SHORT COMMUNICATION

GAS-PHASE ACIDITIES OF ACROLEIN AND METHYL ACRYLATE

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Gas-phase acidities of acrolein and methyl acrylate were measured by bracketing in a flowing afterglow/SIFT apparatus. For acrolein $\Delta G^{\circ}_{acid} = 369 \pm 4$ kcal mol^{-1} and for methyl acrylate $\Delta G^{\circ}_{acid} = 373 \pm 4$ kcal mol^{-1}. These acidities are substantially lower than those of the saturated analogs propionaldehyde and methyl acetate, respectively, even though hydrogens attached to sp^2-hybridized carbon are intrinsically more acidic than those attached to sp^3-hybridized carbon. Resonance stabilization of the neutral form by conjugation of the C=C double bond with the carbonyl group and allenic destabilization of the anionic form of the two acids can account for the relatively low acidities.

The acid–base behavior of chemical species is one of the most fundamental properties of molecules and ions, whether in solution or in the gas phase. Gas-phase acidities, which are the subject of this paper, are defined as the Gibbs free energy change (ΔG°_{acid}) for the ionization of the acid according to equation (1),[1] although most compilations of such data also report the enthalpies (ΔH°_{acid}) of reaction 1.[2]

$$HA \rightarrow H^+ + A^- \qquad (1)$$

Over the past 20 years, gas-phase acidities of a large number of compounds have been determined.[1-7] Surprisingly, the acidities of acrolein (**1**) and methyl acrylate (**2**), two compounds of considerable interest to organic chemists, have not been measured to date. We now report such measurements based on a bracketing method using the tandem flowing afterglow-selected ion flow tube technique (FA-SIFT).[8,9]

$$CH_2=CH—CH=O \qquad CH_2=CH—\overset{\overset{\textstyle O}{\|}}{C}—OCH_3$$

$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$

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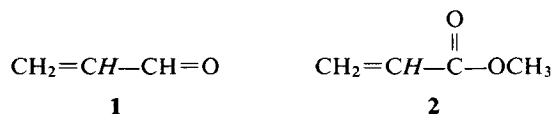
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† The ΔG°_{acid} values quoted in this paper are from Ref. 2 and the ΔH°_{acid} values are calculated as $\Delta G^{\circ}_{acid} + 5.8$ kcal mol^{-1}.[4]

Acrolein is readily deprotonated by HO$^-$ or CH$_3$O$^-$ to form the M $-$ 1 ion **3** (R = H), but injection of **3** (R = H) into the second flow tube leads to significant amounts of decarbonylation.[10] However, the methanol cluster of **3** (R = H), on injection at high energy, yields a relatively pure signal of **3** (R = H).

Deprotonation of neutral reagents was observed when mixing **3** (R = H) with acetaldehyde ($\Delta G^{\circ}_{acid} = 359 \cdot 0$ kcal mol^{-1}, $\Delta H^{\circ}_{acid} = 364 \cdot 8$ kcal mol^{-1}),† acetonitrile ($365 \cdot 2$, $371 \cdot 0$ kcal mol^{-1}), *tert*-butanol ($368 \cdot 0$, $373 \cdot 8$ kcal mol^{-1}) and propionitrile ($367 \cdot 4$, $373 \cdot 2$ kcal mol^{-1}). Deprotonation was *not* observed with toluene ($373 \cdot 7$, $379 \cdot 5$ kcal mol^{-1}) or cycloocta-1,3-diene ($370 \cdot 1$, $375 \cdot 9$ kcal mol^{-1}). Similarly, deprotonation was not observed when **1** was allowed to react with the M $-$ 1 anions of nitromethane ($349 \cdot 7$, $355 \cdot 5$ kcal mol^{-1}), dimethyl sulfoxide ($366 \cdot 4$, $372 \cdot 2$ kcal mol^{-1}), pyrrole ($350 \cdot 9$, $356 \cdot 7$ kcal mol^{-1}), methyl vinyl ketone ($356 \cdot 5$, $362 \cdot 3$ kcal mol^{-1}), acetaldehyde ($359 \cdot 0$, $364 \cdot 8$ kcal mol^{-1}), or ketene ($357 \cdot 8$, $363 \cdot 6$ kcal mol^{-1}), but deprotonation does occur with methoxide ($374 \cdot 0$, $379 \cdot 8$ kcal mol^{-1}) and ethoxide ion ($370 \cdot 8$, $376 \cdot 6$ kcal mol^{-1}). Bracketing these results gives $\Delta G^{\circ}_{acid} = 369 \pm 4$ kcal mol^{-1} and $\Delta H^{\circ}_{acid} = 375 \pm 4$ kcal mol^{-1} as the best estimates for the acidity of acrolein.

