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Enthalpies of Hydration of Alkenes. 4. Formation of Acyclic *tert*-Alcohols

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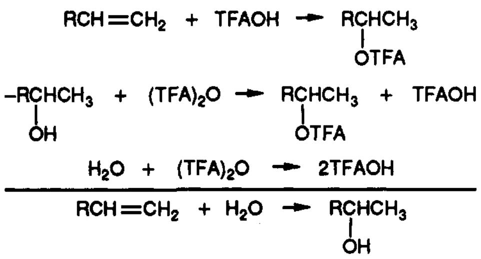
The enthalpies of hydration of a series of acyclic alkenes that lead to *tert*-alcohols were determined. Several pairs of alkenes that give the same alcohol were studied and gave the differences in enthalpy of formation of the alkenes. A consistent difference in ΔH_f of 1.84 kcal/mol was found between di- and trisubstituted alkenes. It was related to the difference in ΔH_f for pairs of exocyclic and endocyclic alkenes. The enthalpies of formation of the alcohols were obtained and were related to data for primary and secondary alcohols.

We have shown that it is possible to determine the enthalpy of hydration of an alkene in the liquid phase via measurements of the enthalpies of reaction of the alkene, alcohol, and water with trifluoroacetic acid (TFAOH) containing trifluoroacetic anhydride $(TFA)_2O$).[1,2] This procedure was used in determining the enthalpies of formation of a series of secondary alcohols. An examination of the available data showed that for a given type of alcohol (primary, secondary, or tertiary) the difference in enthalpy of formation between the alcohol and the alkane formed by replacement of the hydroxy group by methyl was essentially constant. With primary alcohols, the enthalpy difference in the gas phase was 30.8 ± 0.3 kcal/mol, with secondary alcohols it was 32.8 ± 0.3 kcal/mol, and with tertiary alcohols it was 34.5 kcal/mol.[3]



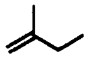
$$RCH{=}CH_2 + TFAOH \rightarrow \underset{\displaystyle OTFA}{RCHCH_3}$$

$$-\underset{\displaystyle OH}{RCHCH_3} + (TFA)_2O \rightarrow \underset{\displaystyle OTFA}{RCHCH_3} + TFAOH$$

$$H_2O + (TFA)_2O \rightarrow 2TFAOH$$

$$RCH{=}CH_2 + H_2O \rightarrow \underset{\displaystyle OH}{RCHCH_3}$$

The data for tertiary alcohols were rather limited, and therefore we have now determined the enthalpies of hydration of a series of acyclic alkenes that would lead to tertiary alcohols. The alkenes and the corresponding alcohols were as follows: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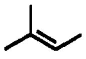
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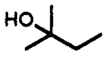
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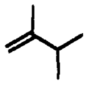
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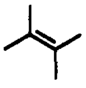
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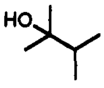
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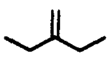
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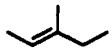
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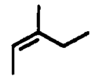
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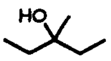
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By choosing pairs of alkenes that lead to the same alcohol, the difference in enthalpies of reaction of the alkenes also gives the difference in their enthalpies of formation.

Table I. Enthalpies of Reaction with Trifluoroacetic Acid[a]

compd	n	ΔH_r (cal/mol)
2-methyl-1-butene (**1**)	5	−10 931 ± 42
2-methyl-2-butene (**2**)	4	−9111 ± 35
2,3-dimethyl-1-butene (**3**)	8	−10 239 ± 33
2,3-dimethyl-2-butene (**4**)	4	−8369 ± 33
2-ethyl-1-butene (**5**)	4	−10 658 ± 23
trans-3-methyl-2-pentene (**6**)	6	−8796 ± 59
cis-3-methyl-2-pentene (**7**)	5	−9014 ± 22
2-methyl-2-butanol (**8**)	6	−21 155 ± 23
2,3-dimethyl-2-butanol (**9**)	6	−21 063 ± 46
3-methyl-3-pentanol (**10**)	5	−21 030 ± 16
water	4	−18 007 ± 30

[a] The uncertainties are given as $2\bar{s}$ where $\bar{s}$ is the standard deviation from the mean.

