JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 5, 575–580 (1992)

HEATS OF FORMATION OF ENOLS. THE DOUBLE-BOND STABILIZING EFFECT OF THE HYDROXYL GROUP

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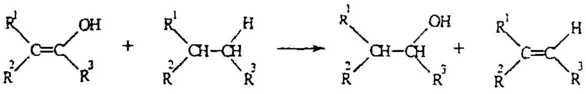
Aqueous solution free energies of ketonization have been combined with enthalpies of reduction of the keto forms and other thermochemical data to yield estimates of the heats of formation of the corresponding enols. A double-bond stabilization term, $D_{OH} = 5\cdot4 \pm 0\cdot5$ kcal mol^{-1} (1 kcal = 4·184 kJ), is obtained for the OH group. This quantity is close to Hine's double-bond stabilization parameter for the methoxyl group (4·9 ± 0·2 kcal mol^{-1}). Comparison with available experimental gas-phase enthalpies of formation suggests that, relative to the keto form, enols are more stable in the gas phase than in water. The differences are unlikely to be due entirely to entropic effects. A wholly enthalpic, gas-phase double-bond stabilization term, $D_{OH} = 8\cdot1 \pm 0\cdot6$ kcal mol^{-1}, may be calculated from the available experimental data. This result indicates that the hydroxyl group more effectively stabilizes the C=C bond in the gas phase than in aqueous solution. An important limitation is that the results reported here apply only to simple enols, that is, monofunctional enols not stabilized by extra resonance or hydrogen-bonding effects.

INTRODUCTION

During the last decade or so, enormous advances in the generation, detection and quantitative study of reactions of simple enols (those monofunctional enols not stabilized by extra resonance or internal hydrogen bonding, and which experience no unusual steric effects) have been made.[1] Comparatively, our knowledge of the thermochemistry of enols has lagged. It is likely that this situation will change, however, owing to the development of methods for determining heats of formation of simple enols in the gas phase.[2–4] Meanwhile, although relatively few data are available, Tureček and Havlas[4a] have been able to compute a group thermodynamic contribution[5] for the enolic functional group: O—(C_d) (H). Additionally, Guthrie[6] has combined gas-phase quantities from the literature with aqueous solution keto–enol equilibrium data[7] to calculate gas-phase heats of formation for simple, unconjugated enols. In doing so, he has taken pains to allow for entropic effects and for the change of state. His results also yield a set of refined group additivity parameters for the enolic group. We report here alternative combinations of experimental results by which the heats of formation of some enols can be calculated. The method also allows an estimate of a double-bond stabilization term, analogous to Hine's parameters,[8] for the OH group.

METHOD

Wiberg *et al.*[9] recently measured the heats of reduction of a series of carbonyl compounds in triglyme solution. With the aid of heats of vaporization, these heats were converted into gas-phase heats of reduction, $\Delta H_{RED}^{KETO\,o}$(g), at 25 °C. These data can be combined with our aqueous solution keto–enol equilibrium measurements to yield approximate values of thermodynamic quantities of potential interest. To do so we use an isodesmic reaction, equation (1):



(1)

The heat of this reaction is approximated by a combination of available heats of hydrogenation of alkenes[10] with the heats of reduction of enols to their alcohols, ΔH_{RED}^{ENOL}. In turn, we estimate the latter quantity by

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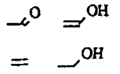
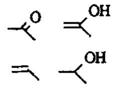
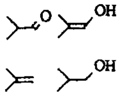
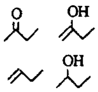
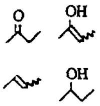
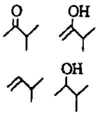
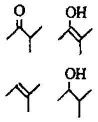
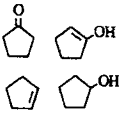
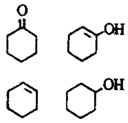
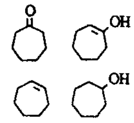
0894-3230/92/090575-06$08.00

Received 13 February 1992
Revised 8 May 1992

Table 1. Experimental data used to derive D_{OH} and $\Delta H_f^{\mathrm{ENOL}}$ (kcal mol^{-1}, 25 °C; 1 kcal = 4·184 kJ)

