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Enthalpies of Interaction of Aliphatic Ketones with Polar and Nonpolar Solvents

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Abstract: Solvation enthalpies [$\Delta H(\text{v} \rightarrow \text{S})$] of a variety of aliphatic ketones including straight-chain, branched, and cyclic compounds have been determined in methanol, dimethylformamide, benzene, and cyclohexane by combining measurements of the heats of solution (ΔH_s) and heats of vaporization (ΔH_v). Values of ΔH_v have been determined by the gas chromatography–calorimetry method, and several of the calculated liquid heat capacities required by this procedure have been verified by experimental measurement. $\Delta H(\text{v} \rightarrow \text{S})$ for most ketones are in the order benzene (most exothermic) > DMF > MeOH > c-C_6H_{12}. Comparison of $\Delta H(\text{v} \rightarrow \text{S})$ values for ketones with values for hydrocarbons of the same carbon skeleton provides a measure of polar interactions of the ketones with solvents. These interactions are largest for the cyclic and 2-ketones, less for the straight-chain symmetrical ketones, and least for the highly branched 2,2,4,4-tetramethyl-3-pentanone, and decrease with increasing ketone size within each group.

Gas-phase studies of solutes, complemented by measurements of the interactions of gaseous species with solvents, have been revived in recent years as a very important approach to an understanding of the intermolecular forces in solutions.[1-3] The significance of these studies to the understanding of solution reactivity and equilibria has been a subject of recent discussions by Taft[4] and Arnett.[5] A considerable research effort has been made in this laboratory to determine the extent to which aromatic compounds[6,7] with a variety of substituent groups, relatively nonpolar aliphatic hydrocarbons,[8] and functional groups introduced into the latter molecules[8,9] interact with polar and nonpolar solvents, in order to evaluate the major intermolecular forces operative in these solutions. The choice of solvents has been limited to nonaqueous ones, thus avoiding several additional complications encountered in aqueous solutions.[2]

The first step toward this goal must be to form a minimum number of empirical generalizations to describe intermolecular interactions, based on an extensive set of data, describing the effects of systematic changes in the structural features of the solute in a variety of polar and nonpolar solvents. The initial investigation in this direction has been carried out by the measurement of enthalpies of solution (ΔH_s) of series of alkanes and alkenes, including straight-chain, branched, and cyclic compounds, in polar solvents (methanol and dimethylformamide), nonpolar but highly polarizable benzene, and nonpolar cyclohexane.[8] There is strong experimental support for one empirical generalization, the existence of methylene group additivity[10] in the solvation enthalpies, $\Delta H(\text{v} \rightarrow \text{S})$, and also in ΔH_s values of alkanes and alkenes. This study showed that alkenes are more strongly solvated than the corresponding alkanes in polar DMF, presumably because of dipole–induced dipole interactions of the solvent with the polarizable π bond of the alkenes, but the alkene–alkane difference in nonpolar cyclohexane is negligible, indicating that in cyclohexane both alkenes and alkanes are solvated almost entirely by dispersion forces. In polar solvents alkenes interact by dispersion, dipole–induced dipole, and perhaps very slightly by dipole–dipole forces, whereas alkanes interact with polar or nonpolar solvents almost entirely by dispersion forces. (In highly polar solvents dipole–induced dipole forces may make a small contribution.) The results were consistent with the premise that a given hydrocarbon group will make the same contribution to dispersion interactions regardless of the nature of the molecule of which it is a part. There is also strong evidence supporting a second empirical generalization,[8] that straight-chain hydrocarbons are better solvated in polar or nonpolar solvents than are branched isomers, and $\Delta H(\text{v} \rightarrow \text{S})$ of alkanes are reduced by nearly 1 kcal/mol for each quaternary carbon atom present in the chain, arising from steric hindrance to solvation by dispersion forces. An additional reduction in the solvation of *trans*-1,2-di-*tert*-butylethylene was also observed, where steric factors prevent the close approach of the solvent dipoles to the π bond of the alkene, thereby diminishing the alkene–alkane difference in $\Delta H(\text{v} \rightarrow \text{polar solvents})$.