The experimental data are presented in Table I. The enthalpies of hydration derived from these data are given in Table II, along with the enthalpy differences for pairs of alkenes. The liquid phase enthalpy differences for **1** and **2**, for **3** and **4**, and for **5** and **6** are essentially the same. The values were converted to those for the gas phase using the known enthalpies of vaporization.[4] The difference between **1** and **2** thus obtained is in excellent agreement with that derived via gas-phase hydrogenation.[5] The difference between **3** and **4** is somewhat smaller than that obtained via hydrogenation, but this may be due to the unusually large difference in reported enthalpies of vaporization (0.81) as compared to 0.29 for **1** and **2**. We suspect that one of the enthalpies of vaporization is in error.

The enthalpies of formation in the liquid phase that may be derived from the present data are given in Table III. The enthalpies of formation of 2-methyl-1-butene (**1**) and of 2-methyl-2-butene (**2**) are available from a recent calorimetric study.[6] The difference in ΔH_f is 1.70 ± 0.36 kcal/mol and is in good agreement with the hydrogenation data. We have taken the value for **1** as the reference since it has the lower standard deviation. The ΔH_f derived for **2** using our enthalpy difference is then −16.39 ± 0.20 kcal/mol, in good agreement with that obtained via combustion calorimetry (−16.27 ± 0.31). Using the enthalpy of formation of water (−68.32 kcal/mol) and the enthalpy of reaction of water with the trifluoroacetic acid/trifluoroacetic anhydride mixture (−18.01 ± 0.03 kcal/mol), the enthalpy of formation of 2-methyl-2-butanol becomes −90.67 ± 0.21 kcal/mol, in very good agreement with that determined by combustion calorimetry, −90.70 ± 0.13 kcal/mol.[7] The good agreement between the values obtained using the hydration data and via combustion ca-

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Table II. Enthalpy Differences (kcal/mol) for Alkenes

	ΔH_r	$\Delta\Delta H$(1)	$\Delta\Delta H$(g)	ΔH(hydrog)	$\Delta\Delta H$
2-methyl-1-butene (1)	−10.93 ± 0.04	1.82 ± 0.06	1.53 ± 0.06	−28.49 ± 0.10	1.57 ± 0.12
2-methyl-2-butene (2)	−9.11 ± 0.04			−26.92 ± 0.06	
2,3-dimethyl-1-butene (3)	−10.24 ± 0.03	1.87 ± 0.05	1.06 ± 0.07[a]	−28.00 ± 0.10	1.37 ± 0.14
2,3-dimethyl-2-butene (4)	−8.37 ± 0.03			−26.63 ± 0.10	
2-ethyl-1-butene (5)	−10.66 ± 0.02	1.86 ± 0.07	1.78 ± 0.09		
trans-3-methyl-2-pentene (6)	−8.80 ± 0.06				
cis-3-methyl-2-pentene (7)	−9.01 ± 0.02	1.65 ± 0.03	1.39 ± 0.09		

[a] See text.

Table III. Enthalpies of Formation (kcal/mol), Liquid Phase, 25 °C

compd	ΔH_f(1)	lit.	ΔH_f(g)
2-methyl-1-butene	[−14.57 ± 0.19][a]	−14.57 ± 0.19	−8.39 ± 0.20
2-methyl-2-butene	−16.39 ± 0.20	−16.27 ± 0.31	−9.92 ± 0.21
2-methyl-2-butanol	−90.67 ± 0.21	−90.70 ± 0.13	−79.07 ± 0.35
2,3-dimethyl-1-butene	−22.73 ± 0.35	−22.85 ± 0.40	−15.74 ± 0.36
2,3-dimethyl-2-butene	−24.60 ± 0.35	−24.48 ± 0.35	−16.80 ± 0.36
2,3-dimethyl-2-butanol	−98.23 ± 0.36		−85.32 ± 0.14
2-ethyl-1-butene	−20.83 ± 0.20	−20.82 ± 0.35	−13.40 ± 0.21
trans-3-methyl-2-pentene	−22.69 ± 0.20	−22.60 ± 0.35	−15.18 ± 0.21
cis-3-methyl-2-pentene	−22.48 ± 0.20	−22.58 ± 0.35	−14.79 ± 0.21
3-methyl-3-pentanol	−96.78 ± 0.21		−83.24 ± 0.29

[a] Literature value.