Compound	$\Delta H_{\mathrm{RED}}^{\mathrm{KETO}}$(g)[a]	ΔG^{K}(aq)[b]	$\Delta H_{\mathrm{RED}}^{\mathrm{ENOL}}$[c]	$\Delta H_{\mathrm{HYDROG}}^{\mathrm{ALKENE}}$(g)[d]	$\Delta H_f^{\mathrm{ALC}}$(g)[d]	$\Delta H_f^{\mathrm{KETO}}$(g)[d]
1. 	−15·41	−8·50	−23·91	−32·58	−56·21	−39·70
2. 	−12·96	−11·81	−24·77	−29·87	−65·20	−51·94
3. 	−16·27	−5·27	−21·54	−28·15	−67·85	−51·58
4. 	−12·9	−11·95	−24·8₅	−30·10	−70·00	−57·05
5. 	−12·9	−10·24	−23·1₄	−27·7[e]	−70·00	−57·05
6. 	−12·6	−11·74	−24·34	−30·19	−75·33	−62·74
7. 	−12·6	−11·74	−24·34	−26·28	−75·33	−62·74
8. 	−10·87	−11·24	−22·11	−26·67	−67·98	−46·55
9. 	−14·08	−9·11	−23·19	−28·35	−68·40	− 54·43[f]
10. 	−10·94	−11·32	−22·26	−26·02	−66·2[g]	−59·15[h]

[a] Ref. 9.

[b] Ref. 7. The ketonization values quoted here include a statistical correction for the number of equivalent enolizable carbon positions.

[c] Defined in equation (2).

[d] Ref. 10.

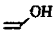
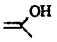
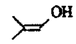
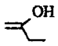
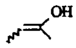
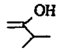
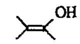
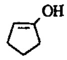
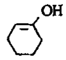
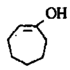
[e] This is a weighted average of the heats of hydrogenation of *cis*- and *trans*-but-2-enes. The weighting factor used is (fraction-*trans*) = 1·7/2·7, where 1·7 kcal mol^{-1} and 1·0 kcal mol^{-1} are the ΔG^{298} values for the equatorial → axial interconversions of methylcyclohexane and hydroxycyclohexane, respectively. The ΔG^{K}(aq) value quoted here (Ref. 7) is for the ketonization of a mixture of (*E*)- and (*Z*)-hydroxybut-2-enes. Taking OH to be smaller than CH_3, the (*Z*)-enol dominates.

[f] Ref. 11.

[g] Value not given in Ref. 10. The number given in this table is the experimental value for cyclohexanol plus an increment (+1·2 kcal mol^{-1}) equal to the difference between the computed $\Delta H_f^{\mathrm{ALC}}$(g) values (MM3, Ref. 9) for cyclohexanol and cycloheptanol.

[h] Wolf[11] gives $\Delta H_f^{\mathrm{KETO}}$(g) = −59·3 kcal mol^{-1} for cycloheptanone. Wiberg *et al.*[9] argue that this figure is too exothermic and implies almost no ring strain. The same objection applies to the value quoted in this table.

Table 2. Double-bond stabilization term(s) for the hydroxyl group and enthalpies of formation of enols (kcal mol^{-1}, 25 °C)[a]

Enol	D_{OH} [eqn (3)]	D'_{OH} [eqn (6)]	ΔH_f [eqn (4)]	$\Delta H'_f$ [eqn (5)]
1. 	8·7	7·6	−32·3	−31·2
2. 	5·1	4·8	−40·4	−40·1
3. 	6·6	6·6	−46·3	−46·3
4. 	5·3	5·2	−45·2	−45·1
5. 	4·6	4·5	−46·9	−46·8
6. 	5·9	5·9	−51·0	−51·0
7. 	4·1	4·1	−52·7	−52·7
8. 	4·6	4·0[b]	−35·9	−35·3[b]
9. 	5·2	5·3[b]	−45·2	−45·3[b]
10. 	3·8	7·7[c]	−43·9	−47·8[c]
Average[d]	5·4 ± 0·5	5·3 ± 0·4[e]		

[a] Experimental errors have not been propagated in deriving these quantities. The energies of reaction and formation (Table 1) are uncertain by 1–3% (usually less). This leads to uncertainties of *ca* 0·2 kcal mol^{-1} in D_{OH}, ΔH_f^{ENOL} and $\Delta H_f'^{\,ENOL}$.

[b] If ΔH_f^{KETO} values from Ref. 10 are used in place of Wolf's values[11] (Table 1, footnote f), then the results become cyclopentanone enol 3·4 and −34·7 kcal mol^{-1} and cyclohexanone enol 4·9 and −44·9 kcal mol^{-1}.

[c] The value of ΔH_f^{KETO}(g) used to obtain these figures may be too exothermic (Table 1, footnote h). If so, the figures in the alternative columns [equations (3) and (4)] are to be preferred.

[d] The error quoted is the standard deviation of the mean. Errors in individual D_{OH} values were not propagated.