These results are qualitatively consistent with a division of the observed overall enthalpies of solute–solvent interaction [$\Delta H(\text{v} \rightarrow \text{S})$] into three terms: the enthalpy of cavity formation (ΔH_c) within the solvent (required to accommodate solute molecules); $\Delta H_{\text{nonpolar}}$, arising from dispersion forces; and the enthalpy of polar interactions (ΔH_{polar}) which arise from additional electrostatic interactions (dipole–induced dipole, di-

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pole-dipole interactions including hydrogen bonding) between polar solvents and polar or polarizable solutes.

The next logical step in this study is to attach a polar functional group (the keto group) in place of the polarizable carbon-carbon double bond to the aliphatic carbon chain in order to investigate the intermolecular forces operative with each of the four solvents, the ΔH_{polar} contribution to $\Delta H(\text{v} \rightarrow \text{S})$ values, and differences in the trends, if any, between ketones and hydrocarbons.[8] Very little is known about the solvation of aliphatic ketones. The only data available in the literature are enthalpies of solution of acetone in several polar solvents,[11] data on the free energy (and in some cases enthalpy) of transfer[12] of isomeric decanones from water to heavy water based on temperature dependence of UV absorption, a gas chromatographic (GC) study[13] of $\Delta S(\text{v} \rightarrow C_{36}H_{74})$ and $\Delta H(\text{v} \rightarrow C_{36}H_{74})$ for some cyclic and 2-ketones at 100 °C, and heats of solution of acetone and acetone-d_6 in a variety of solvents.[14]

In this paper we present an enthalpy study of the solvation of an extensive series of aliphatic ketones, including both symmetrical and nonsymmetrical (methyl) straight chain, branched, and cyclic compounds, by measurement of the enthalpies of solution in methanol (MeOH), *N,N*-dimethylformamide (DMF), benzene (Bz), and cyclohexane (c-C_6). Heats of vaporization for 2-decanone, 2-undecanone, and 6-undecanone have not previously been measured, and conflicting values have been reported for several other ketones (Table II). We have therefore chosen to measure heats of vaporization (ΔH_v) of 12 of the C_5-C_{11} ketones of interest, using a recently developed GC-calorimetry method.[15] The previously unmeasured value for the hydrocarbon 2,2,4,4-tetramethylpentane was also determined (Table III). This technique requires values of ΔC_p $[C_p(\text{l}) - C_p(\text{g})]$. Several liquid heat capacities have been measured to verify those estimated by additivity schemes,[16] and improved parameters have been developed for the estimation of gaseous values. Two or more literature ΔH_v values in good agreement are available for the other ketones. The solvation parameters, $\Delta H(\text{v} \rightarrow \text{S})$, of the ketones will be compared with the corresponding alkane values, in order to assess polar interactions with the four solvents, and the effect of ketone structure on solvent-solute interactions.

Experimental Section

Reagents. The source and drying procedure for the solvents have been described previously.[8] The ketones investigated were commercial samples obtained from Chemical Samples Co. or Aldrich Chemical Co., and are stated to be of 99-99.8% purity. This was confirmed by GC during the ΔH_v determinations. All are liquids at room temperature.

Calorimetry. The calorimetric procedure and apparatus have been described previously.[9] The calorimeters were immersed in water baths maintained at 25.00 °C with regulation to ±0.002 °C or better. Liquid samples were introduced into the calorimeters from 20- or 50-μL syringes with immersed tips, Heats of solution were corrected (0.03 kcal/mol less endothermic) to allow for the sample temperature (22-23 °C).

Heats of Vaporization. Our recently developed method for measuring heats of vaporization[15] by a combination of gas chromatographic retention times (as a function of temperature) and calorimetry in the stationary phase (DC-200 silicone fluid, 100cS) was used.