The M $-$ 1 ion (**3**, R = CH$_3$O) obtained by proton abstraction from methyl acrylate could not be injected without decomposition, even as a methanol cluster.

Hence, bracketing was limited to reacting neutral methyl acrylate with various anions. Deprotonation was observed when mixing methylacrylate with the $M-1$ anions of fluorobenzene ($379 \cdot 0, 384 \cdot 8$ kcal mol^{-1}), methanol ($374 \cdot 0, 379 \cdot 8$ kcal mol^{-1}) and toluene ($373 \cdot 7, 379 \cdot 5$ kcal mol^{-1}). Proton transfer was not observed when mixing methyl acrylate with the $M-1$ anions from acetonitrile ($365 \cdot 2, 371 \cdot 0$ kcal mol^{-1}), cycloocta-1,3-diene ($370 \cdot 1, 375 \cdot 9$ kcal mol^{-1}) and ethanol ($370 \cdot 8, 376 \cdot 6$ kcal mol^{-1}). These data indicate that ΔG_{acid}° for methyl acrylate lies between 371 and 374 kcal mol^{-1}, while ΔH_{acid}° lies between 377 and 380 kcal mol^{-1}.

Our measurements do not give any information about the site of deprotonation. However, ICR experiments with deuterium-labeled acrolein and methyl acrylate[11] show that the acidic site is α to the carbonyl group in both cases (italic hydrogens), as one would expect.

Our ΔH_{acid}° value of ca 375 kcal mol^{-1} for acrolein is considerably higher (the acidity considerably lower) than ΔH_{acid}° of ca 365 kcal mol^{-1} estimated by Graul and Squires,[12] a value close to that for propionaldehyde ($\Delta H_{acid}^{\circ} = 364 \cdot 5$ kcal mol^{-1}). Similarly, methyl acrylate ($\Delta H_{acid}^{\circ} \approx 378 \cdot 5 \pm 4 \cdot 0$ kcal mol^{-1}) is less acidic than the saturated analog methyl acetate ($\Delta H_{acid}^{\circ} = 370 \cdot 9$ kcal mol^{-1}). These findings are interesting because, in the absence of other factors, hydrogens attached to sp^2-hybridized carbon are usually more acidic than those attached to sp^3-hybridized carbon.[13] For example, ethylene ($\Delta H_{acid}^{\circ} = 407 \cdot 7$ kcal mol^{-1}) is substantially more acidic than ethane ($\Delta H_{acid}^{\circ} \approx 420$ kcal mol^{-1}),[14] and acrylonitrile ($\Delta H_{acid}^{\circ} = 373 \cdot 2$ kcal mol^{-1}) is more acidic than propionitrile ($\Delta H_{acid}^{\circ} = 375 \cdot 0$ kcal mol^{-1}), although by only a relatively small amount.

One factor that is likely to contribute to the lower acidity of acrolein and methyl acrylate compared with their respective saturated analogs is that the resonance forms of the deprotonated acrolein or methyl acrylate that bear the negative charge on oxygen are allenic (3b); this makes them significantly less stable than the enolate resonance forms of the deprotonated saturated analogues (4b).

