



# Enthalpies of hydrogenation and formation of enones. Resonance energies of 2-cyclopentenone and 2-cyclohexenone

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The enthalpies of hydrogenation of 2-cyclopentenone, 2-cyclohexenone, 2-methyl-3-isobutoxycyclohex-2-enone, and 5-methylhex-5-en-2-one have been measured and found to be  $-(97.1\pm2.7)\,kJ\cdot mol^{-1}$ ,  $-(109.2\pm2.9)\,kJ\cdot mol^{-1}$ ,  $-(106.1\pm3.0)\,kJ\cdot mol^{-1}$ , and  $-(113.2\pm2.7)\,kJ\cdot mol^{-1}$ , respectively. In combination with the enthalpies of formation of the corresponding alkanones, we obtained the enthalpies of formation  $\Delta_f H^\circ_m$ (cyclopentenone) =  $-(100.3\pm3.0)\,kJ\cdot mol^{-1}$ . By using isodesmic reactions, the resonance energy of cyclic enones is estimated to be  $(13\pm4)\,kJ\cdot mol^{-1}$ .  $\odot$  1998 Academic Press

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### 1. Introduction

As part of our recent study on the structure and energetics of enynones, dienones, and related species,<sup>(1)</sup> we carried out measurements of the molar enthalpies of hydrogenation  $\Delta_{hvd}H_m$  at T = 298.15 K of 2-cyclopentenone, 2-cyclohexenone, and

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r	$\frac{-\Delta_{\rm hyd}H_{\rm m}}{\rm kJ\cdot mol^{-1}}^a$	$\frac{\langle -\Delta_{\rm hyd} H_{\rm m}\rangle}{\rm kJ\!\cdot\!mol^{-1}}$
Cyclopentenone (mass fraction, 0.994)		
0.8122 0.9015	$\begin{array}{c} 98.7 \pm 1.3 \\ 97.5 \pm 1.7 \end{array}$	$\begin{array}{c} 98.1 \pm 1.7 \\ (97.1 \pm 2.7)^b \end{array}$
Cyclohexenone <sup>c</sup> (mass fraction, 0.996)		
0.8448 0.8545	$\begin{array}{c} 108.3  \pm  1.1 \\ 112.2  \pm  2.7 \end{array}$	$\begin{array}{c} 110.2\pm1.9\\ (109.2\pm2.9)^b \end{array}$
2-Methyl-3-isobutoxycyclohex-2-enone (mass fraction, 0.99)		
0.8710 0.8872	$\begin{array}{c} 109.2 \ \pm \ 0.8 \\ 106.7 \ \pm \ 2.9 \end{array}$	$\begin{array}{c} 107.1\pm2.0\\(106.1\pm3.0)^b\end{array}$
5-Methylhex-5-en-2-one (mass fraction, 0.995)		
0.8197 0.8320 0.8180	$\begin{array}{c} 113.0\pm2.1\\ 115.5\pm1.7\\ 114.6\pm1.7\end{array}$	$\begin{array}{c} 114.2\pm1.7\\ (113.2\pm2.7)^b\end{array}$

 TABLE 1. Molar enthalpies of hydrogenation  $\Delta_{hyd}H_m$  at the temperature 298.15 K of four enones; r denotes n(cyclohexene)/n(enone) or n(1-hexene)/n(enone) 

<sup>*a*</sup> Mean value of nine measurements of  $\Delta_{hyd}H_m$ . <sup>*b*</sup> Mean value corrected for  $\Delta_{sol}H_m$  at T = 298 K. <sup>*c*</sup> Mixed solvent mole fraction 0.616 of tetrahydrofuran and *n*-hexane (see text).

2-methyl-3-isobutoxycyclohex-2-enone, members of a class of compounds not well represented in the thermochemical literature.<sup>(2)</sup> Solvent effects on  $\Delta_{\rm hyd}H_{\rm m}$  were also examined, including comparison of a solution-phase  $\Delta_{\rm hyd}H_{\rm m}$  of 5-methylhex-5-en-2-one with a gas-phase study of an alkane of similar size, 2,2,4-trimethylpent-1-ene.

