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Thermochemical Studies of Carbonyl Compounds. 5. Enthalpies of Reduction of Carbonyl Groups

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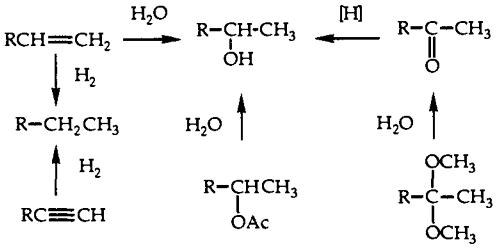
Abstract: The enthalpies of reduction of aldehydes and ketones to the corresponding alcohols have been determined by measuring the enthalpies of reaction of the carbonyl compounds and of the alcohols with lithium triethylborohydride in triglyme. The enthalpy of reduction of ethyl acetate to ethanol was determined in the same fashion. Enthalpies of formation of the carbonyl compounds were derived from the reduction data. The trends in the ΔH_f values for a series of aldehydes and of ketones were examined, and the ΔH_f values also were compared with the predictions derived with the MM3 molecular mechanics procedure.

One of the long-range goals of our calorimetric studies has been to relate the energies of various substituted compounds to the energies of the parent hydrocarbons. Such thermochemical relationships are important because in many cases the heat of formation of the hydrocarbon is known accurately but the heats of formation of the substituted compounds are imprecise, inaccurate, or completely unavailable. A better understanding of the energetic effects of introducing substituents may lead to improved predictive power via empirical relationships or via better parameterization of molecular mechanics procedures.

A key reaction in such a correlation is the reduction of carbonyl compounds. This type of reaction would allow the following to be related:



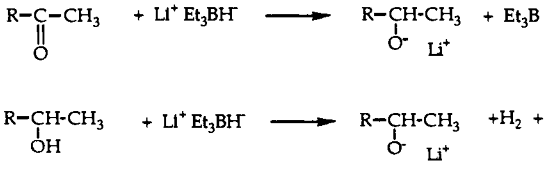
The hydrogenation of alkenes and of alkynes has been studied by Kistiakowsky,[1] Turner,[2] and others.[3] We have developed a procedure for measuring the enthalpy of hydration of alkenes,[4] and we have studied the enthalpies of hydrolysis of ketals,[5] acetals,[6] and orthoesters.[7] The enthalpies of hydrolysis of esters have been studied by Wadsö.[8] A method for measuring the enthalpies of reduction of the carbonyl groups would complete the series of reactions.

Kistiakowsky et al. determined the enthalpy of reduction of some aldehydes and ketones by gas-phase hydrogenation,[9] but this technique is not generally useful. Some information has been obtained via the measurement of the equilibrium constant for the reaction of the carbonyl compound with hydrogen as a function of temperature,[10,11] but such measurements require a very precise determination of the rate of change of the equilibrium constant with temperature and require extrapolation back to room temperature. The most generally useful procedure would appear to involve the measurement of the enthalpy of reaction of both the carbonyl compound and of its reduction products with a metal hydride. The difference between these enthalpies of reaction gives the enthalpy of reduction. The reaction could easily be carried out at room temperature and should be applicable to a wide range of carbonyl compounds.

Table I. Enthalpies of Reaction of Propanal and of 1-Propanol

mass (corr), g	sample, mmol	calib const, cal/K	ΔT, K	ΔH_r,[a] cal/mol
		Propanal		
0.052 991	0.912 38	86.719	0.300 26	−28 539
0.073 231	1.260 87	88.722	0.408 27	−28 729
0.044 495	0.766 10	88.494	0.248 50	−28 705
0.035 722	0.615 04	86.653	0.203 32	−28 646
		1-Propanol		
0.124 704	2.075 29	87.302	0.201 00	−8456
0.166 916	2.777 77	87.482	0.268 85	−8467
0.179 071	2.980 05	86.770	0.294 00	−8559
0.174 471	2.903 50	87.190	0.284 77	−8551

[a] Average ΔH_r for propanal is −28 655 ± 85, and average ΔH_r for 1-propanol is −8508 ± 54.



