Optimized structures have also been computed for the $C_s$ and $C_{2v}$ forms of β-hydroxyacrolein. The calculations predict that the $C_s$ form is more stable than the $C_{2v}$ form, but by only 6.6 kcal. Since the energy difference between these two forms is small, it is reasonable to suggest that the equilibrium structures of this and related compounds may vary with physical state. Intramolecular proton transfer may easily occur leading to the conversion of one equivalent $C_s$ form of β-hydroxyacrolein to the other, through an intermediate of $C_{2v}$ symmetry. These features may account for the discrepancies in the symmetry assignments which have been given to structures of related enolic β-dicarbonyl compounds.

Two limiting cases of proton transfer in formic acid dimer have also been investigated. In the first case, symmetric transfer of both hydrogen-bonded protons occurs while the $HCO_2$ fragments remain rigid. This process gives rise to potential curves, the characteristics of which depend on the intermolecular distance. At the computed equilibrium dimer distance, this curve possesses only a single minimum. However, at the experimental intermolecular distance, the potential curve for this process of proton transfer exhibits a double minimum, in agreement with the results of other studies which employed larger basis sets. It is obvious that the underestimation of the intermolecular distance with the STO-3G basis set is critical to the problem of proton transfer.

In the second case, proton transfer occurs in the formic acid dimer through inversion of the dimer structure. The barrier to this process is lowered as the intermolecular distance is reduced from the experimental distance to the computed equilibrium distance. Since, even at the experimental intermolecular distance, the barrier to proton transfer in this case is lower than it is in the first case, the approximation of rigid $HCO_2$ fragments during proton transfer is not a realistic one. The results of this study suggest that in a concerted reaction, proton transfer accompanied by structural inversion is more favorable than simple proton transfer followed by vibrational relaxation.

**Acknowledgment.** This work was supported by NIH research Grant No. GM 19032 from the National Institute of General Medical Sciences. The support of NIH, and of a Camille and Henry Dreyfus Foundation Teacher-Scholar Grant, is gratefully acknowledged. Thanks are also due to Dr. Ronald Jonas and the Youngstown State University Computer Center for continued assistance.

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# Comparison of Equilibrium Reactions in the Gaseous and Liquid Phases. A New, Improved Theoretical Estimate

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**Abstract:** We have studied available data on four selected simple chemical equilibria: (1) cyclopentadiene ⇄ dicyclopentadiene, (2) ethanol + acetic acid ⇄ ethyl acetate + water, (3) $NO_2 \rightleftarrows N_2O_4$, and (4) norbornene ⇄ nortricyclene. The enthalpy and entropy changes of each component on proceeding from the gas phase to the liquid phase were calculated with an equation that includes heat capacity corrections, but requires only the heat of vaporization, the molar volume, and the normal boiling point of each component. The agreement with experimental results in the liquid phase is improved appreciably over past calculations and was reasonable: $\Delta G_r$ to within 1.5 kcal and $K_{eq}$ to a factor of 10.

Recently Patrick[1] and Benson and Golden[2] published analyses of relationships expected between gas-phase and liquid-phase rates and equilibria. These followed earlier treatments of the subject by Martin,[3] Moelwyn-Hughes,[4] and Mayo.[5] In this paper we wish to examine certain equilibria for which enough data are available or calculable with sufficient accuracy to make a detailed analysis possible.

## Results and Discussion

The general form for our calculations is the thermodynamic cycle shown in Scheme I, below. Reagents at a standard state concentration of 1 M in the gas phase were transformed to a liquid concentration of 1 M through discrete

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Scheme I

$$\begin{array}{lccccccccc}
 & \begin{array}{c}\text{gas}\\ 1\text{ M}\end{array} & \longrightarrow & \begin{array}{c}\text{gas}\\ 1\text{ atm}\end{array} & \longrightarrow & \begin{array}{c}\text{gas}\\ P_{\text{eq}}\end{array} & \longrightarrow & \begin{array}{c}\text{liquid}\\ \text{(eq)}\end{array} & \longrightarrow & \begin{array}{c}\text{solution}\\ 1\text{ M}\end{array}\\
\Delta H & & 0 & & 0 & & -[\Delta H_{\text{v}}^{\circ} + \Delta C_{\text{vap}}(T - T_{\text{B}})] & & +\Delta H_{\text{mix}} & \\
\Delta S & & R\ln(R'T) & & -R\ln P_{\text{eq}} & & -\dfrac{\Delta H_{\text{v}}^{\circ}}{T} + \dfrac{\Delta C_{\text{vap}}(T - T_{\text{B}})}{T} & & -R\ln(V_{\text{m}}/1000) &
\end{array}$$