### 2. Experimental

The compounds 2-cyclopenten-1-one, 2-cyclohexen-1-one, cyclopentanone, and cyclohexanone are commercially available (Aldrich, Acros). The enones were fractionally distilled and stored as refrigerated samples of mass 1.0 g sealed in glass under argon. Sample purity (table 1) was determined by g.l.c. The cycloalkanones were very pure (mass fraction  $\approx 0.998$ ) as obtained. Synthetic methods for obtaining 3-ethynyl-2-cycloalkenones have been given previously.<sup>(3)</sup>

The calorimeter and method have been described elsewhere.<sup>(4,5)</sup> Briefly, portions of a dilute reactant (unsaturate) solution were injected into a reaction flask containing 18.0 cm<sup>3</sup> of the same solvent (Aldrich, mass fraction > 0.99) as the reactant solution and 300 mg of (0.05 mass fraction of Pd, C) catalyst (Aldrich), and stirred magnetically. Hydrogen at a pressure of 0.1 MPa above ambient was conveyed into the flask through a hypodermic needle. The reaction flask contained a thermistor connected as one arm of a Wheatstone bridge circuit which produces a voltage that is amplified and fed into an A/D converter (Alpha Products, Darien, CT 06820), and thence to a microcomputer. The microcomputer is programmed to treat the temperature against time curve obtained during hydrogenation by suitable extrapolations of bridge output (proportional to temperature) taken before and after hydrogenation, in a manner analogous to the extrapolations used in conventional combustion calorimetry.<sup>(6)</sup> Each of the extrapolations, forward and back, intersects with a vertical passing through the inflection point of the *T* against *t* curve. The length of the line segment between these intersections is proportional to  $\Delta T$  for hydrogenation.

Identical volumes of a dilute standard solution of an alkene of known  $\Delta_{hyd}H_m$ , and a similar solution of an unknown were alternately injected into the calorimeter under as nearly as possible identical conditions. The ratio of  $\Delta T$  values for hydrogenation of each reaction pair led to  $\Delta_{hyd}H_m$  at T = 298.15 K of the unknown.

Depending on the molar mass, (60 to 80) mg of cycloalkenone was weighed to  $\pm 2 \cdot 10^{-6}$  g on a Sartorius M3P electronic microbalance and diluted with solvent to a volume of 0.500 cm<sup>3</sup>. The standard was made up so as to be thermochemically equivalent to the sample, *i.e.* it produced approximately the same amount of heat upon hydrogenation as the sample solution. This amount was known for cyclopentenone and cyclohexenone from preliminary experiments on commercial product (Aldrich) of mass fractions 0.98 and 0.97, respectively. Approximate thermochemical equivalence required n(standard)/n(enone) of 0.8 to 0.9, as seen in table 1. Portions of standard and sample (0.0200 cm<sup>3</sup>) were injected into the calorimeter by using a g.l.c. microsyringe fitted with a Cheney adaptor for maximum reproducibility.

Two thermochemical standards (Wiley Organics; mass fraction 0.999) were used in this work. Results in table 1 were calculated from  $\Delta_{hyd}H_m$  values at T =298.15 K of cyclohexene,  $-(118.8 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1},^{(7a,b)}$  or 1-hexene,  $-(126.6 \pm$  $0.8) \text{ kJ} \cdot \text{mol}^{-1}.^{(7c)}$  The value selected for cyclohexene is the arithmetic mean of  $\Delta_{hyd}H_m = -(119.0 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}.^{(7b)}$  in the gas phase at T = 355 K, which would be expected to be slightly more negative than the result at T = 298.15 K, and  $\Delta_{hyd}H_m = -(118.6 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$  measured at T = 298.15 K and corrected for solvent effects.<sup>(7a)</sup> These results have been discussed recently by Steele *et al.*<sup>(7d)</sup> An early result of ours,  $\Delta_{hyd}H_m = -(112.5 \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1}$ , should be discarded.<sup>(8)</sup> Solvents used were *n*-propanol, or tetrahydrofuran, or a mixed solvent system of

Solvents used were *n*-propanol, or tetrahydrofuran, or a mixed solvent system of tetrahydrofuran in *n*-hexane (mol fraction tetrahydrofuran, 0.616). Enthalpies of solution of the reaction products were measured by the same procedure as above. The apparatus was not designed to measure small negative temperature changes but the results showed that the heat effect superimposed on  $\Delta_{hyd}H_m$  at T = 298.15 K was negative and not greater than  $2 \text{ kJ} \cdot \text{mol}^{-1}$ , *i.e.*  $(1 \pm 2) \text{ kJ} \cdot \text{mol}^{-1}$ . Accordingly, the results in table 1 have been adjusted to less negative values by  $1 \text{ kJ} \cdot \text{mol}^{-1}$ , and the experimental uncertainties of the enthalpies and the resonance energies derived from them have been increased to include a  $\Delta_{sol}H_m$  contribution to the uncertainty of the final results.

