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HEATS OF REDUCTION OF KETONES WITH SODIUM BOROHYDRIDE[1]

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Abstract—The heats of reduction of four ketones with $NaBH_4$ in 0·1000M NaOHaq have been measured at 25·00°.

$$4R_2CO + BH_4^- + 4H_2O \rightarrow 4R_2CHOH + B(OH)_4^-$$

The ΔH values expressed in kcal/mole of borohydride ion at 25°, are $-128{\cdot}17 \pm 0{\cdot}52$ for acetone; $-129{\cdot}20 \pm 0{\cdot}71$ for methyl isopropyl ketone; $-126{\cdot}04 \pm 0{\cdot}19$ for cyclopentanone and $-129{\cdot}70 \pm 0{\cdot}31$ for cyclohexanone. The rates of heat production have been obtained and the second order rate constants calculated.

$$r = k[R_2CO][BH_4^-]$$

The specific rate constants at 25° are $2{\cdot}48 \pm 0{\cdot}07 \times 10^{-2}$ M^{-1} sec^{-1} for acetone; $2{\cdot}14 \pm 0{\cdot}08 \times 10^{-2}$ M^{-1} sec^{-1} for methyl isopropyl ketone and $0{\cdot}96 \pm 0{\cdot}04 \times 10^{-2}$ M^{-1} sec^{-1} for cyclopentanone.

The data are compared with thermochemical results obtained by gas phase hydrogenation and by heats of combustion of the pure liquids reported in the literature. The effect of the aqueous medium is to reduce the amount of enthalpy difference between these ketones compared to the gas phase.

The rate data have been compared with the data obtained in isopropyl alcohol as solvent. In water the rate constants are much faster and the relative rate difference between the ketones is decreased.

INTRODUCTION

Sodium borohydride is a powerful reducing agent[3] having high stability in aqueous solution[4–7] above pH 12. In particular borohydride reduces ketones to the corresponding alcohol:

$$4R_2CO + BH_4^- + 4H_2O \rightarrow 4R_2CHOH + B(OH)_4^- \quad (1)$$

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[1] Paper XI, Boron Hydrides; Paper X. R. E. Davis and J. A. Gottbrath, *Inorganic Chem.* in press.

[2] *a.* Alfred P. Sloan Fellow, 1962–1966.
b. Taken in part from the M. S. Thesis, January 1965.

[3] The half-cell electrode potential, E°, is 1·24 volts [W. H. Stockmayer, D. W. Rice and C. C. Stephenson, *J. Amer. Chem. Soc.* **77**, 1980 (1955)].

[4] R. L. Pecsok, *J. Amer. Chem. Soc.* **75**, 2862 (1953).

[5] T. Freund, *J. Inorg. and Nuclear Chem.* **9**, 246 (1959).

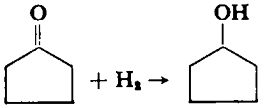
[6] R. E. Davis and C. G. Swain, *J. Amer. Chem. Soc.* **82**, 5949 (1960); Paper I.

[7] R. E. Davis, E. Bromels and C. L. Kibby, *J. Amer. Chem. Soc.* **84**, 885 (1962); Paper III.

If the ketone is in large excess and if the solution is basic no hydrogen gas is formed by hydrolysis of the boron hydride intermediates.[8]

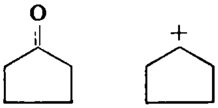
Thus one has a system which can give satisfactory thermochemical measurements that can be used to correlate structure on the energetics of ketones and the corresponding alcohols.

Kistiakowsky[9] has measured the heats of hydrogenation in the gas phase while Seller and Sunner[10] have measured the heats of combustion of some ketones and their alcohols (Table 1). Thus the heat of reduction of a typical ketone such as cyclopentanone is known and the ΔH of reaction (2) can be estimated in several different methods.