Differences:

$$\Delta\Delta H^{\circ}(\text{g}^{+} \rightarrow \text{soln}^{+}) = -\Delta H_{\text{v}}^{\circ} - \Delta C_{\text{vap}}(T - T_{\text{B}}) + \Delta H_{\text{mix}}$$

$$\Delta\Delta S\ (\text{g}^{+} \rightarrow \text{soln}^{+}) = R\ln(R'T) - R\ln P_{\text{eq}} - \frac{\Delta H_{\text{v}}^{\circ}}{T} - \frac{\Delta C_{\text{vap}}(T - T_{\text{B}})}{T} - R\ln\frac{V_{\text{m}}}{1000}$$

**Totals:**

$$\Delta H_{\text{l}}^{+}(1\text{ M}) = \Delta H_{\text{f}}^{\circ} - \Delta H_{\text{vap}}^{\circ} - \Delta C_{\text{vap}}(T - T_{\text{B}}) + \Delta H_{\text{mix}}$$

$$\Delta S_{\text{l}}^{+}(1\text{ M}) = S^{\circ} - R\ln P_{\text{eq}} - \frac{\Delta H_{\text{v}}^{\circ}}{T} - \frac{\Delta C_{\text{vap}}(T - T_{\text{B}})}{T} - R\ln\frac{V_{\text{m}}}{1000}$$

$$\Delta G_{\text{l}}^{+}(1\text{ M}) = \Delta G_{\text{g}}^{\circ}(1\text{ atm}) + RT\ln P_{\text{eq}}(\text{atm}) + \Delta H_{\text{mix}} + RT\ln\frac{V_{\text{m}}}{1000}$$

$V_{\text{m}}$ = molar volume of solute

$T_{\text{B}}$ = normal boiling point (°K)

$\Delta H_{\text{v}}^{\circ}$ = heat of vaporization at $T_{\text{B}}$

$P_{\text{eq}}$ = vapor pressure in atmospheres at $T$

steps for which $\Delta H$ and $\Delta S$ could be calculated. Ideal gas behavior was assumed in the gas phase. Equilibrium constants were expressed in, or converted into, concentration units. Heat capacity corrections are significant and were taken into account as described below. As noted by previous workers,[1,2] for certain steps in Scheme I the enthalpy and entropy changes are related through Trouton's constant or because $\Delta G = 0$. The mixing heat was neglected in the final calculations.

Basic data were obtained from compilations by Cox and Pilcher,[6] Stull, Westrum, and Sinke,[7] from the International Critical Tables,[8] or JANAF Tables.[9] Enthalpies and free energies are given in kilocalories per mole, and entropies are given in calories per degree mole (eu) throughout. The standard state of 1 M is indicated by a (+) superscript; the symbol $\theta$ is $2.3RT$ in kcal/mol.

The largest changes in enthalpy and entropy, in the cycle we are considering, occur in the condensation step. The value of $\Delta H$, however, which is $\Delta H_{\text{vap}}^{0}$ at $T_{\text{B}}$, decreases to zero at the critical temperature and increases as the temperature falls below $T_{\text{B}}$. Recently Shaw[10] assembled a large number of heat capacities for organic compounds, and showed that for most molecules, $\Delta C_{\text{vap}} = C_{\text{p}}(\text{g}) - C_{\text{p}}(\text{l}) = -12 \pm 4$ eu at 25 °C.

If $\Delta H_{\text{vap}} = \Delta H_{\text{vap}}^{0} + \Delta C_{\text{vap}}(T - T_{\text{B}})$, then:

$$\frac{\text{d}P}{\text{d}T} = \frac{\Delta H_{\text{v}}}{T\Delta V_{\text{g-l}}} \simeq \frac{\Delta H_{\text{v}}^{0} + \Delta C_{\text{vap}}(T - T_{\text{B}})}{RT^2/P}$$

$$\frac{\text{d}\ln P}{\text{d}T} = \frac{\Delta H_{\text{v}}^{0} - T_{\text{B}}\Delta C_{\text{vap}}}{RT^2} + \frac{\Delta C_{\text{vap}}}{RT}$$

$$\ln(P/P^0) = -\frac{(\Delta H_{\text{vap}}^{0} - T_{\text{B}}\Delta C_{\text{vap}})}{R}\left[\frac{1}{T} - \frac{1}{T_{\text{B}}}\right] + \frac{\Delta C_{\text{vap}}}{R}\ln(T/T_{\text{B}})$$

$$= -\frac{(\Delta S_{\text{vap}}^{0} - \Delta C_{\text{vap}})}{R}\left[\frac{T_{\text{B}}}{T} - 1\right] + \frac{\Delta C_{\text{vap}}}{R}\ln(T/T_{\text{B}})$$

This can be written as:

$$R\ln P + \frac{\Delta H_{\text{vap}}^{0}}{T} + \frac{\Delta C_{\text{vap}}(T - T_{\text{B}})}{T} = \frac{\Delta H_{\text{vap}}^{0}}{T_{\text{B}}} + \Delta C_{\text{v}}\ln T/T_{\text{B}}$$