$$R-\underset{\underset{O}{\|}}{C}-CH_3 + Li^+ Et_3BH^- \longrightarrow R-\underset{O^-\ Li^+}{CH}-CH_3 + Et_3B$$

$$R-\underset{OH}{CH}-CH_3 + Li^+ Et_3BH^- \longrightarrow R-\underset{O^-\ Li^+}{CH}-CH_3 + H_2 + Et_3B$$

Davis carried out the first study of this type,[12] but it led to relative values rather than the enthalpies of reduction. In some unpublished work, Jackman carried out reductions with lithium aluminum hydride.[13] The requirements for a satisfactory calorimetric experiment are that the reaction is rapid and quantitative and that the products are well-defined. This led us to choose a reducing agent with a single hydride donor (lithium triethylborohydride). It can readily be prepared in pure form, and it will quickly reduce most types of carbonyl compounds. Independent experiments showed that the reaction proceeded quan-

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(1) Kistiakowsky, G. B.; Romeyn, H., Jr.; Ruhoff, J. R.; Smith, H. A.; Vaughan, W. E. *J. Am. Chem. Soc.* **1935**, *57*, 65. Conn, J. B.; Kistiakowsky, G., B.; Smith, E. A. *J. Am. Chem. Soc.* **1939**, *61*, 1868.

(2) Turner, R. B.; Meador, W. R.; Winkler, R. E. *J. Am. Chem. Soc.* **1957**, *79*, 4116. Turner, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 3586.

(3) Skinner, H. A.; Snelson, A. *Trans. Faraday Soc.* **1959**, *55*, 404. Rogers, D. W.; Dejroongruang, K. *J. Chem. Thermodyn.* **1988**, *20*, 675. Roth, W. R.; Lennartz, H. W. *Chem. Ber.* **1980**, *113*, 1806, 1813.

(4) Wiberg, K. B.; Wasserman, D. J. *J. Am. Chem. Soc.* **1981**, *103*, 6563. Wiberg, K. B.; Wasserman, D. J.; Martin, E. *J. Phys. Chem.* **1984**, *88*, 3684. Wiberg, K. B.; Wasserman, D. J.; Martin, E. J.; Murcko, M. A. *J. Am. Chem. Soc.* **1985**, *107*, 6019.

(5) Wiberg, K. B.; Squires, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5512. Wiberg, K. B.; Squires, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 4473. Wiberg, K. B.; Cunningham, W. C., Jr. *J. Org. Chem.* **1990**, *55*, 679.

(6) Wiberg, K. B.; Squires, R. R. *J. Chem. Thermodyn.* **1979**, *11*, 773.

(7) Wiberg, K. B.; Martin, E. J.; Squires, R. R. *J. Org. Chem.* **1985**, *50*, 4717.

(8) Wadsö, I, *Acta Chem. Scand.* **1958**, *12*, 630; **1960**, *14*, 561; **1962**, *16*, 487.

(9) Dolliver, M. A.; Gresham, T. L.; Kistiakowsky, G. B.; Smith, E. A.; Vaughan, W. E. *J. Am. Chem. Soc.* **1938**, *60*, 440.

(10) Buckley, E.; Cox, J. D. *Trans. Faraday Soc.* **1967**, *63*, 895. Buckley, E.; Herington, E. F. G. *Trans. Faraday Soc.* **1956**, *61*, 3615.

(11) Connett, J. E. *J. Chem. Thermodyn.* **1972**, *4*, 135; **1975**, *7*, 1159.

(12) Davis, R. E.; Carter, J. *Tetrahedron* **1966**, *22*, 495.

(13) Jackman, L. M. Private communication. Cf. Jackman, L. M.; Packham, D. I. *Proc. Chem. Soc., London* **1957**, 349.

