Radicals and Ions of Formic and Acetic Acids: An *Ab Initio* Study of the Structures and Gas and Solution Phase Thermochemistry

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The structures of $HCOO^•$, $COOH^•$, $HCOO^-$, $HCOOH^{•+}$, HCOOH, $CH_2COO^{•-}$, $CH_3COO^•$, $CH_2COOH^•$, CH_3COO^-, $CH_3COOH^{•+}$ and CH_3COOH were optimized at HF/6-31G(D) and MP2/6-31G(D) levels. The vibrational frequencies were calculated at the HF/6-31G(D) level and the total energies of these molecules were evaluated at the G2(MP2) level. Gas phase thermodynamic properties, $C_p^⊖$, $S^⊖$, $H^⊖ - H_0^⊖$, $\Delta_f H^⊖$ and $\Delta_f G^⊖$ were calculated as functions of temperature using standard statistical thermodynamic methods. For $HCOO^•$, $COOH^•$, $CH_3COO^•$ and $CH_2COOH^•$, the method of isodesmic reaction was used. The following are recommended values of $\Delta_f H^⊖$ at 298 K in kJ mol^{-1}: $COOH^•$ −193, $CH_2COOH^•$ −243, $CH_2COO^{•-}$ −322, $HCOO^•$ −127, $CH_3COO^•$ −190, all with an uncertainty of ±7 kJ mol^{-1}. Heats of formation of the $RCOO^-$ and $RCOOH^{•+}$ ions were in excellent agreement with those in ref. 1.

On the basis of the structural information from the *ab initio* calculations and an analysis of the solution free energies of the parent compounds, aqueous solution free energies and free energies of formation in solution were calculated for the radicals. The values of $E^⊖(RCOO^•/RCOO^-)$ and other calculated reduction potentials for formate and acetate were shown to be in accord with rates of known redox reactions. Also the $RCOO^•$ radicals were predicted to have abnormally low (actually negative) pK_as for the loss of C–H protons.

The physical chemical properties of the smaller members of the aliphatic series of carboxylic acids are relatively well known. Values of the heats of formation, ionization potentials and proton affinities of the parent molecules are known quite accurately,[1,2] and experimental information on the gas phase thermochemistry of several of the C- and O-centred radicals is available.[3–5] Studies of these radicals have also been made in condensed media.[6,7] However, the short-lived nature of the formyloxyl and acetyloxyl radicals[6,7] has thus far precluded any attempt to obtain thermochemical data for those species in solution, and the relative stabilities of these and the other radical and radical-ion forms remain unclear. Also knowledge of the structures and vibrational frequencies of many of the species is not available.

As well as providing important structural information and vibrational frequencies, *ab initio* calculations carried out at high levels of theory are a valuable source of thermochemical data. For instance, at G2(MP2) level, $\Delta_f H^⊖$ is subject to an uncertainty of only ±20 kJ mol^{-1}, even for open shell systems.[8–10] When coupled with established experimental results for related systems in isodesmic reactions, absolute energies from these calculations are expected to yield heats of formation which are even more reliable. For these reasons we have carried out calculations on several of the ions and radicals, which may be formed from formic and acetic acid. We have previously studied the structures and relative energies of the low lying electronic states of $HCOO^•$ and $CH_3COO^•$ radicals.[11] Here we examine the structures of C-centred species. We also calculate thermodynamic data for these species and the O-centred radicals in the gas phase and in aqueous solution.

*Computation Details.—*Ab initio *calculations.* All calculations presented here were performed with the GAUSSIAN 92 molecular orbital packages.[12] The energies of the species were calculated at the G2(MP2) level of theory.[8] The G2(MP2) procedure includes a geometry optimization with the standard Hartree–Fock method and the 6-31G(D) split-valence basis set [HF/6-31G(D)]; a vibrational frequency calculation at the HF optimized geometry; MP2/6-31G(D) geometry optimization; and two single-point post-HF calculations, QCISD(T)/6-311G(D,P) and MP2/6-311+G(3DF,2P), on the MP2 optimized geometry in order to obtain an accurate estimate of the correlation energy. Harmonic frequency analysis is required by the G2(MP2) procedure for an estimate of the zero point vibrational energy (E_z). This quantity, after scaling, is not particularly sensitive to the accuracy of the frequencies themselves and so HF/6-31G(D) level, with an appropriate empirical correction, is adequate for the purpose. The vibrational frequencies calculated at HF/6-31G(D) level were scaled by a factor of 0.89 (ref. 13) in considering the zero-point energy. Compared with the G2 theory,[10] the G2(MP2) method provides a similar level of accuracy but significant saving in computational time and disk storage. Thus it can be applied to systems of moderate size.[8]

Thermodynamic functions. Ideal gas thermodynamic functions $C_p^⊖$, $S^⊖$, $H^⊖ - H_0^⊖$, $\Delta_f H^⊖$ and $\Delta_f G^⊖$ at 0 and 298.15 K and 1 bar (1 bar = 10^5 Pa) pressure were calculated by standard statistical thermodynamic methods based on the rigid rotor–harmonic oscillator model, and using the frequencies obtained at HF/6-31G(D) level. These frequencies are scaled by a factor of 0.89 in the calculation of thermodynamic functions. In the standard statistical methods, internal rotations are treated as vibrational motions rather than as free or hindered rotors. This approximation may entail some error in the calculated thermodynamic functions $C_p^⊖$, $S^⊖$ and $H^⊖ - H_0^⊖$, which could be avoided in a more detailed treatment.[14] In the present work the lowest vibrational modes in $CH_3COO^•$, CH_3COO^-, $CH_3COOH^{•+}$ and CH_3COOH which correspond to the rotation of CH_3 groups were treated as internal rotations using the free rotor model.

Heats of formation at 0 K, $\Delta_f H_0^⊖$, were derived directly from the G2(MP2) energies according to $\Delta_f H_0^⊖ = E$[G2(MP2) molecule] − Σ E[G2(MP2) elements].† The calculated values of $H^⊖ - H_0^⊖$ were used to evaluate heats of formation at

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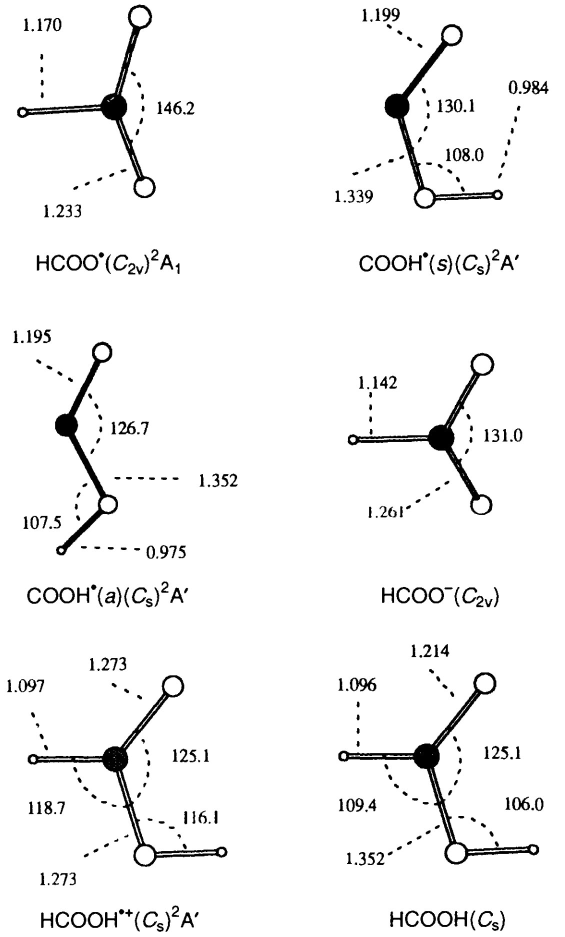
† The G2(MP2) energies for the elements, H_2, O_2, N_2 and Cl_2 were taken from ref. 8. The 'G2(MP2) energy' (−38.054 78 hartrees) for C(graphite) was derived from the G2(MP2) energy for C(atom) (−37.783 90 hartrees, ref. 8) by subtracting the experimental heat of sublimation of graphite at 0 K (711.2 kJ mol^{-1}, ref. 1).