The three terms on the left side of the equation are among the terms that describe $S_{\text{l}}^{+}$ (Scheme I). Substituting, we obtain:

$$S_{\text{l}}^{+}\ (1\text{ M}) = S^0 - \Delta S_{T_{\text{B}}}{}^{0} - \Delta C_{\text{vap}}\ln(T/T_{\text{B}}) + R\ln(1000/V_{\text{m}})$$

and from before

$$\Delta H_{\text{l}}^{+}(1\text{ M}) = \Delta H_{\text{f}}^{0} - \Delta H_{\text{vap}}^{0} - \Delta C_{\text{vap}}(T - T_{\text{B}})$$

The term $\Delta S_{T_{\text{B}}}{}^{0}$ is, of course, Trouton's constant, ~21 eu, and $\Delta C_{\text{vap}}$ is approximately constant, as noted. In Table I we have applied the equations to the equilibria with all liquid components at 25 °C.

**Cyclopentadiene–Dicyclopentadiene.** The gas-phase entropies for the components of this equilibrium were taken from O'Neal and Benson's calculations.[11] Their choice of forward and reverse rate constants, however, gives $\Delta H_{\text{g}}^{0}$ = 19.1 kcal. This is larger by 1.7 kcal than the enthalpy difference of 17.4 one estimates from Cox and Pilcher's compilations. A number of rate constants in the forward and reverse directions in the liquid phase also have been measured. Khambata and Wasserman's value[12] of $\log k_1$ (s$^{-1}$) = (13.0 ± 0.2) − (34.2 ± 0.4)/$\theta$ (paraffin) and Harness, Kistiakowski, and Mears[13] $\log k_{-1}$ (M$^{-1}$ s$^{-1}$) = 6.62 − 17.3/$\theta$ (tetralin) give values of $\Delta H_{\text{l}}^{+}$ = 16.9 kcal, $\Delta S^{+}$ = 31 eu, closest to the ones calculated from the gas-phase data, $\Delta H^{+}$ = 16.6 kcal, $\Delta S^{+}$ = 33.2 eu. The calculated $\Delta G_{\text{l}}^{+}$ from the latter values is 1.0 kcal less than that from the experimental, liquid data.

Calculation of the liquid parameters without taking $\Delta C_{\text{vap}}$ into account gave $\Delta H_{\text{l}}^{+}$ = 16.1 kcal, $\Delta S_{\text{l}}^{+}$ = 38 eu, and $\Delta G_{\text{l}}^{+}$ = 4.8 kcal.

**Ethyl Acetate.** Data are well known for all components, and a recent, careful gas-phase determination of $K_{\text{eq}}$ gave $\Delta H_{\text{r}}^{0} = -3.1 \pm 0.2$ kcal, $\Delta S = \pm 0.4$ eu, and $K_{\text{eq}} = 170$, in reasonable agreement with values of −3.5, −2.85, and 88, respectively, from gas data assembled in Table I. The liquid-phase data include the classic value of Berthelot and St. Gelles,[15] and more recent ones from ICT. Both give $\Delta G_{\text{l}}^{+} = -0.7 \pm 0.1$ kcal, compared with $\Delta G_{\text{l}}$ = 0.8 kcal from our treatment of gas-phase data. Neglect of $\Delta C_{\text{vap}}$ gave $\Delta G_{\text{l}}^{+}$ = −3.8 kcal, $\Delta H_{\text{l}}$ = −1.2 kcal, and $\Delta S_{\text{l}}^{+}$ = 8.7 eu.

**Nitrogen Tetroxide.** In this case, nitrous oxide was chosen as a model for $NO_2$ and *n*-hexane for nitrogen tetroxide. Gas-phase values were taken from JANAF; solution values