Heat Capacities. $C_p(\text{l})$ and $C_p(\text{g})$ were estimated by the additivity rules of Shaw[16] and Benson,[17] respectively. Based on the acetone-2-butanone and acetaldehyde-propionaldehyde $C_p(\text{g})$ differences, the contribution of α-CH_2 is assigned a value of 6.7 (rather than 6.2[17]) cal/mol·K. Additional $C_p(\text{g})$ ketone values have been measured at high temperatures,[19] but the extrapolation to 298 K is too uncertain to be useful in defining group parameters.

Liquid heat capacities of four ketones were measured in a 10-mL vacuum jacketed calorimeter, magnetically stirred, and immersed in a water bath at 25.00 °C, regulated to ±0.002 °C. $C_p(\text{l})$ values were calculated relative to water (17.98 cal/mol·K) and *n*-heptane (53.77 cal/mol·K). Each value was calculated from the mean of four to ten heating curves. Duplicate $C_p(\text{l})$ values determined from separate samples agreed to 0.3 cal/mol·K or better (0.4-0.7%).

Table I. Enthalpies of Solution of Ketones at 25 °C

solute	ΔH_s[a] (MeOH)	ΔH_s[a] (DMF)	ΔH_s[a] (Bz)	ΔH_s[b] (c-C_6)
acetone	0.60[c]	−0.02	0.29	2.69[d]
2-butanone	0.58	0.10	0.10	2.29
2-pentanone	0.59	0.22	0.17	2.04
2-hexanone	0.68	0.40	0.19	2.16
2-heptanone	0.75	0.53	0.24	2.01
2-octanone	0.90	0.70	0.28	2.03
2-nonanone	1.13	0.97	0.39	1.98
2-decanone	1.34	1.29	0.54	2.00
2-undecanone	1.55	1.65	0.64	2.05
3-pentanone	0.63	0.25	0.02	1.97
3-hexanone	0.67	0.41	0.07	1.85
4-heptanone	0.77	0.65	0.16	1.69
5-nonanone	0.94	1.09	0.37	1.70
6-undecanone	1.45	1.53	0.51	1.73
3,3-dimethyl-2-butanone	0.66	0.36	0.15	1.73
2,2,4,4-tetramethyl-3-pentanone	0.92	0.90	0.56	1.00
cyclopentanone	0.82	0.15	−0.25	2.17
cyclohexanone	0.14	0.34	−0.26	1.77
cycloheptanone	0.72	0.30	0.01	1.73

[a] kcal/mol ± 0.05. [b] kcal/mol ± 0.10. [c] Reported (ref 14) 0.58 at 100-1000 times greater concentration. [d] Reported (ref 14) 2.40 at 100-1000 times greater concentration.

Results

Primary Results. Heats of solution of 19 ketones in MeOH, DMF, benzene, and cyclohexane are presented in Table I. The ΔH_s values are averages of three to six determinations measured in the concentration range $1\text{-}5 \times 10^{-3}$ M. No effect of concentration on ΔH_s was noted in this range, and the data are essentially infinite-dilution values, with estimated uncertainties of 0.10 (c-C_6) and 0.05 kcal/mol (MeOH, DMF, Bz).

Calculated values of $C_p(\text{l})$ and $C_p(\text{g})$ are compared with experimental values (Table II), and GC-calorimetry values of ΔH_v, with previous literature values when available. The new experimental values of ΔH_v have overall uncertainties (99% confidence level) of 0.06-0.12 kcal/mol, calculated by consideration of the individual uncertainties in $C_p(\text{l})$, $C_p(\text{g})$ (each conservatively estimated as ±1.0 cal/mol·K), $\Delta H_s(\text{DC-200})$ (±0.02-0.03 kcal/mol), $\Delta H(\text{v} \rightarrow \text{DC-200})$ by GC, and the GC column calibration curve.[15]