Table 1 E_zs [HF/6-31G(D)] and total energies

Species	E_z/kJ mol^{-1}	G2(MP2)/hartree	ΔE[G2(MP2)]/kJ mol^{-1}	G2/hartree	$\langle S^2 \rangle$
$CO_2^{\bullet-}$ (C_{2v}) $^2A_1$	25.0	−188.331 91		−188.338 49[a]	0.760
$HCOO^{\bullet}$ (C_{2v}) $^2A_1$	49.0	−188.833 80	56.0	−188.839 21[b]	0.787
$COOH^{\bullet}$ (C_s-*syn*) $^2A'$	59.9	−188.852 36	7.3		0.764
$COOH^{\bullet}$ (C_s-*anti*) $^2A'$	60.1	−188.855 15	0.0		0.766
$HCOO^-$ (C_{2v})	58.8	−188.965 44	1 433.2	−188.971 38[a]	
$HCOOH^{\bullet+}$ (C_s) $^2A'$	93.7	−189.093 96	1 095.8		0.762
HCOOH (C_s)	97.3	−189.511 31	0.0		
$CH_2COO^{\bullet-}$ (C_{2v}) $^2B_1$	97.9	−227.540 13	1 444.8		0.766
$CH_3COO^{\bullet}$ (C_s) $^2A''$	139.9	−228.072 69	46.6		0.785
$CH_2COOH^{\bullet}$ (C_s) $^2A''$	136.2	−228.090 42	0.0		0.797
CH_3COO^- (C_s)	136.9	−228.196 23	1 448.0		
$CH_3COOH^{\bullet+}$ (C_s) $^2A'$	171.1	−228.354 23	1 033.1		0.754
CH_3COOH (C_s)	175.5	−228.747 73	0.0		

[a] From ref. 15. [b] From ref. 11.



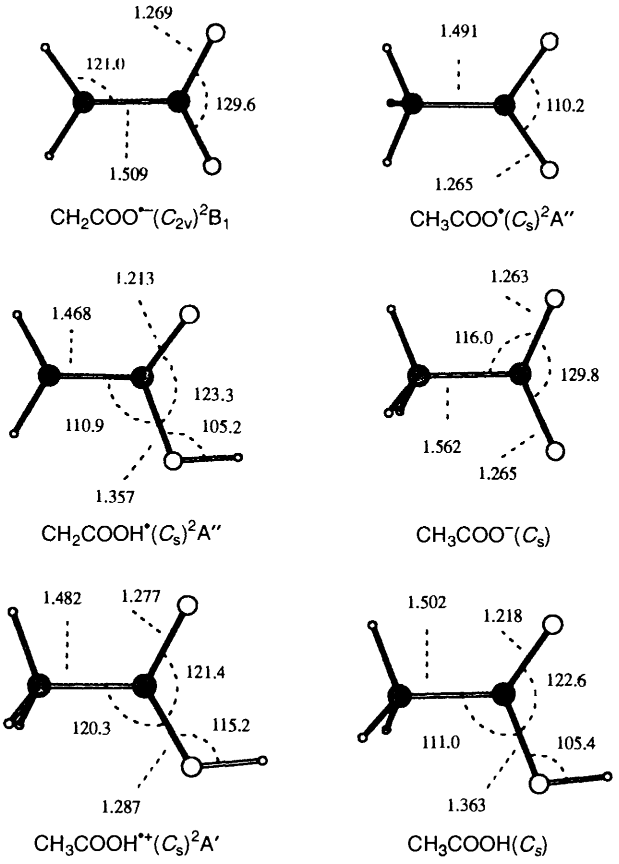
$HCOO^{\bullet}(C_{2v})^2A_1$ $COOH^{\bullet}(s)(C_s)^2A'$

$COOH^{\bullet}(a)(C_s)^2A'$ $HCOO^-(C_{2v})$

$HCOOH^{\bullet+}(C_s)^2A'$ $HCOOH(C_s)$

Fig. 1 MP2/6-31G(D) optimized structures for $HCOO^{\bullet}$, $COOH^{\bullet}$, $HCOO^-$, $HCOOH^{\bullet+}$ and HCOOH. Filled balls represent carbon atoms. Large open balls are oxygen and small open balls are hydrogen. Bond lengths are in angstroms and angles in degrees.

298.15 K. For ionic species the 'ion convention', defined in ref. 1 was followed. Published heats of formation for $COOH^{\bullet}$, $CH_3COO^{\bullet}$ and $CH_2COOH^{\bullet}$ vary by as much as 30 kJ mol^{-1}. For these species and $HCOO^{\bullet}$ the method of isodesmic reaction was used to provide values which we consider to be more accurate. The additional calculations required for the isodesmic reactions were also carried out at the G2(MP2) level. For all species studied, values of $\Delta_f G^{\circ}_{298}$ were derived from the most accurate values of $\Delta_f H^{\circ}_{298}$ and the entropy change of the formation reaction. The values of S°_{298} for the elements were taken from Wagman *et al.*[2]



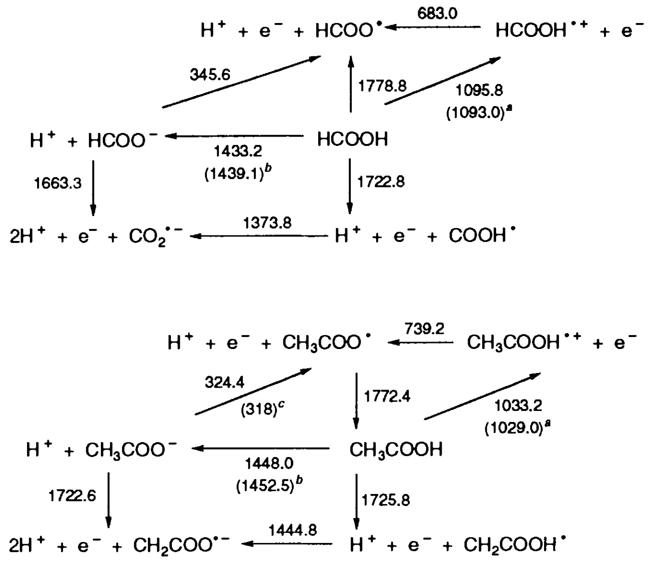
$CH_2COO^{\bullet-}(C_{2v})^2B_1$ $CH_3COO^{\bullet}(C_s)^2A''$

$CH_2COOH^{\bullet}(C_s)^2A''$ $CH_3COO^-(C_s)$

$CH_3COOH^{\bullet+}(C_s)^2A'$ $CH_3COOH(C_s)$

Fig. 2 MP2/6-31G(D) optimized structures for, $CH_2COO^{\bullet-}$, $CH_3COO^{\bullet}$, $CH_2COOH^{\bullet}$, CH_3COO^-, $CH_3COOH^{\bullet+}$ and CH_3COOH. Filled balls represent carbon atoms. Large open balls are oxygen and small open balls are hydrogen. Bond lengths are in angstroms and angles in degrees.

Optimized Structures and Computed Energies.—The MP2/6-31G(D) level optimized structures of the molecules are plotted in Figs. 1 and 2. The characteristic geometric parameters, symmetry types and the electronic states of the radicals are also listed there. The vibrational E_zs and the total energies evaluated at the G2(MP2) level of *ab initio* calculations are reported in Table 1, as well as the relative stabilities within the groups. The G2 values for some of the molecules were available from the literature[10,15] and are listed in Table 1 for comparison. The total energies at the G2(MP2) level for the other 20 compounds involved in the isodesmic reactions are reported in the Appendix, Table A1. Relationships between the G2(MP2)



Scheme 1 Relative G2(MP2) energies in kJ mol⁻¹ (values in parentheses are experimental results corrected to 0 K). [a] From ref. 1. [b] From ref. 16. [c] From ref. 17.

energies of the parent molecules and the radicals and ions are shown in Scheme 1.