0002-7863/91/1513-3447$02.50/0

Table II. Enthalpies of Reaction of Acetone and of 2-Propanol

mass (corr), g	sample, mmol	calib const, cal/K	ΔT, K	ΔH_r,[a] cal/K
		Acetone		
0.045 378	0.781 30	86.410	0.211 11	−23 348
0.044 383	0.764 18	84.537	0.212 22	−23 473
0.047 667	0.820 71	84.172	0.228 70	−23 456
0.058 806	1.012 51	87.040	0.273 53	−23 515
0.075 582	1.301 34	90.582	0.340 70	−23 714
0.058 610	1.009 13	89.096	0.265 96	−23 485
0.072 746	1.252 51	92.230	0.322 02	−23 713
0.079 167	1.363 07	92.618	0.347 55	−23 615
		2-Propanol		
0.199 742	3.323 49	86.458	0.275 76	−7175
0.187 008	3.111 62	86.745	0.256 81	−7160
0.169 779	2.824 94	85.448	0.235 99	−7138
0.127 109	2.114 95	88.227	0.171 22	−7142
0.169 674	2.823 19	90.543	0.220 12	−7060
0.153 618	2.559 87	88.905	0.202 55	−7034
0.186 470	3.102 66	92.690	0.236 05	−7050

[a] Average ΔH_r for acetone is −23 540 ± 92, and average ΔH_r for 2-propanol is −7108 ± 44.

titatively. Triglyme was chosen as the solvent since it was both inert and high boiling. The latter was desired since hydrogen is formed as a product in the reaction of the alcohols, and if the vapor pressure were significant, correction would be needed for the enthalpy of vaporization of the solvent caused by the evolved hydrogen. The other product of the reaction (triethylborane) will remain in solution complexed with the ether solvent.

Two cases were chosen for the initial study, an aldehyde (propanal) and a ketone (acetone). The experimental data for the reaction of propanal and of 1-propanol with lithium triethylborohydride are given in Table I. Both reactions proceeded rapidly and gave good precision. The results of the reactions of acetone and of isopropyl alcohol with the reducing agent are shown in Table II. Here, the reactions were carried out with the use of several different batches of reducing agent and solvent, with different relative amounts of the reagents, and were carried out at different times by two different investigators. The constancy of the values strongly suggest that the procedure is satisfactory and can be relied on to give satisfactory enthalpies of reduction.

The observed enthalpies of reaction for a series of carbonyl compounds are summarized in Table III and lead to the enthalpies of reduction, which are given in Table IV. The enthalpy of fusion of cyclooctanone was determined, allowing the calculation of all of the enthalpies of reaction in the liquid phase. The enthalpies of vaporization of the carbonyl compounds and the corresponding alcohols are quite different; therefore, it is of more interest to examine the data for the gas phase. The enthalpies of vaporization are available for the compounds in this study.[14] The gas-phase ΔH_{red}'s thus obtained are given in the second column of Table IV. The table also provides comparisons with values obtained via other methods. Procedure A is gas-phase hydrogenation, procedures B and C refer to equilibration experiments, and procedure D is oxygen bomb calorimetry.

It can be seen that there is considerable variation in reduction enthalpies for a given compound. With propanal, for example, the previous values range from −15.1 to −16.6 kcal/mol. Our values are frequently somewhat less negative than those previously reported. The procedure that potentially should lead to the best values is gas-phase hydrogenation as reported by Kistiakowsky et al.[9] In the case of alkene hydrogenation, their values have generally stood the test of time. However, there is one potential source of error in their reduction of carbonyl compounds. If any dehydration of the product alcohol occurred on the catalyst at the elevated temperature (84 °C), the alkene would also be reduced and the observed heat of reaction would be too exothermic. Their values are uniformly more negative than ours, and they did not have any way in which to determine whether or not any dehydration occurred. It might be noted that, with cyclopentanone and cyclohexanone, the combustion data also give considerably less negative enthalpies of reduction than those from the gas-phase hydrogenation.

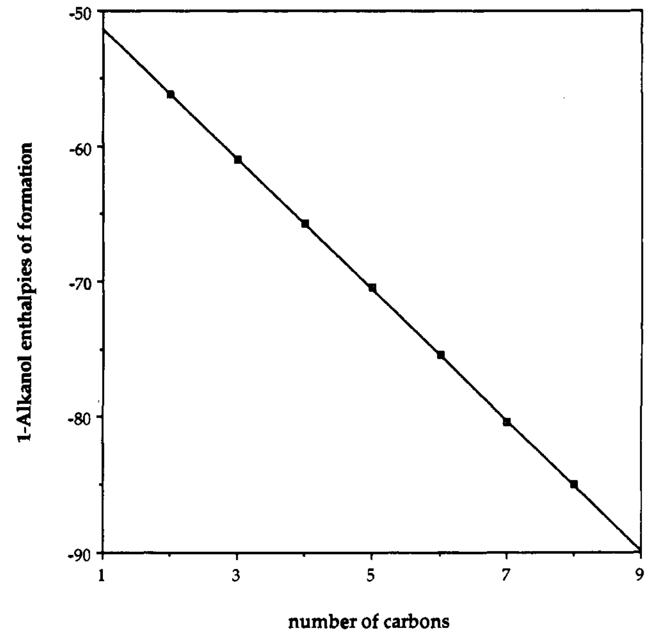

Figure 1. Relationship between enthalpies of formation and the number of carbons for the 1-alkanols.