The calorimeter was operated at ambient temperature (isoperibol operation).<sup>(5*a*)</sup> The temperature difference between isoperibol operation and isothermal operation at T = 298.15 K was within 3 K. Straightforward thermodynamic calculations show

that the effect of isoperibol operation at temperatures that were slightly different from  $T = 298.15 \,\mathrm{K}$  does not influence the measured  $\Delta_{\rm hyd} H_{\rm m}$  by a significant amount. We believe that the measured values in table 1 are the same as the  $\Delta_{\rm hyd} H_{\rm m}$  at  $T = 298.15 \,\mathrm{K}$  to within a tolerance that is a factor of 10 smaller than the stated experimental uncertainties.

### 3. Results and discussion

The uncertainties in table 1 are standard deviations from the mean for nine pairs of hydrogenations, alternating sample with standard (18 hydrogenations in all). They express approximately 95 per cent confidence limits. Entries in parentheses have been corrected by  $1.0 \text{ kJ} \cdot \text{mol}^{-1}$  and their uncertainty estimate has been increased as described above due to uncertainty in the measurement of  $\Delta_{sol}H_m$  at T = 298.15 K.

Thermograms were normal for the compounds in table 1, and reaction times were less than the 10 s instrument system response time. Examination by g.l.c. (60 m wide bore capillary, SE 30, Supelco) of the reaction product showed no evidence of incomplete or competing reactions.

There was a small enthalpy effect superimposed on the reaction enthalpy for the first few hydrogenations. We ascribe it to adsorption of the polar enone on the catalyst or its carbon support. The initial results were more negative than the arithmetic mean of the entire set by  $(2 \text{ to } 6) \text{ kJ} \cdot \text{mol}^{-1}$ . The exothermic effect rapidly diminished, and subsequent results held steady at the values given in table 1. Accordingly, 15 pairs of experimental measurements were made, the last nine of which are reported as individual entries in table 1. We have encountered this effect before and we handled it in a similar way.<sup>(9)</sup> In a mixed solvent system, (tetrahydrofuran + *n*-hexane), the exothermic effect was not observed.

Enthalpies of solution of the reaction products, cyclopentanone and cyclohexanone, were also measured for the mixed solvent system, and  $\Delta_{sol}H_m$  was estimated as  $\langle (2.0 \pm 2.0) \text{ kJ} \cdot \text{mol}^{-1}$ . We have already mentioned that the calorimeter was not designed to measure such small enthalpy effects, which accounts for the large relative uncertainty. The influence of solvent on the measured  $\Delta_{hyd}H_m$  at T = 298.15 K was also assessed by comparing our value of  $\Delta_{hyd}H_m$  (5-methylhex-5-en-2-one), in which one expects no influence of the keto oxygen on the rather distant double bond, with the gas-phase result for a comparable alkene, 2,2,4-trimethylpent-1-ene.

Resonance is a theoretical construct usually thought of as describing intramolecular electronic interactions within isolated molecules. Therefore, resonance energy should properly be measured on samples in the ideal gas state. This is not feasible for any real samples, though it may be well approximated under some circumstances. More to the point, hydrogenation thermochemistry has not been carried out on real gases for many years owing to the low volatility of most samples of interest. In this work, in which a dilute solution of, for example, alkenone in *n*-propanol ( $\approx 0.1$  mass fraction) is hydrogenated to a very dilute solution of alkanone ( $\approx 1 \cdot 10^{-4}$  mass fraction), we argue that the solution-phase

and gas-phase  $\Delta_{hyd} H_m$  differ by less than the  $\approx 2 \text{ kJ} \cdot \text{mol}^{-1}$  error limits assigned to  $\Delta_f H_m$  at T = 298.15 K, and the 4 kJ $\cdot$ mol<sup>-1</sup> assigned to the resonance energy. Following Fuchs and Peacock,<sup>(10)</sup> we note that, for a fixed amount of (neat)

reactant, the enthalpy of hydrogenation in the gas phase  $\Delta_{hvd} H_m(g)$  is given by:

$$\Delta_{\rm hyd}H_{\rm m}({\rm g}) = \Delta_{\rm hyd}H_{\rm m}({\rm sln}) + \Delta_{\rm trans}H_{\rm m}({\rm reactant}) - \Delta_{\rm trans}H_{\rm m}({\rm product}), \quad (1)$$

where  $\Delta_{hyd}H_m(sln)$  is the enthalpy of hydrogenation in solution, and  $\Delta_{trans}H_m$  is the *enthalpy of transfer* of solute from the solution to the gas phase. Hydrogen is rapidly replaced from the gas phase during hydrogenation of the sample, both in solution and on the catalyst surface, so that the overall solution and desorption-adsorption effect for H<sub>2</sub> is negligible. Each enthalpy of transfer is the algebraic sum of  $\Delta_{vap} H_m$  and  $\Delta_{sol} H_m$ , the enthalpies of vaporization and solution of the reactant and product, respectively. Now,

$$\Delta_{\text{hyd}} H_{\text{m}}(\mathbf{g}) = \Delta_{\text{hyd}} H_{\text{m}}(\text{sln}) + \Delta_{\text{vap}} H_{\text{m}}(\text{product}) - \Delta_{\text{vap}} H_{\text{m}}(\text{reactant}) - \Delta_{\text{sol}} H_{\text{m}}(\text{product}) + \Delta_{\text{sol}} H_{\text{m}}(\text{reactant}).$$
(2)