$HCOO^•$, $COOH^•$, $HCOO^-$, $HCOOH^{•+}$ *and* HCOOH. The geometric characteristics and the relative stabilities for the different electronic states of formyloxyl ($HCOO^•$) have been discussed in detail elsewhere.[11] The structure of $HCOO^•$ in its lowest electronic state has C_{2v} symmetry, but an important finding of our previous study is that the $^2A'$ state with C_s symmetry is a separate and well-defined minimum energy point in the lowest potential energy surface. In the present study, we will cite the total energy at the G2(MP2) level of the $^2A_1$ state for direct comparison with other species studied in the present work. At the highest level,[11] the three lowest electronic states ($^2A'$, $^2B_2$ and $^2A_1$) were within an energy gap of about 6 kJ mol⁻¹, with $^2A_1$ the lowest. The three geometric parameters of the anion $HCOO^-$ are intermediate to those of the $^2B_2$ (ref. 11) and $^2A_1$ (Fig. 1) states of formyloxyl radical. This molecule has been included in a reaction pathway study carried out by Francisco and Williams.[18] Their MP2/6-311G(D,P) optimized geometric parameters are very similar to those obtained at the same level with 6-31G(D) basis set.

Both the *anti-* and *syn*-configurations[4] of $COOH^•$ were studied and the two optimized C_s structures are both in $^2A'$ electronic states (*i.e.*, σ radicals). Except for the position of the H-atom, the corresponding geometric parameters of these two configurations are similar as indicated in Fig. 1. At the G2(MP2) level, the anti configuration is more stable by 7.3 kJ mol⁻¹, comparable to the MP2/6-311G(D,P) value of 9.2 kJ mol⁻¹ reported by Jeevarajan *et al.*[19]

For both $HCOOH^{•+}$ and the parent HCOOH, the optimized structures are planar with C_s symmetry. The OCO′ angles in both structures are identical (125.1°) and are almost the same as that of $^2A'$ state of formyloxyl radical (125.5°).[11]

The two oxygen atoms in $HCOOH^{•+}$ are geometrically similar (the O–C bond lengths differ only in the fourth decimal place with values in between the typical single and double O–C bond, and the two OCH angles are within 2.5°).

$CH_2COO^{•-}$, $CH_3COO^•$, $CH_2COOH^•$, CH_3COO^-, $CH_3COOH^{•+}$ *and* CH_3COOH. The MP2/6-31G(D) structures of these species are shown in Fig. 2. A study on the electronic states of $CH_3COO^•$ was reported previously.[11] The two lowest states at the G2(MP2) level are both σ radicals, $^2A''$ (B_2-like in comparison with the formyloxyl radical) and $^2A'$ (A′-like).

The lowest energy form of $CH_2COO^{•-}$ is a π radical, $^2B_1$, of C_{2v} symmetry. The unpaired spin is localized on the C atom of CH_2. The local COO structure (CO: 1.269 Å; OCO: 129.6°) closely resembles that of acetate, CH_3COO^- (CO: 1.263 Å; OCO: 129.8°). Rotating the CH_2 group by 90° leads to a stationary point with $^2B_2$ symmetry, 9.9 kJ mol⁻¹ above the planar equilibrium geometry at the G2(MP2) level. Vibrational frequency analysis indicates that this point corresponds to the transition structure (ν_1 = 381i cm⁻¹) for rotation of the CH_2 group.

Optimized $CH_2COOH^•$ is in the $^2A''$ electronic state with C_s symmetry. The unpaired spin is also mainly on the C atom of the CH_2 group, but with a slight distribution over the C–C–O region. Similar to the situation for $CH_2COO^{•-}$, 90° rotation of the CH_2 group of $CH_2COOH^•$ leads to a transition structure (ν_1 = 339i cm⁻¹) for rotation of the CH_2 group, the $^2A'$ radical. The rotation barrier is much higher than that in $CH_2COO^•$, being 27.8 kJ mol⁻¹ at the G2(MP2) level.

CH_3 substitution has little effect on the local structures as can be seen by comparing the geometries of CH_3COOH and HCOOH (Fig. 1). The corresponding geometric parameters of the radical cation $CH_3COOH^{•+}$ are very close to those in $HCOOH^{•+}$, characterized by two similar C–O bond lengths.

Gas Phase Thermochemical Results.—Values of the thermodynamic functions $C_p^⦵$, $S^⦵$ and $H^⦵ - H_0^⦵$ obtained from the calculated vibrational frequencies, are given in Table 2. For the parent molecules the agreement with the literature values is acceptable. There do not appear to be data available for the other species.

Values of $\Delta_f H_{298}^⦵$ obtained from the G2(MP2) energies by the procedure described in a previous section are given in Table 2. The isodesmic reactions are listed in Table 3 together with derived $\Delta_f H_{298}^⦵$ and experimental results. After a careful comparison of the three sets of data, and other calculated results, we recommend the values listed as $\Delta_f H_0^⦵$(rec) and $\Delta_f H_{298}^⦵$(rec) in Table 2. That comparison is done in the following paragraphs of this section. For species where more than one electronic state or geometric configuration exists, the heats of formation refer to the one with lowest energy at the G2(MP2) level. Thus for $HCOO^•$, $COOH^•$ and $CH_3COO^•$, these are the $^2A_1$ state, $^2A'$ (the *anti* configuration), and the $^2A''$ state (a σ radical) respectively.

Values of $\Delta_f G^⦵$ calculated from the recommended values of $\Delta_f H^⦵$ and the entropy data are listed in the final column of Table 2. From the experimental and calculated $S^⦵$ values of the parent compounds in Table 2, we estimate that the uncertainty in $\Delta_f G^⦵$ introduced by errors in the calculated entropies for radicals will not exceed 1 kJ mol⁻¹.

The parent molecules. In the case of acetic acid, CH_3COOH, the G2(MP2) value of $\Delta_f H_{298}^⦵$ in Table 2 is in good agreement with the experimental result (−432.2 kJ mol⁻¹),[2] which is taken as the recommended value. The discrepancy of 17.5 kJ mol⁻¹ between the G2(MP2) value for HCOOH (−396.1 kJ mol⁻¹) and the value from ref. 2 (−378.6 kJ mol⁻¹) is barely within expected limits for the G2(MP2) procedure, and significantly larger than that obtained for CH_3COOH. In view of this and the fact there is a second experimental value of −371.6 kJ mol⁻¹,[20] $\Delta_f H^⦵$ was checked by carrying out the isodesmic reactions listed under HCOOH in Table 3. The average value of $\Delta_f H^⦵$ from the isodesmic reactions, −376.9 kJ mol⁻¹, supports the lower experimental value of −378.6 kJ mol⁻¹ from ref. 2. The recommended value of $\Delta_f H_{298}^⦵$ for HCOOH is −378 kJ mol⁻¹.