**Table I.** Terms for Calculation of Liquid Equilibria at 25 °C

| Compd | $\Delta H_f^0$ | $\Delta H_{vap}^0$ | $T_B$, °C | 0.012 (25 °C − $T_B$ °C) | $\Delta H_l^+$ | $S^0$ | $-12 \ln (T/T_B)$ | $R \ln (10^3/V_m)$ | $S_l^+$(1 M) |
|---|---|---|---|---|---|---|---|---|---|
| 1,3-Cyclopentadiene | 32.0 | 6.9 | 41 | −0.4 | 24.7 | 65.6 | 0.6 | 5 | 49.0 |
| Dimer | 46.6 | 12.5 | 180 | −1.3 | 32.8 | 86.9 | 5.0 | 3.9 | 64.8 |
| (Calcd: $\Delta H_l^+ = 16.6$ kcal, $\Delta S_l^+ = 33.2$ eu, $\Delta G_l^+$, 6.6 kcal; Found: $\Delta H_l^+ = 16.9 \pm 0.4$, $\Delta S_l^+ = 31 \pm 1.9$, $\Delta G_l^+ = 7.6$ kcal) | | | | | | | | | |
| Ethanol | −56.18 | 10.2 | 78.5 | −0.6 | −67.0 | 67.4 | 2.0 | 5.6 | 50.0 |
| Water | −57.8 | 10.5 | 100 | −0.9 | −69.2 | 45.0 | 2.7 | 8.0 | 29.3 |
| Ethyl acetate | −105.7 | 8.4 | 77 | −0.6 | −114.7 | 86.9 | 1.9 | 4.6 | 68.6 |
| Acetic acid | −103.8 | 12.5 | 114 | −1.1 | −117.4 | 67.4 | 3.1 | 5.7 | 49.0 |
| (Calcd: $\Delta H_l^+ = 0.5$ kcal, $\Delta S_l^+ = -1.1$ eu, $\Delta G_l^+ = 0.8$ kcal; Found: $\Delta G_l^+ = -0.7$ kcal) | | | | | | | | | |
| $NO_2$ | 7.91 | 3.8 | [−90] | 1.3 | 5.4 | 57.3 | −5.85 | 6.2 | 48.4 |
| $N_2O_4$ | 2.17 | 7.5 | [ 69] | −0.5 | −5.8 | 72.7 | 1.7 | 5.5 | 55.5 |
| (Calcd: $\Delta H_l^+ = 16.6$ kcal, $\Delta S_l^+ = 41.3$ eu, $\Delta G^+ = 4.3$ kcal; Found: $\Delta H_l^+ = 19.5$ kcal, $\Delta S_l^+ = 47$ eu, $\Delta G^+ = 5.5$ kcal) | | | | | | | | | |
| Norbornene | 15.1 | 8.1 | [111] | −1.0 | 6.0 | 71.9 | 3.0 | 5.1 | 53.0 |
| Nortricyclene | 14.8 | 8.1 | [111] | −1.0 | 5.7 | 69.7 | 3.0 | 5.1 | 50.8 |
| (Calcd: $\Delta H_l^+ = -0.3$ kcal, $\Delta S_l^+ = -2.2$ eu, $\Delta G_l^+ = 0.4$ kcal at 25 °C; Found: $\Delta G_l^+ = -1.0$ kcal at 111 °C) | | | | | | | | | |

were those of Steese and Whittaker.[16] Agreement is only fair between respective $\Delta H^+$ and $\Delta S^+$ values; the $\Delta G^+ = 5.5$ kcal is reasonably close to our calculated value of 4.3 kcal. The above authors suggested that the extinction coefficients for $NO_2$ in gas and solution may not be equal. This would result in an error in $\Delta S$, but not in $\Delta H$, however.

**Norbornene.** An attempt was made to measure the equilibrium constant for norbornene ⇄ nortricyclene at 111 °C in a liquid mixture refluxed over activated alumina.[17] The measurement was obscured by side reactions leading to polymerization. Despite this, from the apparent values obtained at quite different times starting with either component, it is possible to deduce $K_{eq}(111\ °C) \leq 3.5$ with an uncertainty of a factor of about 2; $1.7 \leq K_{eq}(111\ °C) \leq 3.5$ if it is plausibly assumed that the polymerizing specie is the olefin. The gas-phase equilibrium has not been apparently studied, but gas-phase enthalpies are available,[18] and the entropies can be calculated. The entropy difference was simply taken as $R \ln 3$ (symmetry factor). This correction was neglected by Hall et al.,[18] who erroneously concluded that his results agreed with Schleyer's[17] determination.

We treated the components as hypothetical liquids of bp 111 °C and $\Delta S^0(T_B) = 21$ eu. The observed $\Delta G_l^+ = -1.0$ kcal is reasonably close to that calculated (0.4 kcal). From the experimental solution $K_{eq}$ and $\Delta S = R \ln 3$, we calculate $\Delta H_g = -1.8$ kcal at 111 °C, fairly close to the observed difference of $0.3 \pm 0.5$ kcal at 25 °C.

## Conclusion

The four examples give $\Delta G_l$· within 1.5 kcal of the experimental results in solution. This is reasonable in view of the simplicity of our approach, the uncertainty in source of the data, and the approximations involved. It is noteworthy that the heat capacity corrections (Table I) amount to ±1.3 kcal for the enthalpy term and ±5 eu for the entropy, and that the largest corrections occur when the boiling points of the equilibrium components are separated widely. The correction for the heat capacity of vaporization is thus a significant one and does much to improve the large discrepancies which had been noted earlier in the few comparisons between gas and liquid equilibria.

We agree with Patrick's observation that there are, unfortunately, few examples of equilibrium carried out in both phases.

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