Except for butanal, our results are in reasonably good agreement with the equilibration experiments. It would have been interesting to obtain the enthalpy changes for these experiments from the ΔG at some temperature and the entropy change. However, for these molecules with internal rotors, it is difficult to calculate the entropy change. The enthalpy of reduction of ethyl acetate appears to represent one of the best established data derived from enthalpies of combustion, and here our value is in quite good agreement. While we cannot unambiguously demonstrate that our data are more satisfactory than those reported previously, we do have the largest set of data obtained using a single experimental technique, which appears to be free of some of the problems that may be associated with the other methods. Therefore, we shall see what conclusions may be derived from our data.

The enthalpies of formation of the alcohols are generally better determined than those of the carbonyl compounds. In the case of the 1-alkanols, for example, there is a very good linear relationship between the enthalpies of formation and the number of carbons (Figure 1), just as there is for the alkanes. In the case of cyclopentanol, the ΔH_f derived via combustion is in very good agreement with that obtained via the measurement of the enthalpy of hydration of cyclopentene. The latter measurement for cyclohexene gave a ΔH_f that was quite different than that obtained via combustion. The combustion value had a fairly large standard deviation; therefore, we have used the value derived via hydration. We have used the alcohol data and our reduction enthalpies to calculate enthalpies of formation of the carbonyl compounds, giving the results shown in Table V. Again, a comparison is given with previously reported data.

Very good agreement between our values and the literature values was found with 2-methylpropanal, acetone, and ethyl acetate. In the other cases, the differences were found to range from 0.7 to 1.7 kcal/mol. In this group, the previous determinations of the enthalpy of formation of cyclohexanone cover a considerable range and the same is true for cyclopentanone. Our values are in reasonable agreement with the most recent measurements via oxygen bomb calorimetry.[15] We have previously suggested that the literature value for the enthalpy of formation

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(14) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

(15) Wolf, G. *Helvetica* **1972**, *55*, 1446.

Table III. Enthalpies of Reaction with 0.0355 M Lithium Triethylborohydride in Triglyme (25 °C)

compd	no. of runs	ΔH_r, kcal/mol	compd	no. of runs	ΔH_r, kcal/mol
acetaldehyde(l)	5	−28.16 ± 0.36	ethanol(l)	5	−8.72 ± 0.08
propanal(l)	4	−28.65 ± 0.08	2-propanol(l)	7	−7.11 ± 0.04
butanal(l)	7	−27.91 ± 0.18	1-propanol(l)	4	−8.51 ± 0.05
2-methylpropanal(l)	4	−28.66 ± 0.08	1-butanol(l)	9	−8.34 ± 0.04
acetone(l)	8	−23.54 ± 0.09	2-methyl-1-propanol(l)	4	−7.78 ± 0.03
cyclobutanone(l)	7	−25.08 ± 0.16	cyclobutanol(l)	4	−8.85 ± 0.09
cyclopentanone(l)	5	−21.79 ± 0.12	cyclopentanol(l)	4	−7.39 ± 0.10
cyclohexanone(l)	4	−24.77 ± 0.06	cyclohexanol(l)	8	−6.64 ± 0.11
cycloheptanone(l)	4	−21.19 ± 0.09	cycloheptanol(l)	4	−6.25 ± 0.03
cyclooctanone(c)	4	−18.71 ± 0.08	cyyclooctanol(l)	4	−6.01 ± 0.12
cyclooctanone(l)		−19.32 ± 0.08[a]	ethyl acetate(l)	5	−35.36 ± 0.06

[a] Enthalpy of fusion of cyclooctanone 0.61 ± 0.01 kcal/mol.