$RCOO^-$ *and* $RCOOH^{•+}$ *species.* Recommended heats of formation of the $RCOO^-$ species and those of the $RCOOH^{•+}$ species can be obtained from a consideration of the proton affinities (E_p) of $RCOO^-$, and the adiabatic ionization potentials

Table 2 Ideal gas thermodynamic properties

		J K^{-1} mol^{-1}		kJ mol^{-1}			
	T/K	C_p°	S°	$H^{\circ} - H_0^{\circ}$	$\Delta_f H^{\circ}$[G2(MP2)][a]	$\Delta_f H^{\circ}$(Rec)[a,b]	$\Delta_f G^{\circ}$[a]
$\mathrm{HCOO^{\bullet}}$ ($^2\mathrm{A}_1$)	0	0.0	0.0	0.0	−141.1	−124	
	298	43.4	244.7	10.8	−144.2	−127	−118
$\mathrm{COOH^{\bullet}}$ (*anti*)	0	0.0	0.0	0.0	−197.2	−190	
	298	45.0	251.6	11.1	−200.1	−193	−186
$\mathrm{HCOO^-}$	0	0.0	0.0	0.0	−486.7	−459	
	298	38.8	237.9	10.3	−490.4	−463	−452
HCOOH	0	0.0	0.0	0.0	−388.8	−371	
	298	45.0 (45.7)[c]	248.2 (249.0)[c]	10.9	−396.1	−378	−350
$\mathrm{HCOOH^{\bullet +}}$	0	0.0	0.0	0.0	707.0	722	
	298	46.0	254.7	11.0	699.8	715	741
$\mathrm{CH_2COO^{\bullet -}}$	0	0.0	0.0	0.0	−320.6	−317	
	298	65.4	277.1	13.8	−326.1	−322	−301
$\mathrm{CH_3COO^{\bullet}}$ ($^2\mathrm{A}''$)	0	0.0	0.0	0.0	−187.7	−179	
	298	53.6	284.9	12.5	−198.6	−190	−152
$\mathrm{CH_2COOH^{\bullet}}$	0	0.0	0.0	0.0	−234.2	−234	
	298	70.0	283.4	13.9	−243.8	−243	−205
$\mathrm{CH_3COO^-}$	0	0.0	0.0	0.0	−512.0	−494	
	298	59.2	282.7	13.2	−522.3	−504	−465
$\mathrm{CH_3COOH^{\bullet +}}$	0	0.0	0.0	0.0	604.3	611	
	298	66.7	293.5	14.1	590.7	597	652
$\mathrm{CH_3COOH}$	0	0.0	0.0	0.0	−428.8	−418	
	298	65.1 (66.54)[c]	286.2 (282.5)[d]	13.8	−442.7	−432	−375

[a] Note that the gas phase heats and free energies of formation for ions were computed on the basis of the 'ion convention' (see ref. 1). [b] Recommended, see text. [c] Expt., ref. 53. [d] Expt., ref. 2.

Table 3 Heats of formation from isodesmic reactions

		$\Delta_f H_{298}^{\circ}$/kJ mol^{-1}		
Compound	Isodesmic reaction	G2(MP2)	Isodesmic reaction	Expt.
HCOOH		−396.1		−378.6,[a] −371.6[b]
	$\mathrm{CH_3COOH + CH_4 \longrightarrow HCOOH + C_2H_6}$		−378.5	
	$\mathrm{H_2CO + CH_3OH \longrightarrow HCOOH + CH_4}$		−374.4	
	$\mathrm{CO_2 + CH_3OH \longrightarrow HCOOH + H_2CO}$		−377.7	
	Average		−376.9 ± 1.5[c]	
$\mathrm{HCOO^{\bullet}}$ ($^2\mathrm{A}_1$)		−144.2		−157.7[d]
	$\mathrm{HCOOH + NO_2^{\bullet} \longrightarrow HCOO^{\bullet} + HONO}$		−129.5	
	$\mathrm{HCOO^- + NO_2^{\bullet} \longrightarrow HCOO^{\bullet} + NO_2^-}$		−121.4	
	$\mathrm{HCO^{\bullet} + NO_2^{\bullet} \longrightarrow HCOO^{\bullet} + NO^{\bullet}}$		−128.8	
	Average		−126.6 ± 3.2[c]	
$\mathrm{COOH^{\bullet}}$ (*anti*)		−200.1		−192.5,[d] −223.0[e]
	$\mathrm{HCOOH + HCO^{\bullet} \longrightarrow COOH^{\bullet} + H_2CO}$		−184.2	
	$\mathrm{HCOOH + CH_3CO^{\bullet} \longrightarrow COOH^{\bullet} + CH_3CHO}$		−183.0	
	$\mathrm{HCOOH + COOCH_3^{\bullet} \longrightarrow COOH^{\bullet} + HCOOCH_3}$		−199.5	
	Average		−188.9 ± 6.5[c]	
$\mathrm{CH_3COO^{\bullet}}$ ($^2\mathrm{A}''$)		−198.6		−216.3,[d] −207.5[f]
	$\mathrm{CH_3COOH + NO_2^{\bullet} \longrightarrow CH_3COO^{\bullet} + HONO}$		−190.9	
	$\mathrm{CH_3COCl + NO_2^{\bullet} \longrightarrow CH_3COO^{\bullet} + ONCl}$		−188.6	
	$\mathrm{CH_3CO^{\bullet} + NO_2^{\bullet} \longrightarrow CH_3COO^{\bullet} + NO^{\bullet}}$		−191.3	
	Average		−190.3 ± 1.1[c]	
$\mathrm{CH_2COOH^{\bullet}}$		−243.8		−242.8,[g] −258.0[d]
	$\mathrm{CH_3COOH + CH_2CN^{\bullet} \longrightarrow CH_2COOH^{\bullet} + CH_3CN}$		−246.9	
	$\mathrm{CH_3COOH + CH_2CH_3^{\bullet} \longrightarrow CH_2COOH^{\bullet} + C_2H_6}$		−237.3	
	$\mathrm{CH_3COOH + CH_2COCH_3^{\bullet} \longrightarrow CH_2COOH^{\bullet} + CH_3COCH_3}$		−246.6	
	$\mathrm{CH_3COOH + CH_2COOCH_3^{\bullet} + CH_2COOH^{\bullet} + CH_3COOCH_3}$		−227.3	
	Average		−239.5 ± 9.3[c]	

[a] From ref. 2. [b] From ref. 20. [c] Standard deviations. [d] From ref. 5. [e] From ref. 4. [f] From ref. 21. [g] From ref. 28.

(E_i) of the parent RCOOH molecules. For both formyl and acetyl systems the agreement of the experimental values with the G2(MP2) energies of the E_ps and E_is is excellent (Scheme 1). The experimental E_is and E_ps were used to obtain the $\Delta_f H_{298}^{\circ}$(rec) for the ions in Table 2. These are all within 1 kJ mol^{-1} of the values in ref. 1. The excellent agreement of the present theoretical values of E_p and E_i with experiment suggests that the uncertainties can now be reduced to ±7 kJ mol^{-1}.

The gas-phase E_p for the $\mathrm{CH_3COO^{\bullet}}$ radical (to give $\mathrm{CH_3COOH^{\bullet +}}$) is found to be 739.2 kJ mol^{-1} (Scheme 1). This is higher than the E_p of $\mathrm{HCOO^{\bullet}}$ by 56 kJ mol^{-1} (Scheme 1). On the other hand, the E_p of $\mathrm{CH_3COO^-}$ (1448.0 kJ mol^{-1}) is larger than that of $\mathrm{HCOO^-}$ by only 15 kJ mol^{-1}, indicating that the perturbation due to CH_3 substitution is lower in the anion than in the radical. From Scheme 1, it is interesting to note that CH_3COO^- and $CH_2COO^{\cdot -}$ have almost identical E_ps.

$RCOO^{\cdot}$ *species.* The energy changes in Scheme 1 are equivalent to heats of reaction at 0 K. Thus a value for $\Delta_f H^{\circ}_0$ ($HCOO^{\cdot}$) may be derived from Scheme 1 by using the recommended value $\Delta_f H^{\circ}_0$(rec) for HCOOH (Table 2) and $\Delta_f H^{\circ}_0$ of H^+ (1528 kJ mol^{-1}).[1] Correcting to 298 K with $H^{\circ} - H^{\circ}_0$ data (Table 2), one finds $\Delta_f H^{\circ}_0$ ($HCOO^{\cdot}$) = −123 kJ mol^{-1}. This may be compared with −144.2 kJ mol^{-1} in Table 2 obtained directly from the G2(MP2) procedure. A similar approach for acetoxyl yields $\Delta_f H^{\circ}_{298}$ of $CH_3COO^{\cdot}$ = −185 kJ mol^{-1}, *versus* −198.6 kJ mol^{-1} from the G2(MP2) procedure (Table 2). The differences are primarily due to the corresponding differences between the G2(MP2) calculated values of $\Delta_f H^{\circ}_{298}$ and $\Delta_f H^{\circ}_{298}$(rec) of the parent molecules, HCOOH and CH_3COOH.

