AB INITIO AND SEMI-EMPIRICAL INVESTIGATION OF GAS-PHASE CARBON ACIDITY

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Acidities of a representative range of carbon acids were calculated by various levels of *ab initio* theory and by the semi-empirical methods AM1 and PM3 in order to ascertain what level is necessary in order to obtain consistently reliable results. The semi-empirical methods give good agreement with experiment in about a third of the cases, but are significantly, and sometimes seriously, in error for the rest. The 3–21G *ab initio* method consistently underestimates acidities by a substantial amount. The best results were obtained at the MP2/6–31 + G*//6–31 + G* level. Higher level Møller–Plesset corrections worsened the agreement with experiment.

INTRODUCTION

Gas-phase acidities constitute an ideal testing ground for quantum-mechanical calculations of organic equilibria because there exists a large body of experimental data for comparison.[1] The present investigation was undertaken to study a representative range of carbon acids. Carbon acids, especially those that yield resonance-stabilized anions, are of major importance in synthetic organic chemistry and have also been the subject of many mechanistic investigations. This work is part of a wider study of energy profiles for proton transfers to and from carbon acids, and it was important to determine whether reliable results on the relative energies of carbon acids and their anions could be obtained at a level feasible for the energy profile studies, where quantitative comparisons with experiment are seldom possible.

Numerous calculations of gas-phase acidities of carbon acids have been reported in the recent literature by both semi-empirical[2,3] and *ab initio*[4–8] methods. Of these studies, excellent agreement with experiment was obtained by the G2 method.[8,9] This method, however, is sufficiently time consuming that it would be impractical for other than very simple acids and for nearly all of the projected reaction profile studies. Of the other approaches, results with the semi-empirical methods were mixed and with the lower level *ab initio* methods poor. This study was aimed at the middle ground in the hope of finding a way of obtaining good agreement with experiment at a modest cost in computer time.

COMPUTATIONAL METHODS

The semi-empirical calculations utilized Mopac version 6.0[10] and specifically the AM1[11] and PM3[12] methods. The *ab initio* calculations utilized Gaussian 92.[13] Standard basis sets were used in all calculations: 3–21G[14] and 6–31 + G*.[15,16] Correlation corrections were applied by the Møller–Plesset method.[17–21] The ΔH values reported in Table 1 for the *ab initio* calculations are corrected to constant pressure and for zero point energy differences from 6–31 + G*//6–31 + G* vibrational frequency calculations scaled to 0·9 to account for the overestimation of frequencies by Hartree–Fock methods.[22,23] They are further corrected to 298 K for the contributions of the translational, rotational and vibrational partition functions to ΔH.[24] The vibrational contribution is important only for low-lying frequencies (<500 cm^{-1}) and makes only a slight difference in most of the acidities. The semi-empirical heats of formation were used without correction, as they are parametrized to match experimental heats and so implicitly include the necessary corrections. That all species were true minima was shown by frequency and force calculations that gave no negative eigenvalues.

RESULTS AND DISCUSSION

Table 1 lists experimental acidities in the second column along with calculated acidities at various levels in the succeeding columns. No effort was made to judge the relative reliabilities of the experimental acidities where

Table 1. Gas-phase acidities of carbon acids[a]

Acid	Expt.[b]	AM1	PM3	3-21G	6-31+G*	MP2/6-31+G*//6-31+G*	MP3/6-31+G*//6-31+G*	MP4SDQ=FC/6-31+G*//6-31+G*	MP2/6-31+G*//MP2/6-31+G*
CH_4	416·6 ± 0·8 418·0 ± 3·5[c]	433·7	431·7	454·5	425·6	418·2	421·3	420·7	418·7
C_2H_4	406·0 ± 2·0 407·0 ± 3·0[c] 409·4 ± 0·6[d]	418·5	412·3	434·2	413·8	407·7	410·5	410·1	408·6
C_6H_6	400·7 ± 0·5 401·0 ± 10·0[c]	402·6	395·3	423·3	406·9	397·4	401·8	401·1	
CH_3Cl	396·0 ± 2·3 399·6 ± 2·4[e]	407·8	402·6	400·3	400·9	402·6	403·3	402·5	401·0
CH_3SCH_3	393·2 ± 2·6 390·2 ± 1·5[f]	385·2	380·4	418·1	405·1	395·9	400·1	399·3	
$CH_3CH=CH_2$	390·7 ± 2·4 391·9 ± 2·0	388·2	386·0	417·1	399·7	390·3	395·2	395·1	390·6
$C_6H_5CH_3$	380·8 ± 2·4 381·2 ± 2·5 384·5 ± 7·4	373·6	371·6	407·3	395·0	385·1	389·0	388·2	
C_2H_2	376·7 ± 2·3 377·8 ± 0·6[d]	401·5	392·9	399·2	378·4	374·3	376·8	376·3	375·4
CH_3SOCH_3	373·5 ± 2·3 374·6 ± 2·0	367·7	368·6	400·4	385·4	375·1	378·4	378·7	
CH_3CN	372·9 ± 2·6 373·5 ± 2·0 371·4 ± 4·4 369·0 ± 4·5[c]	378·7	372·4	397·4	381·0	373·6	377·2	377·2	375·1
CH_3COOMe	371·9 ± 4·1 369·1 ± 2·6	369·4	368·4	391·3	382·4	372·6	376·3	376·6	
CH_3COCH_3	370·0 ± 2·0 367·0 ± 3·5	372·8	371·8	393·0	378·6	367·6	372·7	372·1	
CH_3CHO	365·8 ± 2·9 367·0 ± 2·0	371·6	371·5	390·3	375·4	364·7	369·7	367·7	365·3
CH_3NO_2	356·4 ± 2·9 357·6 ± 2·0	347·9	339·8	364·4	360·3	353·9	355·2	355·9	356·2
cyclo-C_5H_6	353·9 ± 2·9 355·5 ± 2·0	355·3	351·4	371·4	362·8	348·6	357·1	357·5	
HCN	351·2 ± 2·0	380·2	371·6	373·5	348·2	345·9	348·0	347·6	347·4