(2)

The present research has been performed in aqueous solution since the synthetic organic chemist seldom performs homogeneous gas phase reactions. In particular the data on the ketones are of interest since the ketone has been used as a model for



the corresponding secondary carbonium ion. The energetics of reactions of the ketone might correlate with the energetics of the carbonium ion reactions.

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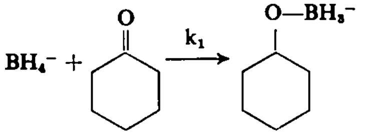
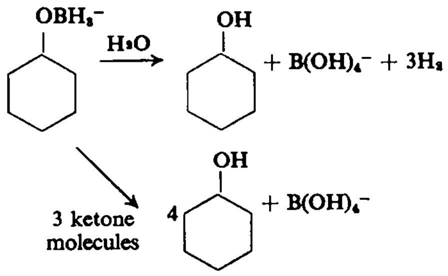
[8] In an earlier paper [R. E. Davis and J. A. Gottbrath, *J. Amer. Chem. Soc.* **84**, 895 (1962)] experimental results were reported of the reduction of mmolar solutions of borohydride with mmolar solutions of ketone. The first reduction step



produces the postulated mono-alkoxy borohydride. But since the ketone concentration was low the greater majority hydrolyzed to produce three moles of hydrogen gas.



rather than reduce the remaining ketone.

[9] J. B. Conn, G. B. Kistiakowsky and E. A. Smith, *J. Amer. Chem. Soc.* **61**, 1868 (1939); summary paper.

[10] P. Seller and S. Sunner, *Acta Chem. Scand.* **16**, 46 (1962). Refs. to the earlier heats of combustion measurement are reviewed in this paper.

TABLE 1. THERMOCHEMICAL DATA HEATS OF HYDROGENATION AT 25°

Ketone	ΔH kcal/mole of Ketone	
Acetone		−13·29[a]
Methyl ethyl ketone		−13·07[a]
Cyclopentanone	−11·32[b]	−12·26[a]
Cyclohexanone	−14·32[b]	−15·23[a]

[a] Data of Kistiakowsky[9] corrected from 82° to 25° by Sellers and Sunner.[10]

[b] Data of Sellers and Sunner.[10]

TABLE 2. EXPERIMENTAL DATA

Acetone	ketone M	Recorder units	Calibration seconds	Recorder units	Coulometer calories	−ΔH kcal/mole
	1·3613	62·90	100·17	71·00	68·82	128·59
	1·230	69·00	100·09	71·00	68·76	127·71
	1·080	91·00	149·0	104·6	102·36	128·79
	1·141	94·01	210·05	146·0	144·30	127·61
					average[a]	128·17
Methyl Isopropyl Ketone					σ	0·52[b]
	0·3250	76·7	133·2	89·2	91·51	129·22
	0·3971	139·8	201·1	137·8	138·15	128·51
	0·3390	75·0	150·9	102·3	103·67	129·87
					average	129·20
Cyclopentanone					σ	0·71
	0·2140	42·0	160·35	112·8	110·16	126·13
	0·1422	64·5	160·20	112·2	110·06	126·12
	0·2464	50·5	170·85	120·4	117·37	126·16
	0·2182	42·5	159·85	109·3	109·82	125·74
					average	126·04
Cyclohexanone					σ	0·19
	0·2696	66·5	119·30	83·8	81·96	129·96
	0·2923	101·2	143·10	99·0	98·31	129·83
	0·2684	88·0	153·17	106·5	105·23[c]	129·61
	0·2252	97·0	144·67	99·3	99·4	129·4
					average	129·70
					σ	0·31

[a] Mean

[b] Value of the estimated standard deviation computed from the Range and the single classification factor for one equivalent degree of freedom using the method of L. H. C. Tippett, *Biometrika* **17**, 364 (1925) and the Tables of E. S. Pearson and H. A. David, *Ibid.* **38**, 393 (1951).