It is evident that from Scheme 1 that $\Delta_f H^{\circ}$ of $RCOO^{\cdot}$ is also accessible experimentally from E_e of $RCOO^{\cdot}$ and $\Delta_f H^{\circ}$ of $RCOO^-$. (Note that an experimental determination of $\Delta_f H^{\circ}$ through the E_p of $RCOO^{\cdot}$ would probably be precluded by its short lifetime.)[6,7] One independent measurement of E_e for $CH_3COO^{\cdot}$ by the retarding potential difference method is 318 ± 20 kJ mol^{-1}.[17] This is in good agreement with the G2(MP2) value (Scheme 1) and strongly supports $\Delta_f H^{\circ}_{298}$ of $CH_3COO^{\cdot}$ = −185 to −199 kJ mol^{-1}. Unfortunately there are no similar measurements of E_e for $HCOO^{\cdot}$. The present value of $\Delta_f H^{\circ}_{298}$ of $HCOO^{\cdot}$ is 20 to 30 kJ mol^{-1} higher (less negative) than the recent experimental value of Holmes, Lossing and Mayer (HLM),[5] −157.7 kJ mol^{-1}. HLM[5] have redetermined $\Delta_f H^{\circ}$ for $CH_3COO^{\cdot}$[*] as well, and a similarly large discrepancy exists with the present calculated value. HLM[5] values are based on appearance potentials of two reactions with a quoted uncertainty of ±13 kJ mol^{-1}. Since these discrepancies are at the upper limit of those expected at the G2(MP2) level, calculations based on isodesmic reactions were carried out to obtain more reliable theoretical values.

For $HCOO^{\cdot}$ the average value of $\Delta_f H^{\circ}_{298}$ from the isodesmic reactions in Table 3 is −126.6 kJ mol^{-1}, in agreement with −123 kJ mol^{-1} from the relative G2(MP2) energies of Scheme 1 as described above. The average of $\Delta_f H^{\circ}_{298}$ of $CH_3COO^{\cdot}$ obtained from the set of isodesmic reactions shown in Table 3 is −190.3 kJ mol^{-1}. It is closer to an older experimental value of −207.5 kJ mol^{-1} which is based on the activation energy for the cleavage of the O–O bond in acetyl peroxide,[21] than to the more recent result of HLM (−216.6 ± 13 kJ mol^{-1}).[5]

A recent thermochemical calculation for $CH_3COO^{\cdot}$, based on absolute energies from density functional theory[22] at a reasonably high level, yielded $\Delta_f H^{\circ}_{298}$ = −232.6 kJ mol^{-1}. However, $\Delta_f H^{\circ}_{298}$ was obtained from the formation reaction

$$CH_3^{\cdot} + CO_2 \longrightarrow CH_3COO^{\cdot}$$

which is not an isodesmic process and the result appears to be substantially in error.

The discrepancy with the recent work of HLM[5] requires comment. HLM[5] determined $\Delta_f H^{\circ}_{298}$ from the appearance potential for R'^+ in the mass spectrometric process believed to correspond to Step 1 of Scheme 2,

$$[RCO_2R']^{\cdot +} \xrightarrow{\text{Step 1}} RCO_2^{\cdot} + R'^{+} \xrightarrow{\text{Step 2}} R^{\cdot} + CO_2 + R'^{+}$$

$$[RCO_2R']^{\cdot +} \xrightarrow{\text{Step 3}} R^{\cdot} + CO_2 + R'^{+}$$

Scheme 2

Experimental and theoretical evidence indicates that the barriers to the exoergic decarboxylations of $HCOO^{\cdot}$ and $CH_3COO^{\cdot}$ (Step 2) must be low.[6,7,11] If the smaller absolute magnitudes for $\Delta_f H^{\circ}_{298}$ suggested by the calculations are correct, Step 2 is exoergic by 49 kJ mol^{-1} for R = H and 59 kJ mol^{-1} for R = CH_3. Thus, when threshold energies for the formation of $RCOO^{\cdot}$ from ester cations are used to determine $\Delta_f H^{\circ}_{298}$ of $RCOO^{\cdot}$, there is the potential complication that the direct decomposition (Step 3) may be a competitive process, and that the measured thresholds may in fact be for the ternary fragmentation. The mechanism of decomposition of the radical cations of esters, an important mass spectrometric process, requires further investigation, but is beyond the scope of the present study. In view of the possibility of an alternate pathway, and in accord with the E_e result for $CH_3COO^{\cdot}$, the $\Delta_f H^{\circ}_{298}$(rec) values for $RCOO^{\cdot}$ radicals in Table 2 were taken as averages derived from the isodesmic reactions in Table 3, namely −127 kJ mol^{-1} and −190 kJ mol^{-1} for $HCOO^{\cdot}$ and $CH_3COO^{\cdot}$, respectively.

$COOH^{\cdot}$. The present calculated value of $\Delta_f H^{\circ}_{298}$ (−200.1 kJ mol^{-1} from G2(MP2) direct calculations or −188.9 kJ mol^{-1} from the isodesmic reactions) is more negative than the value (−174 kJ mol^{-1}) derived by HLM[5] from the data of Schatz *et al.*[23] However, Mozurkewich *et al.*[24] adopted a $\Delta_f H^{\circ}_{298}$ of −209 kJ mol^{-1} for this species, and Ruscic and co-workers[4] obtained an even lower value of −223 kJ mol^{-1} from the photoionisation threshold of the radical and $\Delta_f H^{\circ}_0$ of $COOH^+$. The second of these differs substantially from the present estimates, and would mean that the result from the G2(MP2) isodesmic reactions was in error by 34 kJ mol^{-1}, which is unlikely. More recently HLM[5] have reported −192.5 kJ mol^{-1} from studies of four different appearance potentials. This latter value is in good agreement with two results from solution work: −196.6 kJ mol^{-1} (Schwarz and Dodson)[25] and −194.3 kJ mol^{-1} (Surdhar *et al.*)[26] (see further below). It is also within 3.6 kJ mol^{-1} of the average value obtained from the isodesmic reactions (see Table 3). The recommended value therefore is −193 kJ mol^{-1}.

$CH_2COOH^{\cdot}$. Leroy *et al.*[27] calculated $\Delta_f H^{\circ}_{298}$ for this radical with isodesmic reactions, based on MP4/6-31+G(2DF,P) energies. Our result in Table 3 agrees well with theirs (−238.7 kJ mol^{-1}). The average for the isodesmic reactions and the direct calculation are −239.5 and −243.8 kJ mol^{-1}, respectively. The experimental result of HLM[5] (−257.7 ± 13 kJ mol^{-1}) is based on a single reaction and is about 20 kJ mol^{-1} more negative. The calculated values are in line with a second experimental value of −243 kJ mol^{-1},[28] which we adopt as the recommended value.

$CH_2COO^{\cdot -}$. $\Delta_f H^{\circ}_{298}$(rec) of 322 kJ mol^{-1} for this species was calculated from its proton affinity (see Scheme 1) and $\Delta_f H^{\circ}_{298}$(rec) of $CH_2COOH^{\cdot}$.

Examination of all of the data in Table 3 suggests a maximum uncertainty of ±7 kJ mol^{-1} to be associated with the recommended $\Delta_f H^{\circ}$ values. This uncertainty brings into agreement the average values from the isodesmic reactions and all of the experimental values in which we have confidence. Specifically, the recommended values with an uncertainty of ±7 kJ mol^{-1} permit a selection between the experimental values for $COOH^{\cdot}$ and $CH_2COOH^{\cdot}$, but are not reconcilable with any of the experimental values for $HCOO^{\cdot}$ and $CH_3COO^{\cdot}$.