[e] The value of cycloheptanone enol was not included: see Table 1, footnote h.

equation (2):

$$\Delta H_{RED}^{ENOL} \approx \Delta H_{RED}^{KETO}(g) + \Delta G^{K}(aq) \qquad (2)$$

where ΔG^{K}(aq) is the free energy of ketonization of the enol in aqueous solution[7] [the essential approximation is that $\Delta G^{K}(aq) \approx \Delta H^{K}(g)$; we do not attempt to rationalize such an expectation, but propose merely to examine the empirical utility of the idea]. The heat of reaction of equation (1) may now be estimated in terms of equation (2) and heats of hydrogenation of alkenes.[10] The result, equation (3), measures the stabilization of a C=C bond obtained by substituting one OH for one H:

$$\begin{aligned}\Delta H[\text{eqn (1)}] &\approx D_{OH}\\ &= [\Delta H_{RED}^{KETO}(g) + \Delta G^{K}(aq)] - \Delta H_{HYDROG}^{ALKENE}(g) \qquad (3)\end{aligned}$$

The symbol D_{OH} follows Hine's usage,[8] but our values are obtained in a different way (Hine's parameters[8] are solution-phase ΔG values obtained by experiment, and in some cases with corrections for polar interactions between substituents across the C=C bond).

Heats of formation of enols, appropriate to the gaseous state to the extent that our model is correct, may also be calculated from reaction (1) by use of equation (4). A second method for obtaining $\Delta H_f^{\mathrm{ENOL}}$ values, using the aqueous keto–enol equilibrium data[7] and experimental heats of formation for the ketones, is shown by equation (5). The resulting heats of formation, distinguished by the primed symbol, offer a second way to estimate the double-bond stabilizing effect of the OH group; this is given by equation (6).

$$\Delta H_f^{\mathrm{ENOL}} \approx \Delta H_f^{\mathrm{ALC}}(\mathrm{g}) - \Delta H_{\mathrm{HYDROG}}^{\mathrm{ALKENE}}(\mathrm{g}) - D_{\mathrm{OH}} \quad (4)$$

$$\Delta H'^{\mathrm{ENOL}}_f \approx \Delta H_f^{\mathrm{KETO}}(\mathrm{g}) - \Delta G^{\mathrm{K}}(\mathrm{aq}) \quad (5)$$

$$D'_{\mathrm{OH}} = \Delta H_f^{\mathrm{ALC}}(\mathrm{g}) - [\Delta H_f^{\mathrm{KETO}}(\mathrm{g}) - \Delta G^{\mathrm{K}}(\mathrm{aq})] - \Delta H_{\mathrm{HYDROG}}^{\mathrm{ALKENE}}(\mathrm{g}) \quad (6)$$

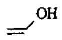
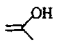
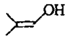
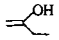
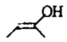
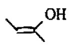
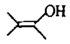
In using equations (2)–(6) we are, in effect, suggesting that aqueous solution free energies of ketonization [$\Delta G^{\mathrm{K}}(\mathrm{aq})$] may be used for gas-phase enthalpies of ketonization [$\Delta H^{\mathrm{K}}(\mathrm{g})$] where the former but not the latter are available. This proposition may be evaluated using information given in Table 1. [The actual comparisons between $\Delta G^{\mathrm{K}}(\mathrm{aq})$ and $\Delta H^{\mathrm{K}}(\mathrm{g})$ are made in Table 3 as are comparisons between our estimated values for $\Delta H_f^{\mathrm{ENOL}}$, equation (4), and other values obtained for these quantities.] Derived double-bond stabilization terms are given in Table 2.

RESULTS AND DISCUSSION

The results calculated from equations (3) and (4) on the one hand and equations (5) and (6) on the other differ in two important ways. Although both sets use the aqueous-phase ΔG values for keto–enol equilibrium, equations (3) and (4) employ Wiberg's heats of reduction [but *not* $\Delta H_f^{\mathrm{KETO}}(\mathrm{g})$], while equations (5) and (6) use $\Delta H_f^{\mathrm{KETO}}(\mathrm{g})$ values (but *not* Wiberg's results). With the exception of cycloheptanone (see footnote c, Table 2), agreement between the two sets is good to excellent. This agreement lends confidence to Wiberg's method of converting his solution data (triglyme solvent) to vapor-phase values. He used heats of vaporization of the pure liquid compounds to do so, but did not use heats of solution.