Table IV. Enthalpies of Reduction

			lit. $\Delta H_{red}(g)$[a]			
compd	ΔH_{red}(l or c)	ΔH_{red}(g)	A	B	C	D
acetaldehyde(l)	−19.44 ± 0.34	−15.41 ± 0.34	−16.51 ± 0.10			
propanal(l)	−20.14 ± 0.09	−15.89 ± 0.14		−15.72 ± 0.16	−16.62 ± 0.18	−15.12 ± 0.30
butanal(l)	−19.57 ± 0.18	−15.12 ± 0.12		−16.85 ± 0.30		−16.57 ± 0.52
2-methylpropanal(l)	−20.88 ± 0.08	−16.27 ± 0.31			−16.27 ± 0.21	−15.59 ± 0.41
acetone(l)	−16.43 ± 0.10	−12.96 ± 0.11	−13.24 ± 0.10	−13.20 ± 0.10		−13.34 ± 0.24
cyclobutanone(l)	−16.23 ± 0.18	−12.73 ± 0.3				
cyclopentanone(l)	−14.40 ± 0.16	−10.87 ± 0.18	−12.25 ± 0.15			−11.63 ± 0.62
cyclohexanone(l)	−18.13 ± 0.12	−14.08 ± 0.15	−15.18 ± 0.15			−14.36 ± 0.72
cycloheptanone(l)	−14.94 ± 0.09	−10.94 ± 0.3				
cyclooctanone(c)	−12.70 ± 0.14					
cyclooctanone(l)	−13.32 ± 0.14	−9.31 ± 0.3				
ethyl acetate(l)	−17.92 ± 0.13	−5.96 ± 0.15				−6.44 ± 0.16

[a] Key: A, hydrogenation (ref 1); B, equilibrium (ref 10); C, equilibrium (ref 11); D, combustion (ref 14).

Table V. Enthalpies of Formation of Carbonyl Compounds (kcal/mol)

compd	ΔH_{red}(l)	product (ΔH_f(l))	ΔH_f(l)	ΔH_v[a]	ΔH_f(g)[c]	lit.[a]
acetaldehyde	−19.44 ± 0.34	EtOH (−66.39 ± 0.10)[a]	−46.95 ± 0.35	6.15 ± 0.03	−40.80 ± 0.35	−39.70 ± 0.12
propanal	−20.14 ± 0.09	1-PrOH (−72.32 ± 0.12)[a]	−52.18 ± 0.15	7.09 ± 0.10	−45.09 ± 0.18	−44.36 ± 0.21
butanal	−19.57 ± 0.18	1-BuOH (−78.23 ± 0.10)[a]	−58.66 ± 0.20	8.05 ± 0.10	−50.61 ± 0.22	−48.95 ± 0.33
2-methylpropanal	−20.88 ± 0.08	*i*-BuOH (−79.99 ± 0.21)[a]	−59.11 ± 0.22	7.54 ± 0.30	−51.57 ± 0.37	−51.58 ± 0.21
acetone	−16.43 ± 0.10	2-PrOH (−76.03 ± 0.12)[a]	−59.60 ± 0.15	7.37 ± 0.01	−52.23 ± 0.14	−51.94 ± 0.17
cyclopentanone	−14.40 ± 0.16	c-C_5H_9OH (−71.80 ± 0.25)[b]	−57.40 ± 0.30	10.21 ± 0.05	−47.19 ± 0.30	−46.55 ± 0.41[d]
cyclohexanone	−18.13 ± 0.12	c-$C_6H_{11}OH$ (−84.13 ± 0.16)[b]	−66.00 ± 0.20	10.77 ± 0.05	−55.23 ± 0.21	−54.43 ± 0.45[d]
ethyl acetate	−17.92 ± 0.13	2 EtOH (−66.39 ± 0.10)[a]	−114.86 ± 0.19	8.40 ± 0.05	−106.46 ± 0.20	−106.14 ± 0.14

[a] Reference 14. [b] Reference 4. [c] This work. [d] Wolf, G. *Helvitica* **1972**, *55*, 1446.