Derived Results. The values of ΔH_s and ΔH_v have been combined to give enthalpies of transfer from vapor to each of the four solvents (Table III): $\Delta H(\text{v} \rightarrow \text{S}) = \Delta H_s - \Delta H_v$. The enthalpies of transfer among solvents are not tabulated, but can be readily derived from the data of Table I: $\Delta H(S_1 \rightarrow S_2) = \Delta H_s(S_2) - \Delta H_s(S_1)$. The additional interactions of ketones with solvents compared to that of the nonpolar hydrocarbons, which arise from substitution of the polar carbonyl group in place of a hydrocarbon methylene group, are derived by subtracting the values of $\Delta H(\text{v} \rightarrow \text{S})$ of alkanes[8] from the corresponding quantities of ketones with the same carbon skeleton.

Discussion

Heats of Vaporization. Of the nine ΔH_v determinations by the GC-calorimetry method reported in Table II which duplicate recent values by the vapor pressure procedure,[20] seven agree within ±0.05 kcal/mol or better, and none disagrees by appreciably more than the combined uncertainties. On the other hand, values for 2-hexanone,[21] 3-hexanone,[22] and 5-

Table II. Heats of Vaporization[a] of Ketones at 25 °C

compd	ΔH_s[b] DC-200	calcd[c] C_p(l)[d]	calcd[c] C_p(g)	slope[e]	ΔT, K[f]	ΔH_v[g] cor	H_v(lit.)[h] p_v	H_v(lit.)[h] cal
acetone		30.2	18.0				7.48 ± 0.02	7.37 ± 0.01
2-butanone			24.7				8.29 ± 0.02	8.34 ± 0.01
2-pentanone	1.00	44.8	30.2	3487.59	34.5	9.16 ± 0.07	9.18 ± 0.02	9.14 ± 0.05
2-hexanone	1.05	52.0	35.7	4001.41	34.5	10.27 ± 0.08	10.25 ± 0.02	10.09 ± 0.02
2-heptanone	0.96	59.2	41.2	4607.40	32.8	11.34 ± 0.07	11.47 ± 0.24	
2-octanone	1.03	66.5	46.7	5079.53	35.6	12.43 ± 0.08	12.38 ± 0.02	
2-nonanone	1.05	73.8	52.2	5091.41	79.4	13.53 ± 0.14	13.48 ± 0.02	
2-decanone	1.01	81.0	57.7	5723.50	69.1	14.55 ± 0.11		
2-undecanone	1.08	88.3	63.2	6183.07	69.5	15.65 ± 0.11		
3-pentanone	0.91	44.8	31.4	3590.37	35.0	9.24 ± 0.07	9.23 ± 0.02	9.22 ± 0.03
3-hexanone	0.90	52.0	36.9	4010.07	35.0	10.11 ± 0.06	10.11 ± 0.02	10.01 ± 0.05
4-heptanone	0.82	59.2	42.4	4535.50	34.1	11.04 ± 0.09	11.16 ± 0.02	
5-nonanone	0.89	73.8	53.4	5485.87	35.6	13.12 ± 0.09	13.15 ± 0.24	12.74 ± 0.02
6-undecanone	0.92	88.3	64.4	6062.40	69.5	15.18 ± 0.12		14.51 ± 0.12[i]
t-BuCOMe	0.95						9.15 ± 0.02	9.05 ± 0.02
t-BuCO-*t*-Bu	0.59						10.84 ± 0.02	10.85 ± 0.02[j]
cyclopentanone	1.20						10.19 ± 0.10[k]	10.21 ± 0.05
cyclohexanone	1.13						10.73 ± 0.15,[k] 10.81[l]	10.77 ± 0.05
cycloheptanone	1.28						11.84 ± 0.15,[k] 11.89[l]	