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[*] To gain some experimental input one may estimate $\Delta_f H^{\circ}_{298}$ of $HCOO^{\cdot}$ from the recommended values of $\Delta_f H^{\circ}_{298}$ for $HCOO^-$ and $HCOOH^{\cdot +}$ using the G2(MP2) E_e of $HCOO^-$ and E_p of $HCOOH^{\cdot +}$ from Scheme 1. The values of $\Delta_f H^{\circ}_{298}$ of $HCOO^{\cdot}$ are −118 and −126 kJ mol^{-1}, respectively. Thus they bridge the purely theoretical result of −123 kJ mol^{-1} and do not improve the agreement with ref. 5.

Table 4 Thermodynamic properties (kJ mol^{-1}) of radicals of formic and acetic acid at 298 K and 1 bar

Species	$\Delta_f G^\ominus(g)$[a]	$\Delta G^\ominus(soln)$[b]	$\Delta_f G^\ominus(aq)$[c]
HCOOH	−350	−22	−372
$COOH^•$	−186	−18	−204[d]
$HCOO^•$	−118	−10[e]	−128[f]
$HCOO^-$	−452	−1416	−351
$CO_2^{•-}$	−341[g]	−1381	−205[d]
CH_3COOH	−375	−22	−397
$CH_2COOH^•$	−205	−22[h]	−227[f]
$CH_3COO^•$	−152	−10[e]	−162[f]
CH_3COO^-	−465	−1421	−369
$CH_2COO^{•-}$	−301	−1417	−201[i]

[a] From column 8 of Table 2, unless otherwise stated. [b] From substitution of $\Delta G^\ominus$(aq) and $\Delta_f G^\ominus$(g) in eqn. (5), unless otherwise stated. [c] From ref. 2, unless otherwise stated. [d] Based on the data of references 19, 25 and 26. Uncertainty ±6 kJ mol^{-1}. [e] See text. Uncertainty ±5 kJ mol^{-1}. [f] From substitution of $\Delta_f G^\ominus$(g) and $\Delta G^\ominus$(soln) in eqn. (5). [g] From ref. 15. [h] Assumed equal to that of CH_3COOH. Uncertainty ±2 kJ mol^{-1}. [i] From $\Delta_f G^\ominus$(aq) of $CH_2COOH^•$ and the experimental pK_a of $CH_2COOH^•$ in refs 30 and 31.

Solution Phase Thermochemical Results.—There is now extensive information on the redox reactions of $HCOO^-$ and CH_3COO^- ions[7,25,26,29] in aqueous solution, and on the pK_as[19,30,31] and kinetics of reaction of the radicals derived from them.[29,32] The purpose of this section is to demonstrate that the gas phase free energies of formation in Table 2 and well established solution data for $HCOO^-$ and CH_3COO^- and the parent acids are consistent with this information. Free energies of formation in solution, $\Delta_f G^\ominus$(aq), and free energies of solution, $\Delta_f G^\ominus$(soln), are derived below. Comparisons with experimental redox and pK_a studies are made in subsequent subsections, respectively.

Free energies. Data for aqueous solutions at 298 K and 1 bar are shown in Table 4. Free energies of formation in column four were taken from the sources indicated or were calculated as explained below. Gas phase free energies of formation from Table 2 are reproduced in column two and free energies of solution are listed in column three. It should be noted that for ions, $\Delta_f G^\ominus$(aq) corresponds to the free energy changes for reactions (1) and (2) for positive and negative species, respectively.[2]

$$\mathrm{ESSB(D^+)} + \mathrm{H^+} \longrightarrow \mathrm{D^+} + \tfrac{1}{2}\mathrm{H_{2(g)}} \qquad (1)^*$$

$$\mathrm{ESSB(A^-)} + \tfrac{1}{2}\mathrm{H_{2(g)}} \longrightarrow \mathrm{A^-} + \mathrm{H^+} \qquad (2)$$

Use of this established convention (ref. 33, p. 244) makes it possible to calculate pK_as [*i.e.* $\Delta G^\ominus$(ionization)] and $E^\ominus$ values directly from the differences in $\Delta_f G^\ominus$(aq) for different species. It should also be noted that the 'conventional' free energies of solution used for ions are defined as the free energy changes in reactions (3) and (4) for positive and negative ions

$$\mathrm{D^+_{(g)}} + \mathrm{H^+} \longrightarrow \mathrm{D^+} + \mathrm{H^+_{(g)}} \qquad (3)$$

$$\mathrm{A^-_{(g)}} + \mathrm{H^+_{(g)}} \longrightarrow \mathrm{A^-} + \mathrm{H^+} \qquad (4)$$

respectively.[2] For a given species the free energy of solution, $\Delta G^\ominus$(soln), is related to $\Delta_f G^\ominus$(aq) and $\Delta_f G^\ominus$(g) by expression (5). Here k has values of +1, −1 and 0 for positive,

$$\Delta G^\ominus(\mathrm{soln}) = \Delta_f G^\ominus(\mathrm{aq}) - \Delta_f G^\ominus(\mathrm{g}) + k\Delta_f G^\ominus(\mathrm{H^+_{(g)}}) \qquad (5)$$

negative and neutral species, respectively, and $\Delta_f G^\ominus(\mathrm{H^+_{(g)}})$ is the free energy of formation of the gaseous proton at 298 K (1517 kJ mol^{-1}), the value appropriate to the 'ion convention' used here.[1]

The values of $\Delta_f G^\ominus$(aq) for the parent acids and their anions in column four of Table 4 are well established.[2] For $CO_2^{•-}$ $\Delta_f G^\ominus$(aq) was taken as the mean of the values calculated from $E^\ominus(CO_2/CO_2^{•-})$ (−203 kJ mol^{-1})[25] and $E^\ominus(CO_2^{•-}, H^+/HCO_2^-)$ (−207 kJ mol^{-1}).[26] It may be noted that the recent revision of the pK_a of $COOH^•$ from 1.4 to −0.2 in ref. 19 does not require a correction to these reduction potentials, since both $E^\ominus(CO_2/CO_2^{•-})$ and $E^\ominus(CO_2^{•-}, H^+/HCO_2^-)$ were determined at pHs of 3 or higher,[25,26] well above even the old pK_a value. However, the value of $\Delta_f G^\ominus$(aq) = −204 kJ mol^{-1} for $COOH^•$ in Table 4, calculated from $\Delta_f G^\ominus$(aq) of $CO_2^{•-}$ and the revised pK_a of −0.2, is to be preferred over the values derived from the old pK_a.[25,26,34]

For $COOH^•$, HCOOH and CH_3COOH, $\Delta_f G^\ominus$(soln) was obtained from the difference between $\Delta_f G^\ominus$(aq) and $\Delta_f G^\ominus$(g). The values for the last two are identical and the difference for $COOH^•$ lies within the combined experimental errors of $\Delta_f G^\ominus$(aq) and $\Delta_f G^\ominus$(g), in agreement with assumptions made in refs. 25 and 26. Hence for these systems $\Delta_f G^\ominus$(soln) is not strongly sensitive to the size of the aliphatic group. Therefore $\Delta_f G^\ominus$(soln) of $CH_2COOH^•$ was taken to be the same as that of CH_3COOH (−22 kJ mol^{-1}), from which it differs only by the loss of one H atom (Fig. 2). $\Delta_f G^\ominus$(aq) of $CH_2COOH^•$ was obtained from that result and $\Delta_f G^\ominus$(g), with the aid of eqn. (5). The pK_a of $CH_2COOH^•$ is 4.5,[30,31] and from $\Delta G_{\mathrm{ionization}}$ and $\Delta_f G^\ominus$(aq) of $CH_2COOH^•$ the value of $\Delta_f G^\ominus$(aq) for $CH_2COO^{•-}$ was calculated to be −201 kJ mol^{-1}. Use of eqn. (5) then yields $\Delta_f G^\ominus$(soln) = −1417 kJ mol^{-1}.