R
|
CH$_2$=$\bar{C}$—C=O ⟷ CH$_2$=C=C—O$^-$

3a   3b

R = H or CH$_3$O

R
|
CH$_3$—$\bar{C}$H—C=O ⟷ CH$_3$—CH=C—O$^-$

4a   4b
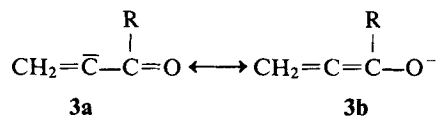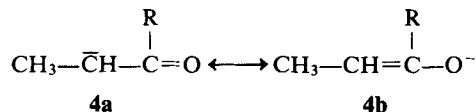
An estimate of the destabilizing influence of the two cumulated C=C double bonds in 3 can be deduced

from the heat of formation of penta-1,2-diene ($\Delta H_{f}^{\circ} = 33 \cdot 6$ kcal mol^{-1}),[15] which is $8 \cdot 3$ kcal mol^{-1} larger than that for penta-1,4-diene ($\Delta H_{f}^{\circ} = 25 \cdot 3$ kcal mol^{-1}).[15]

A second factor that would tend to lower the acidity of acrolein and methyl acrylate is the stabilization of these molecules in their neutral form by conjugation of the C=C double bond with the carbonyl group. For example, comparing the heat of formation of *trans*-but-2-enal ($\Delta H_{f}^{\circ} = -24 \cdot 0$ kcal mol^{-1})[15] with that of the unconjugated but-3-enal ($\Delta H_{f}^{\circ} = -19 \cdot 4$ kcal mol^{-1})[15] shows a stabilization of $4 \cdot 6$ kcal mol^{-1}.

It is noteworthy that the $10 \cdot 5$ kcal mol^{-1} difference in ΔH_{acid}° between acrolein and propionaldehyde is close to the sum ($8 \cdot 3 + 4 \cdot 6 = 12 \cdot 9$ kcal mol^{-1}) of the destabilization of penta-1,2-diene by the cumulated double bonds and the conjugative stabilization of acrolein. We also note *ab initio* (4–31G) calculations[11] that suggest that ΔH° for the reaction MeO$^-$ + CH$_2$=CHCH=O → CH$_2$=C=CHO$^-$ + MeOH is $-4 \cdot 8$ kcal mol^{-1}. Combining this result with ΔH_{acid}° (MeOH) = $379 \cdot 8$ kcal mol^{-1}, one obtains $\Delta H_{acid}^{\circ} = 375 \cdot 0$ kcal mol^{-1} for acrolein, in excellent agreement with our experimental value of 375 ± 4 kcal mol^{-1}.

The acrylonitrile–propionitrile pair ($\Delta \Delta H_{acid}^{\circ} = -2 \cdot 1$ kcal mol^{-1}) shows a behavior that is intermediate between that of the ethylene–ethane pair on the one hand ($\Delta \Delta H_{acid}^{\circ} = -14 \cdot 0$ kcal mol^{-1}), and that of the acrolein–propionaldehyde ($\Delta \Delta H_{acid}^{\circ} \approx +10 \cdot 5$ kcal mol^{-1}) and methyl acrylate–methyl acetate ($\Delta \Delta H_{acid}^{\circ} \approx +7 \cdot 6$ kcal mol^{-1}) pairs on the other. This may be attributed to the fact that the cyano group stabilizes negative charge more by a polar and less by a resonance effect compared to a carbonyl group.[16–18] This would reduce the importance of the allenic resonance form (5b) and with it the destabilizing effect on the anion.

CH$_2$=$\bar{C}$—C≡N ⟷ CH$_2$=C=C=N$^-$

5a   5b
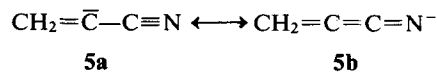
On the other hand, comparison of the heats of formation of *trans*-but-2-ene nitrile ($\Delta H_{f}^{\circ} = 33 \cdot 6$ kcal mol^{-1})[15] with that of but-3-ene nitrile ($\Delta H_{f}^{\circ} = 37 \cdot 7$ kcal mol^{-1})[15] indicates that the stabilization of the neutral acrylonitrile by conjugation ($4 \cdot 1$ kcal mol^{-1}) is about the same as that for acrolein ($3 \cdot 9$ kcal mol^{-1}).

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