Table IV. Equilibration of Methylenecyclobutane and 1-Methylcyclobutene

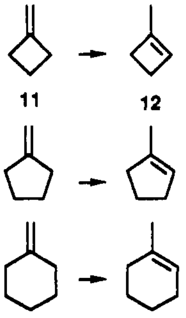
T (K)	K	T (K)	K
298.11	5.43	283.14	5.72
293.14	5.52	268.04	6.01
287.57	5.62	265.75	6.06

lorimetry again validates our procedure and provides a good check on the experimental data.

The enthalpies of formation of 2,3-dimethyl-1-butene (**3**) and 2,3-dimethyl-2-butene (**4**) have been determined by combustion calorimetry, giving a difference in ΔH_f(l) of 1.63 ± 0.53 kcal/mol,[8] which is in satisfactory agreement with our data. Since the standard deviations for the two compounds were essentially the same, they were adjusted equally to fit our enthalpy difference. Then, the enthalpy of formation of 2,3-dimethyl-2-butanol was obtained from the enthalpy of hydration. No other experimental data are available for this alcohol.

The enthalpies of formation of 2-ethyl-1-butene (**5**), *trans*-3-methyl-2-pentene (**6**), and *cis*-3-methyl-2-pentene (**7**) have been determined by combustion calorimetry.[7] The differences among these values are in excellent agreement with the hydration data (±0.08 kcal/mol), suggesting a net uncertainty in the enthalpies of formation of about ±0.10 kcal/mol. It therefore seems reasonable to reduce the uncertainty from the experimental value (±0.35 kcal/mol) to ±0.20 kcal/mol. By use of the enthalpy of formation of **5** and its enthalpy of hydration, ΔH_f of 3-methyl-3-pentanol was found to be −96.78 ± 0.36 kcal/mol. Again, no other experimental data are available for this alcohol.

Having these data, we are now in a position to examine them to see what trends may be found. With **1** and **2**, and with **3** and **4**, the difference in enthalpy of formation in the liquid phase was the same within experimental error, 1.84 kcal/mol. The same difference was found between **5** and **6**, but the difference between **5** and **7** was slightly smaller (1.65 kcal/mol). The 1.84 kcal/mol difference may be taken as the base for comparing the exo/endo energy differences for cyclic compounds (liquid phase) such as the following:[3]



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ΔH = −0.54 kcal/mol

ΔH = −3.65 kcal/mol

ΔH = −1.97 kcal/mol

It can be seen that the enthalpy difference for the cyclohexane derivatives is very close to that for the acyclic cases. The larger difference found with the cyclopentane derivatives is expected since methylenecyclopentane will have a larger number of eclipsing interactions than methylcyclopentene, and for this reason is destabilized. The literature value for the difference in enthalpy between the cyclobutane derivatives (−0.94 kcal/mol)[9] was determined by hydrogenation in acetic acid solution and was not corrected for the differences in heats of solution. It therefore appeared desirable to obtain new data for these compounds.

It was not possible to obtain consistent results for the trifluoroacetolysis of the alkenes **11** and **12**. However, they were readily equilibrated in the presence of sodium on alumina.[10] The equilibrium constants obtained at several temperatures are given in Table IV. The enthalpy difference thus obtained was −535 ± 24 cal/mol. The smaller difference as compared to cyclohexyl is expected since the introduction of a trigonal center into a cyclobutane ring raises its strain energy by about 1 kcal/mol.[11]

We were interested in examining the difference in energy between tertiary alcohol and the corresponding alkanes having a methyl group in the place of the hydroxy group. The data are presented in Table V. The enthalpies of vaporization of **9** and **10** have not been reported, and therefore we have measured the change in vapor pressure with temperature using an ebulliometer and have calculated these quantities. The average difference between alcohols and alkanes in the gas phase was 35.3 ± 0.7 kcal/mol, which is considerably larger than for the primary and secondary alcohols.