[a] All values are ΔH in kcal mol^{-1} for the reaction HA = H$^+$ + A$^-$ at 298 K. The ΔE values from the *ab initio* calculations are corrected to constant pressure, for ZPE differences and for the contributions of the partition functions to ΔH.
[b] except where noted otherwise, experimental values are from Ref. 1a.
[c] Ref. 1b.
[d] Ref. 1c.
[e] Ref. 1d.
[f] Ref. 1e.

more than one value was available for a given compound. The uncertainties could be considered as a criterion, but they bear no necessary relation to accuracy.

The semi-empirical methods are inconsistent. They give good agreement [< 3 kcal mol^{-1} error (1 kcal = $4 \cdot 184$ kJ)] with experiment in about a third of the cases, and very poor agreement (> 10 kcal mol^{-1} error) in about a quarter. In general, they do better for compounds in the mid-range of acidities. The 3–21G *ab initio* results underestimate badly (> 20 kcal mol^{-1} error) the acidities in all but two or three cases, and come close only with CH$_3$Cl. They are superior to the semi-empirical results only in consistency of the direction and approximate magnitude of error. The 6–31 + G* results also tend to underestimate acidities, but by much less than 3–21G. The results on C$_2$H$_2$ and HCN are in good agreement with experiment.

There is marked improvement when Møller–Plesset correlation corrections are introduced. Single-point MP2 corrections at the 6–31 + G* geometry give results that agree within 3 kcal mol^{-1} with at least one experimental value in 13 out of 16 cases, and the errors on the remaining three are not excessive ($3 \cdot 3$, $5 \cdot 3$ and $5 \cdot 3$ kcal mol^{-1}). Optimization at the MP2/6–31 + G* level requires much more CPU time but gives agreement within 2 kcal mol^{-1} in eight of the nine cases studied, and the remaining one, HCN, is only $3 \cdot 8$ kcal mol^{-1} off. The single-point MP2 values for these nine cases are not as good. Only six are within 2 kcal mol^{-1}, but eight are within 3 kcal mol^{-1}. The agreement worsens with higher level Møller–Plesset corrections at the 6–31 + G* geometry. MP4SDQ gives acidities that are off by more than 3 kcal mol^{-1} in 9 of 16 cases, hardly better than MP3. Calculations at MP4SDTQ were done in a few cases, and did better at the expense of a considerable increase in CPU time. Since MP2 usually overestimates correlation corrections, there may be a fortuitous but, if so, consistent cancellation of errors at this level.

Figure 1 displays a plot of experimental acidities vs acidities calculated at the MP2/6–31 + G*//6–31 + G* level. Where more than one experimental value for a given acid was available, all the values were used. Although they differ in both methods employed and reported experimental uncertainties, there is no completely objective way of separating poor from good values, and including them all should minimize the influence of deviant points on the correlation. The line through the points is calculated by the method of linear least squares and follows the equation

$$y = 32 \cdot 5368 + 0 \cdot 915014x \qquad (1)$$

where y is the experimental acidity and x is the calculated acidity. The correlation coefficient is $0 \cdot 989$ and the standard deviation of y is $2 \cdot 75$. The experimental acidity to be expected for a carbon acid that has not been measured can thus be predicted by calculation and
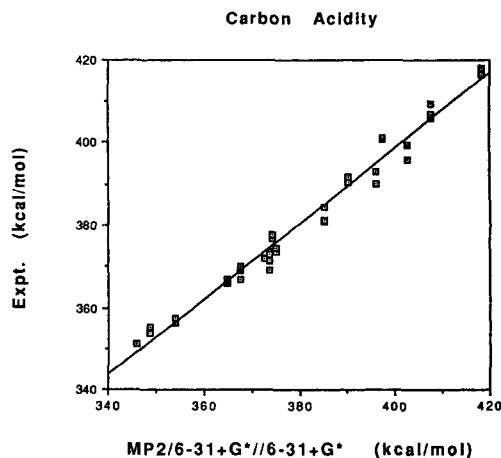

Figure 1. Plot of experimental gas-phase acidities vs acidities calculated at the MP2/6–31 + G*//6–31 + G* level. The line through the points is calculated by the method of linear least squares. Where more than one experimental value is available for a given acid (most cases), there is a point for each value

equation (1) with an error hardly larger than the experimental uncertainty.

In summary, there is a good probability that single-point MP2 corrections on 6–31 + G* structures for acids and their conjugate bases will give gas-phase acidities that agree with experiment essentially within experimental uncertainty, which in most cases is no better than ± 2–3 kcal mol^{-1}. Of the six examples that overlap with those studied by the G2 method,[8] three are predicted better by G2 and there is no significant difference in agreement for the other three. While G2 can certainly be expected to give results closer to experiment over a wide range of acids, the present method requires only modest expenditures of CPU time and is thus applicable to considerably larger acids than is G2. Moreover, the present method has proved to be entirely feasible for reaction profile studies of identity-reaction deprotonations of acetaldehyde[25] and acetonitrile (unpublished results), and can be expected to be feasible for similar studies on a wide range of carbon acids.

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