In these calculations we have approximated gas-phase heats of ketonization by aqueous solution free energy values. It is important, therefore, to compare our results with authentic gas-phase data where possible. As

Table 3. Comparison of derived $\Delta H_f^{\mathrm{ENOL}}$ values with literature values (kcal mol^{-1}, 25 °C)

Enol	$\Delta H_f^{\mathrm{ENOL}}(\mathrm{g})$, exp.[a]	Tureček[b]	Guthrie[c]	Eqn (4)[d]	$\Delta G^{\mathrm{K}}(\mathrm{aq})$[e]	$\Delta H^{\mathrm{K}}(\mathrm{g})$[f]
1. 	$-30{\cdot}6$[b,g]	$-33{\cdot}4$	$-30{\cdot}5$	$-32{\cdot}3$	$-8{\cdot}5$	$-9{\cdot}1$
2. 	$-42{\cdot}1$,[b] $-40{\cdot}6$[h]	$-41{\cdot}9$	$-42{\cdot}2$	$-40{\cdot}4$	$-11{\cdot}8$	$-9{\cdot}8$,[b] $-11{\cdot}2$[h]
3. 	$-49{\cdot}5$[b]	$-49{\cdot}7$	$-47{\cdot}7$	$-46{\cdot}3$	$-5{\cdot}3$	$-2{\cdot}1$
4. 	$-46{\cdot}8$[b]			$-45{\cdot}2$	$-11{\cdot}95$	$-10{\cdot}3$
5(E). 	$-50{\cdot}7$[b,i]	$-48{\cdot}8$	$-53{\cdot}1$	$-46{\cdot}9$[j]	$-10{\cdot}2$[j]	$-6{\cdot}4$
5(Z). 	$-51{\cdot}1$[b,i]					$-6{\cdot}0$
7. 	$-57{\cdot}6$[b]	$-56{\cdot}2$	$-57{\cdot}5$	$-52{\cdot}7$	$-10{\cdot}0$	$-5{\cdot}1$

[a] These values were determined by electron-impact ionization techniques. Tureček[4a] gives an average uncertainty of ±1·9 kcal mol^{-1}.

[b] Ref. 4.

[c] Ref. 6.

[d] This work.

[e] Ref. 7.

[f] Calculated as $\Delta H_f^{\mathrm{KETO}}(\mathrm{g})$ (Ref. 10) less $\Delta H_f^{\mathrm{ENOL}}(\mathrm{g})$, exp. The average uncertainty is *ca* ±2 kcal mol^{-1} and is due almost entirely to the experimental uncertainty in $\Delta H_f^{\mathrm{ENOL}}(\mathrm{g})$.

[g] Refs. 2a, 3.

[h] Refs. 2a, 12.

[i] Tureček *et al.*[4b] argue convincingly that the figures quoted in this table are more accurate than the experimental values reported in Ref. 2a.

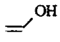
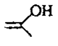
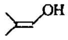
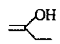
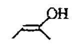
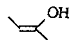
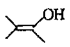
[j] Calculated using weighted average of (Z)- and (E)-enols. We estimate the Z isomer to be *ca* 65% of the mixture; see Table 1, footnote e.

noted in the Introduction, Tureček and co-workers computed a group thermodynamic contribution for the enolic group from $\Delta H_f^{ENOL}(g)$ data; they also summarized the available $\Delta H_f^{ENOL}(g)$ values.[4] Guthrie[6] calculated $\Delta H_f^{ENOL}(g)$ and group thermodynamic contributions for the enolic group by combining a variety of data from the literature. In Table 3 are given experimental $\Delta H_f^{ENOL}(g)$ values together with those calculated by Tureček[4] and by Guthrie[6] using their optimized group thermodynamic contributions. Also given in Table 3 are our values for ΔH_f^{ENOL} calculated from equation (4). Experimental aqueous- and gas-phase energies of ketonization complete Table 3.

In Table 4 our double-bond stabilization terms from equations (3) and (6) are compared with a set of gas-phase $D_{OH}(g)$ values calculated by substituting the experimental $\Delta H_f^{ENOL}(g)$ values listed in Table 3 into equation (6). All D_{OH} values are based on reaction (1).