[a] kcal/mol. [b] Heat of solution in DC-200 silicone fluid (GC stationary phase) at 25 °C, kcal/mol ± 0.02-0.03. [c] cal/mol·K. See Experimental Section. [d] Exptl C_p(l): acetone, 30.0, 30.2; 2-pentanone, 44.3; 3-pentanone, 45.4, 45.3; 5-nonanone, 73.4, 73.1. [e] Of plot of ln GC-corrected retention time vs. $1/T$. [f] Mean temperature of GC measurements −298.15 K. [g] Corrected exptl ΔH_v. [h] Literature values from vapor pressure measurements (ref 19) or vaporization calorimetry (ref 20, 21). [i] Estimated. [j] I. Wadsö, *Acta Chem. Scand.*, **20,** 544 (1966). [k] G. Wolf, *Helv. Chim. Acta,* **55,** 1446 (1972). [l] E. F. Meyer and C. A. Hotz, *J. Chem. Eng. Data,* **21,** 274 (1976).

Table III. Enthalpies of Transfer[a] of Ketones from Vapor to Solvents at 25 °C

solute	$-\Delta H(\mathrm{v} \rightarrow \mathrm{MeOH})$ ketone	$-\Delta H(\mathrm{v} \rightarrow \mathrm{MeOH})$ ket-RH[b]	$-\Delta H(\mathrm{v} \rightarrow \mathrm{DMF})$ ketone	$-\Delta H(\mathrm{v} \rightarrow \mathrm{DMF})$ ket-RH[b]	$-\Delta H(\mathrm{v} \rightarrow \mathrm{Bz})$ ketone	$-\Delta H(\mathrm{v} \rightarrow \mathrm{Bz})$ ket-RH[b]	$-\Delta H(\mathrm{v} \rightarrow c\text{-}C_6)$ ketone	$-\Delta H(\mathrm{v} \rightarrow c\text{-}C_6)$ ket-RH[b]
acetone	6.88	3.5[c]	7.50	4.7[c]	7.19	4.1[c]	4.79	1.0[c]
2-butanone	7.71	3.4[c]	8.19	4.5[c]	8.19	4.0[c]	6.00	1.0[c]
2-pentanone	8.57	3.3	8.94	4.4	8.99	3.7	7.14	1.1
2-hexanone	9.59	3.2	9.87	4.4	10.08	3.7	8.30	1.0
2-heptanone	10.59	3.2	10.81	4.3	11.10	3.7	9.33	1.0
2-octanone	11.53	3.2	11.73	4.3	12.15	3.7	10.40	0.9
2-nonanone	12.40	3.2	12.56	4.3	13.14	3.7	11.55	1.0
2-decanone	13.21	3.0	13.26	4.2	14.01	3.5	12.55	0.8
2-undecanone	14.10	2.9	14.00	4.1	15.01	3.5	13.60	0.8
3-pentanone	8.61	3.3	8.99	4.4	9.22	4.0	7.27	1.2
3-hexanone	9.43	3.1	9.69	4.2	10.03	3.7	8.25	1.0
4-heptanone	10.27	2.9	10.39	3.9	10.88	3.5	9.35	1.0
5-nonanone	12.18	2.9	12.03	3.8	12.75	3.3	11.42	0.8
6-undecanone	13.73	2.5	13.65	3.7	14.67	3.2	13.45	0.6
t-BuCOMe	8.49[d]	2.9	8.79[d]	4.2	9.00[d]	3.5	7.42[d]	0.9
t-BuCO-*t*-Bu	9.93	2.1[e]	9.95	3.4[e]	10.29	2.5[e]	9.85	0.7[e]
cyclopentanone	9.38	3.5	10.05	4.7	10.45	4.3	8.03	1.2
cyclohexanone	10.63	3.9	10.43	4.4	11.03	4.0	9.00	1.1
cycloheptanone	11.15	3.4	11.57	4.5	11.86	3.6	10.14	1.0