Table VI. Comparison of Enthalpies of Reduction of Carbonyl Compounds and Alkenes[a]

carbonyl compd	ΔH_{red}	alkene	ΔH_{red}
formaldehyde	−22.1 ± 0.2	ethene	−32.6 ± 0.1
acetaldehyde	−15.4 ± 0.3	1-propene	−29.9 ± 0.1
propanal	−15.9 ± 0.1	1-butene	−30.1 ± 0.1
butanal	−15.1 ± 0.2	1-pentene	−30.0 ± 0.3
2-methylpropanal	−16.3 ± 0.3	3-methyl-1-butene	−30.2 ± 0.1
acetone	−13.0 ± 0.1	isobutene	−28.2 ± 0.1
2-butanone	−12.9 ± 0.3	2-methyl-1-butene	−28.3 ± 0.1
3-methyl-2-butanone	−12.6 ± 0.4	2,3-dimethyl-1-butene	−27.8 ± 0.1
2-pentanone	−12.8 ± 0.5	2-methyl-1-pentene	−27.6 ± 0.4
cyclopentanone	−10.9 ± 0.2	methylenecyclopentane	−28.3 ± 0.3

[a] The data were taken from this work and ref 14.

of butanal is in error.[16] These considerations lead us to conclude that our derived heats of formation are the more satisfactory of those currently available.

We were interested in comparing the enthalpies of formation of the aldehydes and ketones with those of the corresponding alkenes in which O has been replaced by CH_2. The data are summarized in Table VI and are shown in Figure 2. The circles are drawn to correspond to an uncertainty of 0.2 kcal/mol. A fairly satisfactory linear relationship was found with a slope of 1.9, showing that the carbonyl compounds are more sensitive to substituents than are the alkenes. This is in accord with the observation that, whereas the difference in enthalpy of formation between isobutene and 1-butene is −4.1 ± 0.3 kcal/mol, that between acetone and propanal is −7.1 ± 0.2 kcal/mol.[14] It is not

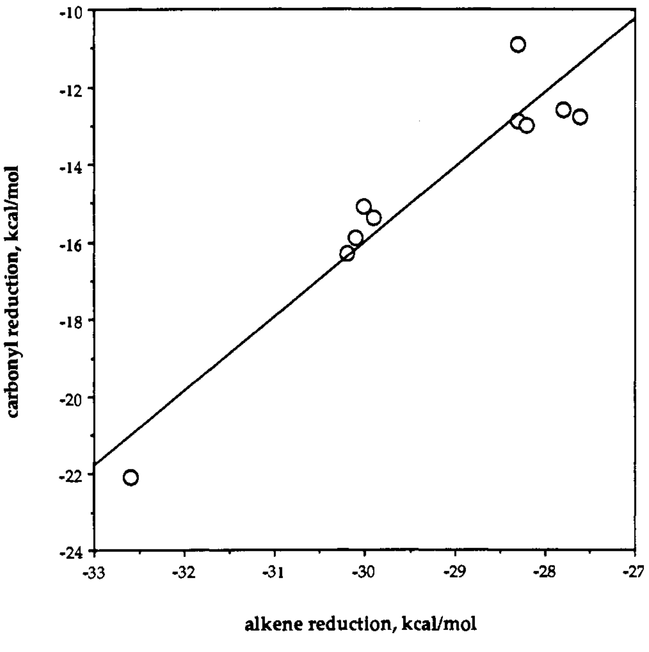

Figure 2. Relationship between the enthalpies of reduction of carbonyl compounds and of the corresponding alkenes.

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(16) Wiberg, K. B. *J. Am. Chem. Soc.* **1986**, *108*, 5817.