[c] Sample calculation $\frac{105{\cdot}23\ \text{cal.}}{106{\cdot}50\ \text{units}} \times \frac{88{\cdot}00\ \text{units}}{0{\cdot}67091 \times 10^{-3}\ \text{moles}} = 129{\cdot}6_1 \times 10^3$ cal/mole of $NaBH_4$.

RESULTS

Enthalpies of reduction. Acetone is rapidly reduced to isopropanol by borohydride ion in dilute base. The concentration of acetone was varied from 1·08 to 1·51M while the sodium borohydride concentration was varied from 1·9 × 10^{-3}M to 4·0 × 10^{-3}M. The mean value of ΔH at 25° was −128·17 ± 0·52 kcal/mole of borohydride. The data are reported in Table 2. A graph of the time-temperature curve for a solution containing 1·05M acetone in 0·1M sodium hydroxide after a sample bulb of 27·53 mg

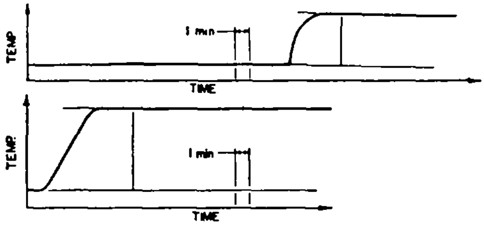


Fig. 1. Experimental Data for Run 34. The reduction of 1·05M acetone in 0·1M base with 27·530 mg $NaBH_4$ at 25·00 ± 0·002°. The calibration curve is also shown.

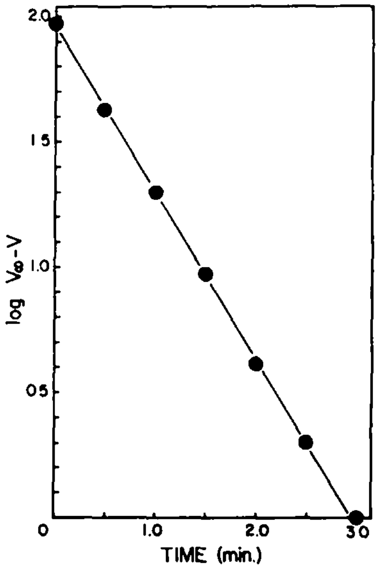


Fig. 2. Rate of heat production of the data from Fig. 1 for acetone with $NaBH_4$.

of sodium borohydride has been crushed under the surface is shown in Fig. 1. The rate of heat production is described by a first order process (Fig. 2). The electrical calibration for this same experiment ≠ 34 is shown in the lower half of Fig. 1. The data are typical and give evidence to the general character and reliability of these experiments. Acetone was the first ketone studied and only one thermochemical experiment was rejected by the "Q test".

The ketones were dissolved in the dilute sodium hydroxide solutions and used quickly. Repeated experiments using solutions which had stood at 25° for different short times gave identical heats of reaction. Thus base-catalyzed condensation reactions are not a problem. Likewise the basic ketone solutions did not produce any temperature rise in the submarine calorimeter.

Methyl isopropyl ketone was reduced by borohydride at a somewhat slower rate than acetone, in keeping with the increased inductive effects of the alkyl groups and the somewhat larger spacial requirements of the isopropyl group compared to a methyl group. The $\underline{\Delta H}$ was $-129{\cdot}20 \pm 0{\cdot}71$ kcal/mole of borohydride.

Cyclopentanone has the slowest rate of reduction of the ketones studied in this investigation and its reduction time extends for over 60 minutes before more than ten half-times have expired. This is due in part to the limit of solubility of the ketone. Nevertheless the data of Table 2 have a mean standard deviation of only 0·2%. This ketone represents the practical lower limit of slowly reduced ketones that can be studied in our present equipment. This has frustrated the study of cycloheptanone (estimated to be slower by a factor of 5 from the cyclopentanone) and cycloöctanone (estimated to be slower by nearly 100). The problem is further complicated by the decreased aqueous solubility of these materials which reduces the molarity of the ketone and therefore of the pseudo first order rate constant. While isopropanol has served as a medium for borohydride reductions,[11] the thermochemistry is complicated by the transesterifaction equilibria that would exist in this solvent.