[a] kcal/mol. [b] $\Delta H(\mathrm{v} \rightarrow \mathrm{S})$ of ketone $-\Delta H(\mathrm{v} \rightarrow \mathrm{S})$ of alkane or cycloalkane with same carbon skeleton. RH values from ref 8. [c] Based on extrapolated value of ΔH_v(hydrocarbon). [d] $\Delta H_v = 9.15$ kcal/mol. [e] Based on $\Delta H_v = 9.21 \pm 0.06$ for 2,2,4,4-tetramethylpentane by GC-calorimetry method.

nonanone[21] measured by direct vaporization calorimetry, and an estimated value for 6-undecanone based on these,[21] are appreciably low, and are believed to be in error. Because C_p(g) group parameters for cyclic and branched ketones have not been firmly established, we have chosen to use literature values of ΔH_v (generally the mean of two or more determinations) in determining $\Delta H(\mathrm{v} \rightarrow \mathrm{S})$ of five ketones.

The ketone liquid heat capacities measured experimentally showed a mean difference with the calculated values of 0.39 cal/mol·K, and in no case exceed 0.7 cal/mol·K. It appears that the C_p(l) and C_p(g) additive values used in the ΔH_v determinations are likely to be well within the estimated ±1.0 cal/mol·K uncertainty.

Trends in ΔH_s and $\Delta H(\mathrm{v} \rightarrow \mathrm{S})$. With few exceptions ΔH_s values of the ketones are endothermic, and are in the order c-C_6 > MeOH > DMF > Bz. ΔH_s also becomes more endothermic with increasing ketone chain length in the solvent order DMF > MeOH > Bz. Values in c-C_6 are relatively constant from C_5 to C_{11}, but are more endothermic for the 2-ketone than for the symmetrical ones. This is unlike the behavior of alkanes and alkenes,[8] which closely follow methylene group additivity in all four solvents.

Solvation enthalpies [$\Delta H(\mathrm{v} \rightarrow \mathrm{S})$] in all four solvents become more exothermic with increasing ketone molecular weight, as opportunities for dispersion interactions increase. For the 2-ketones from acetone to 2-undecanone methylene increments are DMF, −0.83 ± 0.10; MeOH, −0.92 ± 0.10; Bz, −0.98 ± 0.09; c-C_6, −1.10 ± 0.07 kcal/mol, and are roughly constant within the 0.08–0.17 kcal/mol uncertainties in the individual $\Delta H(\mathrm{v} \rightarrow \mathrm{S})$ values. The "symmetrical" ketones (including 3-hexanone) show similar but slightly smaller (by 0.05–0.07 kcal/mol) methylene increments. However, the increments in ketone solvation enthalpies are probably somewhat less uniform than in the alkane series, particularly among the few simplest compounds. This is also reflected in ΔH_{v} values of the 2-ketones, where the increments are smaller among simpler compounds, but reach a steady value of about 1.10 kcal/mol between the higher homologues. An uneven trend is to be expected, because, for each additional methylene group in the chain, three changing factors affect the energetics of the solvation process: additional dispersion interactions, increased enthalpy of cavity formation, and an increasing extent of "steric hindrance" to keto-group solvation. The first two of these probably vary fairly uniformly with each additional methylene group, but the latter is more profoundly affected in the change acetone → 2-butanone than by the addition of a methylene group higher in the series. Meyer[13,23] has suggested that dipole–dipole interactions in pure liquid ketones fall off rapidly with increasing size, as the mean distance between dipoles increases. Meanwhile, however, dispersion interactions increase with each added methylene group, and dipole–induced dipole (induction) interactions remain constant. While we have reservations about the quantitative estimates of the forces involved, this could be a useful approach to the problem, if the implicit assumptions are reasonably valid.