The experimental uncertainties in $\Delta H_f^{ENOL}(g)$ ($\pm$ *ca* 2 kcal mol^{-1}) are substantial.[4a] Nevertheless (except for the results for vinyl alcohol), there appear to be consistent (although small) differences between the experimental gas-phase heats of formation of enols and those calculated by us using equation (4) [or equation (5)]: our results are less exothermic, especially for the more highly alkylated enols. Similar differences exist between the gas-phase heats of ketonization and the aqueous solution free energies of ketonization: relative to the keto form, the enol is more stable in the gas phase than in aqueous solution. The differences are unlikely to be found in the gas-phase entropies of ketonization. These would have to range from $\Delta S^K(g) \approx -6$ to -16 k cal mol^{-1}, but these values are, in fact, known to be positive.[6,13b] Differential heats of solution for enol and keto forms almost certainly play a role. Water, which is protic and very polar, can stabilize the more polar keto isomer both through its dielectric and its hydrogen-bond donor ability. The small differences between $\Delta G^K(aq)$ and $\Delta H^K(g)$ are probably compounded from several effects.[13]

Table 4. Comparison of derived double-bond stabilization terms (Table 2) with calculated gas-phase D_{OH}[a] (kcal mol^{-1}, 25 °C)

Enol	D_{OH} [eqn (3)]	D'_{OH} [eqn (6)]	$D_{OH}(g)$[a]
1. 	8.7	7.6	7.0
2. 	5.1	4.8	6.8[b], 5.3[c]
3. 	6.6	6.6	9.8
4. 	5.3	5.2	6.9
5(E). 	4.6[d]	4.5[d]	9·0
5(Z). 			8·5
7. 	4.1	4.2	9.0
Average[e]	5.7 ± 0.7	5.5 ± 0.6	8.1 ± 0.6[b]

[a] Calculated as $D_{OH}(g) = \Delta H_f^{ALC}(g) - \Delta H_f^{ENOL}(g) - \Delta H_{HYDROG}^{ALKENE}(g)$. All quantities are experimental values; the uncertainty in the individual $D_{OH}(g)$ values is *ca* ± 2 kcal mol^{-1}.

[b] Calculated using $\Delta H_f^{ENOL}(g) = -42{\cdot}1$ kcal mol^{-1} for acetone enol.[4]

[c] Calculated using $\Delta H_f^{ENOL}(g) = -40{\cdot}6$ kcal mol^{-1}.[2a]

[d] Enol is a weighted average of Z and E isomers; see Table 1, footnote e, and Table 3, footnote j.

[e] The error quoted is the standard deviation of the mean. Errors in individual D_{OH} values were not propagated.

The same sort of difference exists between the gas-phase double-bond stabilization terms and those calculated using $\Delta G^K(aq)$ data. $D_{OH}(g)$, a purely enthalpic term, averages $8{\cdot}1 \pm 0{\cdot}6$ kcal mol^{-1} whereas D_{OH} from equations (3) and (6) is *ca* 2·5 kcal mol^{-1} smaller, especially if the vinyl alcohol data are excluded from the comparison. The hydroxyl group appears to stabilize the C=C bond [see equation (1)] more in the gas phase than it does in aqueous solution. Confidence in the results of equations (3) and (6), and therefore in this conclusion, is increased by noting that Hine's value[8b] for the double-bond stabilizing effect of a methoxyl group, a solution-phase free energy parameter, is $4{\cdot}9 \pm 0{\cdot}2$ kcal mol^{-1}, very close to our value for D_{OH}.

It is important to note some limitations to the conclusions given here. Enols stabilized by extra conjugation or by intramolecular hydrogen bonding, or which experience unusual steric interactions, are not expected to be covered by our analysis, nor are they accommodated by the group thermodynamic terms calculated by Tureček[4] and Guthrie.[6] This point was made clear by both authors. It seems certain also that enols in which additional heteroatoms are attached to the C=C bond are to be excluded. It is known, for example, that the cumulative effects of methoxyl groups on alkene stability are not additive: the relative stabilities of isomeric polymethoxyalkenes depend on the number, positions and stereochemical relationships of CH_3O groups[14,15] [we note also that the keto isomer may be affected by the presence of multiple hydroxy (alkoxy) groups; geminal groups attached by heteroatoms to a saturated carbon can produce stabilization[16]].

CONCLUSION

Solution-phase keto–enol equilibrium data can be combined with the enthalpies of reduction of carbonyl compounds and other data to yield, via the isodesmic reaction equation (1), estimates for the heats of formation of enols and a double-bond stabilization quantity for the hydroxyl group. These results appear to be slightly different in magnitude from their purely enthalpic gas-phase analogues. For simple unconjugated enols, the kind considered here, enthalpies of formation are roughly 3–5 kcal mol^{-1} more exothermic in the gas phase than calculated by equation (4) or (5). Similarly, the enthalpy of stabilization conferred by the hydroxyl group on a C=C bond is *ca* 2·5 kcal mol^{-1} more in the gas phase than in aqueous solution. Hydroxyl and methoxyl groups have very similar double-bond stabilizing effects in solution. With the cited differences between gas and solution phases in mind, results in one medium may be usefully transferred to the other.

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