mol$^{-1}$.

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