From Table 4 the solution free energies of $HCOO^-$, $CH_2COO^{•-}$ and CH_3COO^- are the same within the present uncertainty, −1418 ± 10 kJ mol^{-1}. The value of −1381 kJ mol^{-1} for $CO_2^{•-}$ is 37 kJ mol^{-1} less. However, it is similar to values of −1382, −1380 and −1389 kJ mol^{-1}, which can be calculated from recent experimental electron affinity data in ref. 15 for NO_2^-, N_3^- and OCN^-, respectively. Thus the total absence of a non-polar group probably contributes to the difference from $HCOO^-$ and CH_3COO^-. However, although there is experimental support[35,36] for the value of $\Delta_f H_0^\ominus$ obtained in ref. 15 and used here, it has not been confirmed by spectroscopic studies, and more detailed discussion of $\Delta_f G^\ominus$(soln) of $CO_2^{•-}$ is unwarranted at this time.

Since they have similar geometry and polarity, one would expect $\Delta_f G^\ominus$(soln) for $CH_3COO^•$ to be close to that of CH_3NO_2 (−8.7 kJ mol^{-1}).[37] Also the magnitude of $\Delta_f G^\ominus$(soln) of $CH_3COO^•$ should be reduced from the value for the parent acid by the contribution of a single OH $\cdots$ O hydrogen bond, which is near 9.2 kJ mol^{-1} in water.[38] The average of these approaches gives $\Delta_f G^\ominus$(soln) = −10 kJ mol^{-1}, corresponding to a net change of 12 kJ mol^{-1} from $\Delta_f G^\ominus$(soln) for the parent acid (−22 kJ mol^{-1}). This change was also assumed to apply to $\Delta_f G^\ominus$(soln) of $HCOO^•$. The values of $\Delta_f G^\ominus$(aq) for the two O-centred radicals were then obtained from the $\Delta_f G^\ominus$(g) values by using eqn. (5).

Reduction potentials. The reduction potentials for the cell reaction (6) with R = H and CH_3 can be calculated from the

$$\mathrm{RCOO^•} + \tfrac{1}{2}\mathrm{H_{2(g)}} \longrightarrow \mathrm{RCOO^-} + \mathrm{H^+} \qquad (6)$$

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* ESSB(X) means 'stoichiometric quantities of elements in their standard states at 1 bar required to produce one mol of X'. The subscript (g) indicates that a molecular species is present in the gas phase at 1 bar, absence of a subscript that it is present at a concentration of 1 mol dm^{-3} in aqueous solution.

Table 5 Standard reduction potentials

Process	$E^\ominus$/V
$CH_3COO^\bullet + H^+ + e^- \longrightarrow CH_3COOH$	2.4
$HCOO^\bullet + H^+ + e^- \longrightarrow HCOOH$	2.5
$CH_3COO^\bullet + e^- \longrightarrow CH_3COO^-$	2.1
$HCOO^\bullet + e^- \longrightarrow HCOO^-$	2.3
$CH_2COOH^\bullet + H^+ + e^- \longrightarrow CH_3COOH$	1.8
$CH_2COO^{\bullet -} + H^+ + e^- \longrightarrow CH_3COO^-$	1.7
$CO_2^{\bullet -} + H^+ + e^- \longrightarrow HCOO^-$	1.5[a]

[a] Experimental value from ref. 26.

values of $\Delta_f G^\ominus$(aq) in Table 4 and the relation $E^\ominus = -\Delta G^\ominus(6)/F$, where F is the Faraday constant. These correspond to the values of $E^\ominus(RCOO^\bullet/RCOO^-)$, the standard reduction potentials for the half reactions (7) with

$$RCOO^\bullet + e^- \longrightarrow RCOO^- \tag{7}$$

R = H and R = CH_3. Standard reduction potentials for any other half reactions can be calculated in a similar manner. Those of interest here are given in Table 5.

There are no experimental reduction potentials with which the present data can be compared. They are, however, consistent with observed rates of redox reactions. Thus the $SO_4^{\bullet -}$ radical ion with $E^\ominus(SO_4^{\bullet -}/SO_4^{2-}) = 2.43$ V (ref. 39) reacts at a significant rate with both $HCOO^-$ and CH_3COO^- ions.[29] Conductivity studies mentioned in ref. 32 indicate that reaction (8) occurs with the former.

$$SO_4^{\bullet -} + HCOO^- \longrightarrow H^+ + CO_2^{\bullet -} + SO_4^{2-} \tag{8}$$

The electron transfer process, reaction (9) apparently is not

$$SO_4^{\bullet -} + HCOO \longrightarrow HCOO^\bullet + SO_4^{2-} \tag{9}$$

observed. These results can be understood in the light of the data in Table 5, which show that, while (8) is strongly exergonic (0.9 V), (9) is only marginally so (0.1 V). Thus the rate of (9) would be negligible. For CH_3COO^- on the other hand $E^\ominus(CH_3COO^\bullet/CH_3COO^-)$ is lower and (10), the counter-

$$SO_4^{\bullet -} + CH_3COO^- \longrightarrow CH_3COO^\bullet + SO_4^{2-} \tag{10}$$

part of (9) is exergonic by 0.3 V. Here the experimental data show that the electron transfer process (10) dominates over the H atom abstraction (11).

$$SO_4^{\bullet -} + CH_3COO^- \longrightarrow H^+ + CH_2COO^{\bullet -} + SO_4^{2-} \tag{11}$$

The yields of carbon dioxide[40] and methyl radicals[7c] from the rapid subsequent decomposition of $CH_3COO^\bullet$, *viz* reaction (12) demonstrate that (10) represents over 80% of the overall

$$CH_3COO^\bullet \longrightarrow CH_3^\bullet + CO_2 \tag{12}$$

reaction. Analogous reactions occur with many other carboxylic acids.[40]

In contrast to $SO_4^{\bullet -}$, $OH^\bullet$ with $E^\ominus(OH^\bullet/OH^-) = 1.90$ V[39] would not be capable of removing an electron from either $HCOO^-$ or CH_3COO^-, and should only undergo H abstraction. This is in agreement with observations of EPR studies[7c] and other experiments.[29] Further information comes from studies of photo-induced oxidation. The effective reduction potential of the flavin triplet, $E^\ominus(Fl^{Triplet}/Fl^{\bullet -})$, calculated from $[E^\ominus(Fl/Fl^{\bullet -}) + E(Fl^{Triplet})]$,[41] is 1.8 V.[42] While this species reacts quite rapidly with amines and other species of lower reduction potential[43,44] the rate of electron transfer from unsubstituted carboxylate ions, such as propionate or acetate, is negligible.[45] Hence $E^\ominus(CH_3COO^\bullet/CH_3COO^-)$ must be equal to or larger than 1.8 V,[41,46] while being significantly smaller than $E^\ominus(SO_4^{\bullet -}/SO_4^{2-})$ (= 2.4)[39] as mentioned above. The value of 2.1 V in Table 5 is consistent with these observations. Likewise, the apparent slowness of reaction (9) is consistent with $E^\ominus(HCOO^\bullet/HCOO^-) = 2.3$ V. It is worth pointing out that this was calculated from $\Delta_f H^\circ_{298}$ of $HCOO^\bullet = -127$ kJ mol^{-1}. A $\Delta_f H^\circ_{298}$ of -157 kJ mol^{-1} would make $E^\ominus(HCOO^\bullet/HCOO^-)$ 0.3 V lower, and formate should then be susceptible to electron transfer to $SO_4^{\bullet -}$ as is observed for acetate with calculated $E^\ominus(CH_3COO^\bullet/CH_3COO^-) = 2.1$ V.

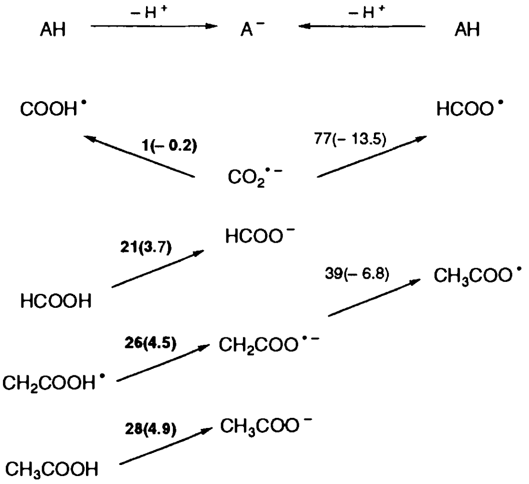

Fig. 3 Comparison of free energies of interconversion in kJ mol^{-1} at pH = 0 and pK_as (in parenthesis) of radicals and parent acids. Experimental values in bold face.