We do not know  $\Delta_{vap}H_m$  for all of the reactants and products in table 1, but we draw an analogy between unsaturation in ketones and unsaturation in alcohols. Polak and Benson<sup>(11)</sup> found that  $\Delta_{\text{vap}} H_{\text{m}}(\text{prop-2-en-1-ol}) = (47.3 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1}$ and  $\Delta_{\text{vap}} H_{\text{m}}(\text{propanol(l)}) = (47.5 \pm 0.04) \text{ kJ} \cdot \text{mol}^{-1}$  at T = 298.15 K. Wadsö observed the value  $\Delta_{\text{vap}} H_{\text{m}}(\text{propanol(l)})$  to be  $(47.3 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$ .<sup>(12)</sup> Comparison of the saturated and unsaturated alcohols indicates that the double bond has little influence on  $\Delta_{yap}H_m$ , a conclusion supported by our previous and more general work.<sup>(13)</sup>

Enthalpies of solution are largely determined by the size of the cavity in the solvent system made by intrusion of solute molecules<sup>(14)</sup> which, in turn, correlates directly with the size, shape, and functionality of the solute.<sup>(13)</sup> For hydrogenation of the two simple cycloalkenones in table 1, product and reactant are almost exactly the same size and have a similar electron distribution, differing only in the presence or absence of the double bond. In the light of these observations, we believe that the last four terms in equation (2) nearly cancel pairwise, leaving  $\Delta_{hvd}H_m(g) \approx \Delta_{hvd}H_m(sln)$  within the limits of the other sources of experimental error. It should be noted that the actual process occurring along with hydrogenation in the calorimeter is an enthalpy change of the system due to *dilution* of  $a \approx 0.15$ mass fraction alkenone solution to a very dilute alkanone solution. This thermal effect can be assumed to be very much smaller than the difference between  $\Delta_{sol}H_m$ (reactant) and  $\Delta_{sol}H_m$ (product), hence the arguments in this section follow a fortiori.

A factor that has not yet been accounted for is the possibility of association between the solvent and solute, for example, the polar OH group of *n*-propanol and the double bond in the reactant. Such an association would be broken during hydrogenation, and the enthalpic effect would depend upon the strength of the reactant-solvent association. This enthalpy would, if present, appear as a difference

in  $\Delta_{sol}H_m$ (reactant) and  $\Delta_{sol}H_m$ (product) in the solvent chosen as the calorimeter fluid. At present, we do not have an accurate direct measure of this strength, but Roth and Lennartz<sup>(15)</sup> have measured  $\Delta_{sol}H_m$  for cyclopentene, cyclopentane, cyclohexane, and cyclohexane and found them to differ by slightly more than  $1 \text{ kJ} \cdot \text{mol}^{-1}$  in methanol and by less than  $1 \text{ kJ} \cdot \text{mol}^{-1}$  in cyclohexane.

In order to judge the systematic error brought about by any combination of the factors described above, we measured  $\Delta_{hyd}H_m$ (5-methylhex-5-en-2-one), in which the keto oxygen and the  $\alpha$ -methyl double bond are well separated from one another and should have no mutual intramolecular energetic influence. We compare our measurement with the gas-phase  $\Delta_{hyd}H_m$ (2,2,4-trimethylpent-1-ene) obtained by Kistiakowsky.<sup>(7b)</sup> The results are  $\Delta_{hyd}H_m = -(113.2 \pm 1.7) \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta_{hyd}H_m = -(113.8 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$ , respectively, indicating no significant difference and no significant solvent error. For completeness, we note that the temperatures at which these experiments were carried out were different (T = 298.15 K and T = 355.15 K, respectively), that  $\Delta_{hyd}H_m$  of a C<sub>7</sub>  $\alpha$ -methyl terminal alkene has not been measured in the gaseous phase, and that  $\Delta_{hyd}H_m$ (g) for the C<sub>6</sub> and C<sub>5</sub>  $\alpha$ -methylalkenes at T = 355.15 K are larger,  $-117 \text{ kJ} \cdot \text{mol}^{-1}$  compared with  $-119 \text{ kJ} \cdot \text{mol}^{-1}$ , than the compound we chose as the most apposite for comparison. The standard molar enthalpies of formation in the gas phase at  $T = 100 \text{ km}^{-1}$ 