$$4R_2CO + BH_4^- \rightarrow (R_2CHO)_4B^- \tag{3}$$

$$(R_2CHO)_4B^- + xR'OH \rightleftharpoons (R_2CHO)_{4-x}(R'O)_xB^- + xR_2CHOH \tag{4}$$

It would be unlikely that all the transesterifaction equilibria as (4) would be isoenthalpic. In aqueous medium the borate eaters hydrolyse completely

$$(RO)_4B^- + 4H_2O \rightarrow (HO)_4B^- + 4ROH \tag{5}$$

and nearly instantaneously to produce borate anion and thus produce a comparable thermochemical standard state for all the ketones. The specific rate constants of reduction in isopropanol are also slower than in water (Table 3).

TABLE 3. RELATIVE RATES OF KETONE REDUCTION AT 25°

Ketone	Isopropyl alcohol Relative rate titration data	Water Thermochemical data
Acetone	1·00[a]	1·00[e]
Methyl isopropyl	0·431[b]	0·89[f]
Cyclopentanone	0·20[c]	0·40[g]
Cyclohexanone	7·1[d]	—[h]

Data of Ref. 11, (a)–(d).

[a] $k_2 = 63{\cdot}0 \times 10^{-4}\ M^{-1}$ at 25°.

[b] $k_2 = 14{\cdot}7 \times 10^{-4}\ M^{-1}sec^{-1}$ at 25°.

[c] $k_2 = 31{\cdot}8 \times 10^{-4}\ M^{-1}sec^{-1}$ at 25°.

[d] $k_2 = 450 \times 10^{-4}\ M^{-1}sec^{-1}$ extrapolated to 25°.

[e] $k_2 = 2{\cdot}30 \times 10^{-2}\ M^{-1}sec^{-1}$. Reported by W. H. Stockmayer, R. R. Miller and R. J. Zeto, *J. Phys. Chem.* **65**, 1076 (1961) by a titration method. Value by thermochemistry is $2{\cdot}48 \pm 0{\cdot}07 \times 10^{-2}\ M^{-1}\ sec^{-1}$.

[f] $k_2 = 2{\cdot}14 \pm 0{\cdot}08 \times 10^{-2}\ M^{-1}sec^{-1}$, this study.

[g] $k_2 = 0{\cdot}959 \pm 0{\cdot}041 \times 10^{-2}\ M^{-1}sec^{-1}$, this study.

[h] Rate constant observed depends upon the rate of heat transfer to the thermistor element in this ketone.

Cyclohexanone, a six membered ring containing a carbonyl function with an exo double bond is the most rapidly reduced ketone of Table 2 and also releases the largest amount of heat. The value of $\underline{\Delta H}$ is $-129{\cdot}70 \pm 0{\cdot}31$ kcal/mole of borohydride. Since the thermistor element is placed in a separate tube containing a small amount of silicone oil as a heat transfer liquid, there is a short time lag in the temperature recorder and the actual temperature of the solution. This only affects the observed