Finally, this study provides an opportunity to compare the experimental results with the predictions of molecular mechanics. The energies of the compounds were calculated using MM3[12] and are summarized in Table VI. With most of the compounds, the deviation from the experimental values was on the order of only 0.5 kcal/mol, which may

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Table V. Comparison of Alcohols and Hydrocarbons (kcal/mol)

compd	$\Delta H_f(1)$	ΔH_v	$\Delta H_f(g)$	ΔHf(alkane)	$\Delta\Delta H_f$
2-methyl-2-propanol	−85.86 ± 0.20	11.14 ± 0.02	−74.72 ± 0.21	−40.12 ± 0.18	34.6 ± 0.3
2-methyl-2-butanol	−90.70 ± 0.13	11.63 ± 0.30	−79.07 ± 0.35	−44.48 ± 0.23	34.6 ± 0.4
2,3-dimethyl-2-butanol	−98.23 ± 0.36	12.91 ± 0.20	−85.32 ± 0.41	−48.47 ± 0.31	36.9 ± 0.5
3-methyl-3-pentanol	−96.78 ± 0.21	13.54 ± 0.20	−83.24 ± 0.29	−48.08 ± 0.27	35.2 ± 0.4

Table VI. Comparison with Molecular Mechanics Calculations (kcal/mol)

	MM3					
compd	ΔH_f^a	POP	TORS	ΔH_f^b	obsd (g)[c] ΔH_f	$\Delta\Delta H_f$
2-methyl-1-butene	−8.94	0.08	0.42	−8.44	−8.39	0.05
2-methyl-2-butene	−10.05	0.00	0.00	−10.05	−9.92	0.08
2,3-dimethyl-1-butene	−16.56	0.11	0.42	−16.03	−15.74	0.29
2,3-dimethyl-2-butene	−16.90	0.00	0.00	−16.90	−16.80	0.10
2-ethyl-1-butene	−13.85	0.26	0.84	−12.83	−13.40	−0.57
trans-3-methyl-2-pentene	−15.03	0.09	0.42	−14.52	−15.18	−0.66
cis-3-methyl-2-pentene	−15.11	0.00	0.42	−14.69	−14.79	−0.10
2-methyl-2-propanol	−74.86	0.00	0.00	−74.86	−74.72	0.14
2-methyl-2-butanol	−79.01	0.22	0.42	−78.37	−79.07	−0.70
2,3-dimethyl-2-butanol	−83.89	0.26	0.42	−83.21	−85.32	−2.11
3-methyl-3-pentanol	−82.96	0.26	0.84	−81.86	−83.24	−1.38
2,2-dimethylpropane	−41.06	0.00	0.00	−41.06	−40.12	0.94
2,2-dimethylbutane	−44.61	0.00	0.42	−44.19	−44.48	−0.29
2,2,3-trimethylbutane	−48.35	0.00	0.00	−48.35	−48.87	−0.52
3-methylpentane	−41.61	0.23	0.84	−40.55	−41.13	−0.58

[a] Energy of the more stable conformer. [b] Energy corrected for the higher energy conformers (POP) and for the torsional correction (TORS). [c] This work and ref 4.