Table VII. Comparison of Present Data with MM3 Predictions

compd	ΔH_f obs	ΔH_f MM3	ΔH_{red} obs	ΔH_{red} MM3
acetaldehyde	−40.8	−39.9	−15.4	−16.2
ethanol	−56.2	−56.1		
propanal	−45.1	−44.7	−15.9	−16.3
1-propanol	−61.0	−61.0		
butanal	−50.6	−49.6	−15.1	−16.3
1-butanol	−65.7	−65.9		
2-methylpropanal	−51.6	−52.1	−16.3	−15.5
2-methyl-1-propanol	−67.9	−67.6		
acetone	−52.2	−51.7	−13.0	−13.6
2-propanol	−65.2	−65.3		
cyclobutanone		−21.0[a]	−12.7	−13.9
cyclobutanol		−34.9[a]		
cyclopentanone	−47.2	−45.9	−10.9	−12.5
cyclopentanol	−58.1	−58.4		
cyclohexanone	−55.2	−54.5	−14.1	−15.2
cyclohexanol	−69.3	−69.7		
cycloheptanone	−59.3[b]	−55.1	−10.9	−12.4
cycloheptanol		−67.5		
cyclooctanone	−65.1[b]	−58.0	−9.3	−10.8
cyclooctanol		−68.8		
ethyl acetate	−106.5	−110.0	−6.0	−2.2

[a] MM2 values. For the cyclobutane derivatives, some of the MM3 parameters are not established. [b] These literature values (ref 15) would imply almost unstrained rings and may not be correct.

surprising that alkyl groups stabilize carbonyl to a greater extent than carbon–carbon double bonds because of the strong charge polarization in the carbonyl group leading to an electron deficient carbon.

One of the objects of our study was to see how well currently available procedures for molecular modeling could predict the enthalpies of formation of carbonyl compounds. The MM3 procedure[17] was applied to each of the compounds in this study, giving the results in Table VII. The predicted enthalpies of reduction were in most cases approximately 1 kcal/mol more exothermic than the observed values. This appears to result largely from the estimate of the energies of the carbonyl compounds. A small adjustment in the parameter used for the carbonyl group in converting steric energies to enthalpies of formation would make the agreement between experimental and prediction quite satisfactory.

Experimental Section

Lithium Triethylborohydride. The procedure was based on that reported by Brown et. al.[18] A double Schlenk flask of 600-mL total capacity fitted with a coarse fritted-glass filter was heated in an oven (190 °C), cooled under reduced pressure, and filled with argon. To one side was added 5.5 g (0.7 mol) of lithium hydride, a magnetic stirrer, and 100 mL of diethyl ether freshly distilled from benzophenone ketyl. The mixture was stirred at 0 °C, and 35 mL (0.26 mol) of triethylborane was added over a 15-min period. The flask was fitted with an oven-dried reflux condenser. The mixture was stirred at 0 °C for 1 h and then gradually warmed to room temperature. An exothermic reaction occurred, and the mixture refluxed gently. After it was stirred at room temperature overnight, the solution containing the product was decanted through the glass filter and the solvent was removed under reduced pressure. Approximately 10 mL of benzene was distilled onto the white paste, and with gentle warming the product dissolved completely. When the solution cooled to room temperature, crystals of the product formed. The benzene was decanted from the crystals and was removed under reduced pressure. The crystals were removed in an argon-filled glovebox, giving 18.3 g (67%) of the product.

Compounds. All of the compounds were commercial samples and, except for cyclooctanone, they were dried and distilled, collecting a center fraction. Sample homogeneity was tested with a Hewlett-Packard gas chromatograph with a 50 m × 0.25 mm OV-101 capillary column and a flame ionization detector. The compounds had a minimum purity of 99.6%, and in most cases it was 99.9%. In the case of cyclooctanone, purification was carried out with use of zone refining, giving a product with 99.9% purity. All transfers were made either in a drybox or via a vacuum line in order to avoid contamination of the samples by water.

The solvent (bis(methoxyethoxy)ethane (triglyme)) was purified by distillation. Just prior to the start of a calorimetric experiment, it was passed through freshly ignited alumina directly into the reaction vessel.

Calorimetric Experiment. The reactivity of the reducing agent made it necessary to carry out the experiments with exclusion of air and moisture. A modified calorimetric vessel and head were constructed that allowed a sealed system to be used.[19] The experiment was carried out with the automated calorimetric system previously described.[20]

Acknowledgment. This investigation was supported by the Office of Basic Energy Sciences, Department of Energy.

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(17) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551.

(18) Brown, H. C.; Khuri, A.; Kim, S. C. *Inorg. Chem.* **1977**, *16*, 2229.

(19) The details of the calorimetric vessel may be found in Crocker, L. S. Ph.D. Thesis, Yale, 1989.

(20) Wiberg, K. B.; Squires, R. R. *J. Chem. Thermodyn.* **1979**, *11*, 773.