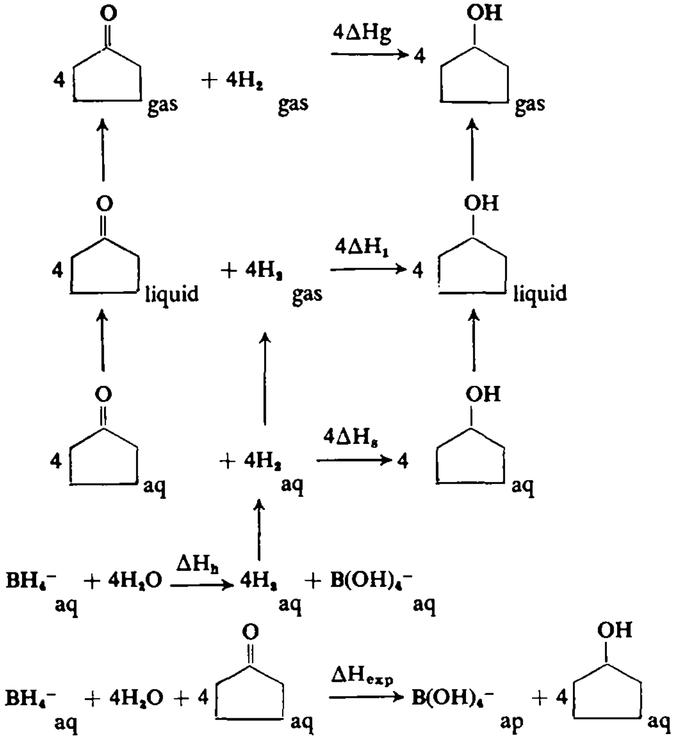
[1] H. C. Brown and K. Ichikawa, *Tetrahedron* **1**, 221 (1957); *J. Amer. Chem. Soc.* **84**, 373 (1962).

first order kinetic rate constant, not the final ΔH when thermal equilibrium has been established. The reaction of 19·11 mg of sodium borohydride with 0·067M cyclohexanone in 0·1M sodium hydroxide is complete within a few minutes at 25°. Therefore we will not use the thermochemical rates with cyclohexanone to compare the relative rates for the ketone reduction. These data are available in isopropyl alcohol solution[11] and reproduced in Table 3 along with the relative rates in pure water.

The problem of the time lag in the thermistor is a special case of the thermal maximum kinetic technique used by Bell[12] to study some rather fast reactions with half-times as low as 0·2 seconds. If one knew the value of the first order heating constant for the thremistor and its tiny oil bath, one can compute the rate at which heat is produced in the aqueous solution.

DISCUSSION

The present data can be compared with the data obtained in the gas phase hydrogenation of a ketone as cyclopentanone. Thus the complete thermodynamic cycle would be represented:



$$\Delta H_{exp} = \Delta H_h + 4\Delta H_s$$

The important point to note is that the solution data contain the difference between the heat of solution of the cyclopentanone and the heat of solution of the alcohol. For acetone and isopropyl alcohol, its reduction product, the difference in heats of

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[12] R. P. Bell and J. C. Clunie, *Proc. Roy. Soc.* A212, 16 (1952) and R. P. Bell, V. Gold, J. Hilton and M. H. Rand, *Disc. Faraday Soc.* 17, 151 (1954).

solution is 2·26 kcal/mole.[13] The heats of reduction of a series of ketones in aqueous solution contain a constant ΔH_h term, the heat of hydrolysis of borohydride ion producing only dissolved hydrogen gas. Thus the experimentally determined differences in strain energies in the ketone and its alcohol can be compared in aqueous solution and in the pure neat liquids or in the gas phase. In Table 4 the results have been compared on the basis of four moles of ketone being reduced per mole of borohydride. Then the difference in heat has been related to cyclopentanone as standard in each case.

TABLE 4. COMPARISON OF THE HEATS OF REACTION IN Kcal

Ketone	$-\Delta H_{exp}$	$-\Delta H_{exp} - \Delta H_0$	$-\Delta H_{exp} - \Delta H_0$, Per mole of ketone
Cyclohexanone	129·70	3·64	0·91[d]
Acetone	128·17	2·13	0·53[d]
Cyclopentanone	126·04[a]	0	0[d]
	$-4\Delta H_1$[c]	$-4(\Delta H_1 - \Delta H_{so})$	Neat liquids
Cyclohexanone	57·28	12·00	3·00[e]
Acetone	53·16	7·88	1·97[e]
Cyclopentanone	45·28[b]	0	0[e]

[a] Standard ΔH_0.
[b] Standard ΔH_{so}.
[c] Four times the ΔH_1 value listed in Table I.
[d] In aqueous solution.
[e] In the pure liquids.