The standard molar enthalpies of formation in the gas phase at T = 298.15 K,  $\Delta_{\rm f} H^{\circ}_{\rm m}$ (cyclopentanone) =  $-(197.4 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1} \, {}^{(16)}$  and  $\Delta_{\rm f} H^{\circ}_{\rm m}$ (cyclopentanone) =  $-(231.1 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1} \, {}^{(16)}$  lead to  $\Delta_{\rm f} H_{\rm m}$ (cyclopentenone) =  $-(100.3 \pm 3.0) \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta_{\rm f} H_{\rm m}$ (cyclohexenone) =  $-(121.9 \pm 3.0) \text{ kJ} \cdot \text{mol}^{-1}$  at T = 298.15 K, the two main target compounds of this study. Uncertainties in  $\Delta_{\rm f} H^{\circ}_{\rm m}$  are given as the root-mean-square of the experimental uncertainties. We lack the necessary  $\Delta_{\rm f} H^{\circ}_{\rm m}$  values of the hydrogenation products for calculating  $\Delta_{\rm f} H^{\circ}_{\rm m}$  of the remaining two compounds in table 1 at T = 298.15 K.

## 4. Resonance energies of cylopentenone and cyclohexenone

We are in a position to evaluate the resonance energies of these cyclic enones. Following from reference 2, the enthalpy of the following isodesmic reaction:

$$cycloalkenone + cycloalkane = cycloalkene + cycloalkanone,$$
 (3)

may be equated with the resonance energy of the enone. Inspection shows that this enthalpy equals the difference in enthalpies of hydrogenation of the enone and the parent olefin. For cyclopentenone, taking the enthalpy of hydrogenation of cyclopentene as  $-(112.5 \pm 1.7) \text{ kJ} \cdot \text{mol}^{-1}$  from reference 17, we deduce a resonance energy of  $(15.4 \pm 3.2) \text{ kJ} \cdot \text{mol}^{-1}$ . Likewise, for cyclohexenone, from references 7(a) and 7(b), we deduce a resonance energy of  $(9.6 \pm 3.0) \text{ kJ} \cdot \text{mol}^{-1}$ . An arithmetic mean of the resonance energy of  $(13 \pm 4) \text{ kJ} \cdot \text{mol}^{-1}$  for cyclic enones is thus suggested.

There are disappointingly few species with which comparisons can be made.<sup>(2)</sup> The first is with (E)-2-butenal for which the gas-phase enthalpy of hydrogenation of  $-(104.2 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$  has been reported.<sup>(18)</sup> That of the corresponding

olefin, (E)-2-butene, has been measured as  $-(114.6 \pm 0.6) \text{ kJ} \cdot \text{mol}^{-1}$ ,<sup>(19)</sup> resulting in a resonance energy of  $(10.2 \pm 0.6) \text{ kJ} \cdot \text{mol}^{-1}$ . The enthalpies of combustion, and thus of formation, of (E)-2-cycloheptadecenone and cycloheptadecanone have been determined,<sup>(20)</sup> and corresponding sublimation enthalpies either directly measured,<sup>(21)</sup> or derived.<sup>(22)</sup> The resulting enthalpies of formation of the gaseous ketones,  $-(460.3 \pm 10.9) \text{ kJ} \cdot \text{mol}^{-1}$  and  $-(408.3 \pm 13.4) \text{ kJ} \cdot \text{mol}^{-1}$ , can be numerically combined to derive an enthalpy of hydrogenation of the 2cycloheptadecenone,  $-(52.0 \pm 17.3) \text{ kJ} \cdot \text{mol}^{-1}$ . We lack thermochemical information about (E)-cycloheptadecene but, by analogy with other cycloalkenes with more than seven carbon atoms, or long acyclic olefins with double bonds that are not in the terminal position,<sup>(23)</sup> we believe that its hydrogenation enthalpy will not be very different from that of these species, approximately  $-(110 \text{ to } 120) \text{ kJ} \cdot \text{mol}^{-1}$ . Used without reservation, we would conclude that 2 -cycloheptadecenone has a resonance energy of some (50 to 60) kJ  $\cdot \text{mol}^{-1}$ . We are very doubtful of this last value, but suspect no error except in the measurement of the enthalpy of formation of either large-ring ketone.

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