Table VII. Vapor Pressure as a Function of Temperature for 2,3-Dimethyl-2-butanol

T (K)	p (obsd)	p (cald)	T (K)	p (obsd)	p (cald)
339.835	99.00	98.90	322.320	38.60	38.52
339.025	95.10	94.99	320.920	35.50	35.48
337.980	90.00	90.14	319.355	32.30	32.32
335.280	78.50	78.53	318.290	30.30	30.31
336.960	73.20	73.31	317.110	28.20	28.21
333.220	70.40	70.52	314.440	23.90	23.90
331.140	63.00	63.13	313.640	22.70	22.73
329.330	57.30	57.23	312.480	21.10	21.11
328.020	53.20	53.25	309.960	18.00	17.93
327.185	50.90	50.84	307.865	15.60	15.61
325.540	46.50	46.35	305.730	13.50	13.52
324.550	43.80	43.81	303.540	11.50	11.63
323.540	41.40	41.34			

Table VIII. Enthalpies of Vaporization (kcal/mol)

compd	A	B	C	std dev (mm)	ΔH_v (298 K)
2-pentanol	−8065.04	33.9267	−0.017017	0.08	13.02
2,3-dimethyl-2-butanol	−9094.62	41.2754	−0.029189	0.08	12.91
3-methyl-3-pentanol	−10273.9	47.8667	−0.038912	0.08	13.54

be considered as quite satisfactory. In a few cases, somewhat larger deviations were found.

Experimental Section

Materials. Trifluoroacetic acid and trifluoroacetic anhydride were obtained from Aldrich. All of the alkenes and 2-methyl-2-butanol were obtained from Wiley Organic. They were analyzed by GC using a 50-m capillary column of cross-linked methylsilicone on fused silica and found to have a purity greater than 99.9%. The one exception was 2,3-dimethyl-2-butene, which was 99.7% pure. 2,3-Dimethyl-2-butanol and 3-methyl-3-pentanol were obtained from Aldrich. They were distilled from calcium hydride, collecting a center fraction. Analysis by GC gave purities of 99.8% and 99.7%, respectively.

Calorimetric Measurements. The calorimetric studies were carried out using the automated reaction calorimeter previously described.[1-3] The calorimetric solvent consisted of 0.25 M trifluoroacetic anhydride in trifluoroacetic acid. All of the alkenes were found to react rapidly and quantitatively with this solvent. Unlike the less substituted alkenes, it was not necessary to add a strong acid catalyst for the alkenes in this study.

Equilibration of 1-Methylcyclobutene and Methylenecyclobutene. Sodium on alumina was prepared from 1 g of freshly activated alumina and 0.3 g of sodium at 140 °C (30 min).[9] Methylenecyclobutane[13] (2 g, purified by GC using 30% silver nitrate in ethylene glycol) was vacuum transferred to the flask containing the catalyst, and it was filled with nitrogen. The flask was placed in a thermostat, and the contents were stirred using a magnetic stirrer. The bath temperature was maintained ±0.02° and was measured using a Hewlett-Packard quartz thermometer. After the mixture was allowed to equilibrate for at least 8 h, a small sample was removed and analyzed via capillary GC. A second sample was removed 1 h later and analyzed. If it agreed with the first, the data were recorded.

Vapor Pressure Measurements. The vapor pressure of 2,3-dimethyl-2-butanol and of 3-methyl-3-pentanol was measured as a function of temperature using an ebulliometer. The pressure was measured using a Wallace and Tiernan absolute pressure gauge, and the temperature was measured using a Hewlett-Packard quartz thermometer. The experimental data for 2,3-dimethyl-2-butanol are summarized in Table VII. The data were fit to the equation

$$p = \exp(A/T + B + CT)$$

using a nonlinear least-squares procedure. The constants thus derived are given in Table VIII. The enthalpies of vaporization were then given by

$$\Delta H_v(298) = R(CT^2 - A)$$

A very conservative uncertainty of ±0.2 kcal/mol was assigned to the ΔH_v values.

Registry No. 1, 563-46-2; 2, 513-35-9; 3, 563-78-0; 4, 563-79-1; 5, 760-21-4; 6, 616-12-6; 7, 922-62-3; 8, 75-85-4; 9, 594-60-5; 10, 77-74-7; 11, 1120-56-5; 12, 1489-60-7; 2-methyl-2-propanol, 75-65-0; 2,2-dimethylpropane, 463-82-1; 2,2-dimethylbutane, 75-83-2; 2,2,3-trimethylbutane, 464-06-2; 3-methylpentane, 96-14-0.

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