Cyclopentanone has a puckered non-planar ring[14] with six sets of bond oppositions[15] and the reduction product, cyclopentanol, has ten sets of bond oppositions.[15] Thus steric strain is produced in the product and the amount of heat released is the smallest for the five-membered ring ketone. Pitzer[16] has estimated the torsional strain in cyclopentanone to be 2·8 kcal/mole less than that of cyclopentane. The replacement of two methylene hydrogens by the carbonyl oxygen reduces the strain energy difference by 0·95 kcal/mole[15–17] per hydrogen while the change in the C—C—C angle going from C—CH_2—C to C—CO—C introduces about 0·9 kcal/mole of angle strain. Thus cyclopentanone can be estimated to have about 1·9 kcal/mole less strain energy than cyclopentane. In the pure neat liquids the ΔH_s of cyclopentanone differs by 1·97 kcal/mole of ketone from the ΔH_1 of acetone which is assumed to be completely strain free.

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[13] At infinite dilution:

$$R_2CO \xrightarrow{\Delta H_1} R_2CO_{aq}$$

$$R_2CHOH \xrightarrow{\Delta H_s} R_2CHOH_{aq}$$

$\Delta H_s - \Delta H_1 = -2{\cdot}26$ kcal/mole for acetone and isopropyl alcohol. *International Critical Tables* Vol. 5; p. 148.

[14] J. G. Aston, S. C. Schumann, H. L. Fink, and P. M. Doty, *J. Amer. Chem. Soc.* **63**, 2029 (1941).

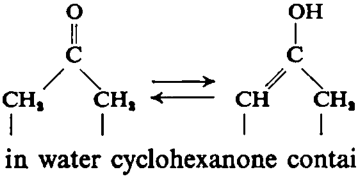
[15] H. C. Brown, J. H. Brewster and H. Shechter, *J. Amer. Chem. Soc.* **76**, 467 (1954).

[16] W. E. Donath and K. S. Pitzer, *J. Amer. Chem. Soc.* **81**, 2313 (1959).

[17] The potential barrier to rotation in acetone is 1·40 kcal/mole while that in propane is 3·30 kcal or 0·95 kcal/mole per C—H bond. J. A. McCoubrey and A. R. Ubbelohde, *Quart. Rev.* **5**, 364 (1951).

However an aqueous solution has a great leveling effect on these energy differences and the difference between cyclopentanone and acetone is reduced to 0·53 kcal/mole of ketone. Differential solvation of these ketones and their alcohols between the pure liquids and their aqueous solutions is also reflected in the rates of reduction. Ketone reduction with borohydride is generally much faster in water than in isopropyl alcohol and the relative rate difference become less in water than in isopropyl alcohol (Table 3). In isopropyl alcohol cyclopentanone is reduced at 0·2th the rate of acetone while in water the rate is only 0·4th the rate of acetone. This is a factor of two in the change in relative rates and this is also reflected in the relative heat change of 3·7.

The effect of water on ketones can be examined by noting the percentage of enol.



It has been reported that in water cyclohexanone contains 20 × 10^{-3}% enol while cyclopentanone[18] contains 4·8 × 10^{-3}%. The enol form has been stablized by the involvement of the hydroxy group in the hydrogen bonding of the solvent and the difference in the percentage of enol decreased from that in the pure ketone by the presence of the water. Likewise a change in solvent from 95% ethanol[19] to pure water[20] raises the percentage of enol in 2-carbethoxycyclohexanone from 57% to 76%.