The present value of $E^\ominus(CH_3COO^\bullet/CH_3COO^-) = 2.1$ V is significantly smaller than a previous estimate of 2.4 V by Eberson,[47] based on earlier thermochemical data, but closer to Pearson's more recent prediction of 2.0 V.[48] It is evident from these estimates and from our $E^\ominus(HCOO^\bullet/HCOO^-)$ that the first two members of the series of aliphatic $RCOO^\bullet$ radicals have redox potentials just below those of $NO_3^\bullet$ and $SO_4^{\bullet -}$ $[E^\ominus(NO_3^\bullet/NO_3^-) = 2.3$ and $E^\ominus(SO_4^{\bullet -}/SO_4^{2-}) = 2.4]$.[39] At first sight this conclusion may seem surprising, since $RCOO^\bullet$ radicals have frequently been postulated to occur in electrolysis at relatively low potentials.[49] However, it has been pointed out that the radicals involved in electrode processes like the Kolbe electrosynthesis are stabilized by adsorption on the electrode.[49,50] The production of free aliphatic $RCOO^\bullet$ radicals by electrolysis in water at positive potentials is not thermodynamically favourable.[50]

pK_a *Values.* The ionization energies and pK_as (in parenthesis) of the parent molecules and the C-centred and O-centred radicals, calculated from the data in Table 4, are presented in Fig. 3. One interesting result is the extreme instability of the $RCOO^\bullet$ radicals with respect to deprotonation of the R group to form the more stable C-centred radicals, *viz* reactions (13) and (14). Normally pK_ss of H–C protons are in the region of 20

$$HCOO^\bullet \longrightarrow H^+ + CO_2^{\bullet -} \tag{13}$$

$$CH_3COO^\bullet \longrightarrow H^+ + CH_2CO_2^{\bullet -} \tag{14}$$

to 50.[51] For H–COO$^\bullet$ and H–$CH_2COO^\bullet$ they are drastically reduced: -13.5 and -6.8 respectively.

Reactions (13) and (14) are strongly exergonic (Fig. 3), and one must consider the possibility of the sequences (9) + (13)

Table A1 G2(MP2) energies and heats of formation (298 K) for compounds used in isodesmic reactions

		$\Delta_f H^{\circ}_{298}$/kJ mol ^{1}	
Compound	E[G2(MP2)]/hartree	Calc.	Expt.[a]
CH_4	−40.409 66[b]	−66.0	−74.8
$CH_2CH_3^{\bullet}$	−78.968 28	140.0	120.2
C_2H_6	−79.628 93[b]	−68.8	−84.7
$HCO^{\bullet}$	−113.695 97[b]	34.6	43.1
H_2CO	−114.336 08[b]	119.1	−108.6
CH_3OH	−115.531 81[b]	−203.3	−200.7
$CH_2CN^{\bullet}$	−131.866 24	271.7	249.8[c]
CH_3CN	−132.519 90	82.1	73.7[c]
$CH_3CO^{\bullet}$	−152.931 65	−10.7	−10.0[d]
CH_3CHO	−153.573 11	−167.4	−166.2
CO_2	−188.356 62[b]	−419.8	393.5
$CH_2COCH_3^{\bullet}$	−192.154 95	−23.1	−41.0
CH_3COCH_3	−192.809 14	−212.9	−217.6
$NO^{\bullet}$	−129.736 22[b]	77.6	90.3
$NO_2^{\bullet}$	−204.830 47	13.8	33.1
NO_2	−204.915 36	−209.1	−186.3
HONO(*cis*)	−205.455 07	−98.7	−76.7
$COOCH_3^{\bullet}$	−228.064 23	−173.8	−166.7
$HCOOCH_3$	−228.721 88	−374.2	−350.2
$CH_2COOCH_3^{\bullet}$	−267.301 35	−222.3	−240.6
CH_3COOCH_3	−267.958 50	−420.8	−445.3
ONCl	−589.464 65	34.9	51.7
CH_3COCl	--612.735 22	−251.1	−243.5

[a] From refs 1, 2, 5 and 28 unless otherwise indicated. [b] From ref. 8. [c] From ref. 54. [d] From ref. 55.

and (10) + (14) as sources of $CO_2^{\bullet -}$ and $CH_2CO_2^{\bullet}$. The evidence cited for $CH_3^{\bullet}$ and CO_2 production from $SO_4^{\bullet}$ oxidation of CH_3COO in the previous subsection indicates that, despite the large driving force, reaction (14) does not compete effectively with (12). This feature can be attributed to the large solvent reorganization required for (14), and one may assume that the rate of (13) will be affected in the same way. Reaction (12) and its counterpart for $HCOO^{\bullet}$ do not require massive solvent reorganization, and there is evidence that $k_{12} \geq 10^{11}$ s ^{1}.[52]

Another feature in Fig. 3 is the fact that the experimental pK_a of the $CH_2COOH^{\bullet}$ radical closely resembles that of the parent acid (pK_as of 4.5 and 4.9 respectively). This is corroborated by the almost identical gas phase E_ps calculated here for $CH_2COO^{\bullet}$ and CH_3COO (see Scheme 1). The similarity of the gas and solution acidities is maintained by the essential equality in the solution free energies of the ions and neutrals for the two systems (Table 4, column three). In contrast, for the $COOH^{\bullet}$ radical both the gas and solution phase data exhibit a greater acidity than the parent acid (Scheme 1 and Fig. 3).

Conclusions

The *ab initio* calculations have provided optimized structures for the parent acids, their anions and radicals, as well as absolute G2(MP2) energies and heats of formation. Differences in G2(MP2) energies of the parent molecules and ions in Scheme 1 gave E_ps and E_is in excellent agreement with experiment. The G2(MP2) gas phase heat of formation for CH_3COOH agreed well with experiment. The agreement was not as good in the case of HCOOH, and isodesmic reactions were used here. The results of these confirmed the accuracy of the more negative heat of formation, −378 kJ mol ^{1}, currently in the literature.

The calculations of $\Delta_f H^{\circ}_{298}$ for the radicals $COOH^{\bullet}$ and $CH_2COOH^{\bullet}$ supported the less negative values of recent experimental studies, namely −193 and −243 kJ mol ^{1}. For $HCOO^{\bullet}$ and $CH_3COO^{\bullet}$ on the other hand our recommended values of $\Delta_f H^{\circ}_{298}$ of −127 and −190 kJ mol ^{1}, respectively, were 17 and 30 kJ mol $^{-1}$ more positive than even the closest experimental result from appearance potential studies. In the case of $CH_3COO^{\bullet}$ the present value is supported by an independent determination of the E_e. We believe the present $\Delta_f H^{\circ}_{298}$(rec) values are correct to within ± 7 kJ mol ^{1}.

Gas phase free energies of formation, were derived from the present heats of formation and entropy data. These were combined with solution free energy information for related molecules and used to derive free energies of formation of the radicals in water. A self consistent set of gas and solution phase thermodynamic data has therefore been obtained. The solution phase results were shown to be in accord with a range of experimental observations on redox reactions and acidities of the radicals and their parent ions, a feature which strongly supports the heats of formation recommended here.

Finally the pK_as of the $HCOO^{\bullet}$ and $CH_3COO^{\bullet}$ radicals with respect to deprotonation at the C–H sites were found to be remarkably low: −13.5 and −6.8, respectively. This is due to the strong stabilization of the negative charge on the oxygen atoms. Nevertheless experimental results imply that the deprotonation is kinetically unable to compete with the elimination of CO_2, which is known to be extremely rapid for small aliphatic acyloxyl radicals.

Acknowledgements

The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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Paper 4/02165G
Received 12*th April* 1994
Accepted 9*th June* 1994