If acetone and isopropyl alcohol are assumed to be both strain-free, then one concludes (both from the data of Sellers and Sunner[10] and of this investigation) that cyclohexanone has some strain energy which is released as the strain-free cyclohexanol is formed. Others[15,21] have suggested that cyclohexanone is strained by 1·6 kcal[21] or by 1·0 kcal[10] compared to its alcohol even though Pitzer[16] suggests that the compound is unstrained. Examination of Table 4 shows that while the difference in the heats of reduction of cyclohexanone and acetone is 1·03 kcal/mole of ketone in the pure liquids, the leveling effect in aqueous solution is clearly seen as the difference is now only 0·4 kcal/mole of ketone. While this is a small thermochemical difference, the better model for cyclohexanone would be methyl isopropyl ketone. The $\underline{\Delta H}$ for reduction with borohydride is −129·2 kcal/four moles of methyl isopropyl ketone and −129·7 kcal/four moles of cyclohexanone.

The values of the heats of reduction by borohydride are very large. This is due to (a) the weakness of the boron-hydrogen bond and its extreme hydridic character. The extremely large heat is also affected by (b) the extremely strong boron-oxygen bonds formed in the borate ion and (c) the strength of the hydrogen-hydrogen bond or the hydrogen-carbon bond formed.

The $\Delta H°$ of the hydrolysis of borohydride at 25° is −63·73 kcal/mole[22,23]

$$BH_4^- + 4H_2O \rightarrow B(OH)_4^- + 4H_2$$

$$\Delta H° = -63{\cdot}7 \text{ kcal/mole}$$

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[18] G. Schwarzenbach and C. Wittwer, *Helv. Chim. Acta* **30**, 656, 669 (1947).

[19] W. Dieckmann, *Ber. Dtsch. Chem. Ges.* **55**, 2470 (1922).

[20] G. Schwarzenbach, M. Zimmermann and V. Prelog, *Helv. Chim. Acta* **34**, 1954 (1951).

[21] N. L. Allinger, *J. Amer. Chem. Soc.* **81**, 572 (1959).

[22] W. D. Davis, L. S. Mason and G. Stegman, *J. Amer. Chem. Soc.* **71** 2775 (1949).

[23] W. H. Stockmayer, D. W. Rice and C. C. Stephenson, *J. Amer. Chem. Soc.* **77**, 1981 (1955).

Since the four moles of hydrogen gas are used to then convert four moles of ketone to the alcohol, the observed heat is quite large.[24]

In conclusion it can be stated that while exo carbonyl double bonds stabilize a five membered ring and destabilize a six-membered ring, the effects in aqueous solutions are much smaller than expected on the basis of other thermodynamic data obtained in the gas phase or in the neat liquid.

EXPERIMENTAL

Materials. Sodium borohydride (Metal Hydrides, Inc.) was heated at 40·0° for 1 hr with 30 times its wt. of freshly distilled diglyme. The warm solution then was filtered at 38–40° through a fine pore sintered glass filter. The filtrate was allowed to cool slowly to 0° and the $NaBH_4$ (solvated) removed by filtration. The diglyme was removed under high vacuum using an Abderhalden pistol.

The diglyme (Ansul 141 ether) was stirred with 2% by wt. of CaH_2 for several hr, filtered and then distilled at 58° *in vacuo* from CaH_2 or LAH at 11 mm press. under N_2.

Acetone (Spectrophotometric grade, Matheson, Coleman and Bell) was homogeneous (99·93% or better) on a four foot column of 25% 1,2,3-tris-cyanoethoxypropanol on firebrick.

Methyl isopropyl ketone (Matheson, Coleman and Bell) was distilled using a Heli-pak column. The material was homogeneous (99·9 or better) on a four foot dioctyl phthalate column.

Cyclohexanone was dried and distilled through a Heli-pak column; the fraction collected at 153° (743·5 mm) was homogeneous on a six foot 20M carbowax column on 60/80 firebrick.

Cyclopentanone (Arapohoe Chemicals) was shaken with K_2CO_3 and then distilled at 126° (740 mm) through a Heli-pak column. The material was homogeneous on a 20M Carbowax column. For each ketone traces of the corresponding alcohol and hydrocarbon derivatives could be easily detected using the VPC columns.

Calorimeter. A 37 gallon insulated tank controlled to 25·00 ± 0·001° (checked against NBS standards) served as the constant temp bath for the submarine calorimeter. The calorimeter, a silvered Pyrex vacuum bottle,[25] was 20 cm long and had a total volume of 425 ml. It had a stirring rod, a sample holder and crusher, a heating element and a thermistor. The stirring motor was run at a very steady rate. The heater was constructed from 80′ of No. 35 manganin wire wound noninductively around a 6 mm Pyrex rod. The wire was then painted with Glyptal and baked at 110°. The element was then placed in a slightly larger tube and the element covered with Silicone oil to serve as a heat transfer agent. A Veco 32A 24 thermistor (2070 ohms) served as the temp sensing element. A Sargent (SR-S-72180) Recorder (1 mv full scale) served as a null-point device to graphically record the potential.

A Sargent Coulometric Current Source (No. 30974) with a resistance of 77·26 ± 0·01 ohms was used as a power source for the manganin heater. Current regulation was constant to ±0·1% or better. Generally the unit was set to supply 193·0 ± 0·1 milliamperes.

Operation. Freshly recrystallized and vacuum dried $NaBH_4$ was weighed (to ±0·01 mg) into small sample bubbles. The thin-walled bubbles were then fastened to the sample-holder rod above the crusher plate in the bottom of the colorimeter.

Samples of the ketone were dissolved in dil. 0·1000M NaOH and diluted to a volume of 257·05 ± 0·04 ml at 24·9°. A home made transfer pipet (calibrated by water) of 247·36 ± 0·03 ml delivery volume was then used to transfer the solution to the calorimeter. The calorimeter was quickly assembled and then placed in the constant temp bath. The calorimeter heater was then used to raise the temp to 25·00°. Using these procedures thermal equilibrium was reached quickly and a good recorder base line established.

The bulb of $NaBH_4$ was then crushed (bulb blank was always less than 1 cal, and the heat of solution of 0·02000 ± 0·00002 gm $NaBH_4$ in 0·1M NaOH was 5 cal/mole) and the time-temp curve recorded. After 10 half-lives or more, the heat equiv of the calorimeter and the final solution was

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[24] The largest heat of reaction of borohydride we have measured is that of the reaction of borohydride with iodate. The ΔH is nearly −1000 kcal/mole of borohydride. This is due to the fact that the hydride hydrogens are converted into water and the observed ΔH contains four times the heat of formation of liquid water.

[25] C. M. Criss, Ph.D. Thesis, Purdue University (1961).

determined by electrical calibration using the coulometric source. Generally the current of 193·0 ± 0·1 milliamperes was run through the heater (77·26 ± 0·01 ohms) for 100 to 210 ± 0·05 sec. The factor 4·1833 was used to convert joules to calories. Since the heat input to the calorimeter could be measured by the recorder displacement the heat of reaction could be determined using a simple proportion method.[25]

Each reaction was repeated at least 4 times to obtain the average and experiments were performed at different initial concentrations of ketone and $NaBH_4$. All data were treated by the proper statistical[25] methods[26,27]. The age of the ketone in the dil NaOHaq did not correlate (ANOVA method) with the ΔH of reaction. Hence it is concluded that the borohydride was reducing the original ketone, not some base-catalyzed transformation or condensation product.

Kinetics. Since the ketone was in large excess, the second order rate expression

$$\text{rate} = k_2(\text{ketone})(BH_4^-)$$

reduces to

$$\text{rate} = k_1(BH_4^-)$$

This is a first order rate expression indicating a first order rate of heat (Q) production.

$$\frac{dQ}{dt} = k_1(BH_4^-)$$

The value of k_1 has been computed from the raw data of the temp-time recorder tracings. If k_1 is divided by the initial ketone concentration, the value of k_2 is obtained.

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[26] F. S. Acton, *Analysis of Straight-Line Data*. J. Wiley, New York (1959).

[27] E. L. Bauer, *A Statistical Manual for Chemists*. Academic Press, New York (1960).