It has previously been suggested[8] for alkanes that the differences in $\Delta H(\mathrm{v} \rightarrow \mathrm{S})$ between various solvents arise primarily from the greater cavity formation energy (solvent–solvent forces) of the polar solvents, but that solvent–solute dispersion interactions do not vary greatly from solvent to solvent. With ketone solutes there is superimposed an additional dipole–dipole interaction between the carbonyl dipole and the solvent dipole (MeOH, DMF), or a dipole–induced dipole interaction between the carbonyl and solvent (strongest with benzene). The cavity formation energy, an endothermic contribution, increases in the order c-C_6 < Bz < MeOH < DMF. The (exothermic) polar interactions increase in the order c-C_6 < MeOH < Bz < DMF. The latter term predominates only for acetone. For all but the smallest ketones $\Delta H(\mathrm{v} \rightarrow \mathrm{Bz})$ is more exothermic than $\Delta H(\mathrm{v} \rightarrow \mathrm{DMF})$.

Comparison of $\Delta H(\mathrm{v} \rightarrow \mathrm{S})$ for Ketones and Alkanes. *n*-Alkanes or cycloalkanes having the same carbon skeletons as the ketones have been used as nonpolar solute models for the ketones. Slight imperfections exist in this model because of the different geometry at the carbonyl carbon and the slightly larger molar volumes (3.3–9.5 mL) of the hydrocarbons. The difference in $\Delta H(\mathrm{v} \rightarrow \mathrm{S})$ between a ketone and the corresponding hydrocarbon can be attributed principally to polar interactions involving the carbonyl group. The difference in nonpolar solvents (0.6–1.2 kcal/mol in c-C_6), which tends to decrease with ketone size, has been attributed entirely to carbonyl dipole–hydrocarbon solvent induced dipole interactions,[13,23] on the premise that carbonyl dispersion interactions are only slightly larger than in methylene. It is also possible that the difference results from larger dispersion interactions by the carbonyl than by methylene. Were the latter entirely correct the $\Delta H(\mathrm{v} \rightarrow \text{c-}C_6)$ difference between ketones and hydrocarbons would not be expected to vary with molecular size, and this suggests that dipole–induced dipole forces must be at least partially responsible. Comparison of the $\Delta H(\mathrm{v} \rightarrow \text{c-}C_6)$ difference for the hindered ketone 2,2,4,4-tetramethyl-3-pentanone and the analogous hydrocarbon (2,2,4,4-tetramethylpentane), and that for the straight-chain isomer 5-nonanone (vs. nonane), shows essentially no difference; this is consistent with either extra carbonyl interactions by dispersion forces or with Meyer's induction model[23] *if* steric factors do not impede approach of a nonpolar solvent to the carbonyl.

The interactions of benzene with ketones also involve dispersion and induction forces. The hydrocarbon model compounds interact with benzene only by dispersion forces, the net interaction being slightly smaller than with cyclohexane (equal[8] or slightly larger dispersion forces, larger cavity energy in benzene). $\Delta H(\mathrm{v} \rightarrow \mathrm{Bz})$ is 1.2–2.5 kcal/mol more exothermic than $\Delta H(\mathrm{v} \rightarrow \text{c-}C_6)$ for all ketones except 2,2,4,4-tetramethyl-3-pentanone. Also, $\Delta H(\mathrm{v} \rightarrow \mathrm{Bz})$ is 3.2–4.3 kcal/mol more exothermic for ketones than for hydrocarbon models. Obviously, ketones undergo induction interactions with benzene at least four times stronger than with cyclohexane. Previous calculations of induction forces[13,23] use an equation which predicts benzene values only 40% larger than cyclohexane values, and this is clearly an unsatisfactory approximation. Data of Table III indicate that 2,2,4,4-tetramethyl-3-pentanone relative to its hydrocarbon model is not as favorably solvated as is 5-nonanone, and, indeed, the branched ketone is only about 0.4 kcal/mol more solvated in benzene than in cyclohexane. 2,2,4,4-Tetramethyl-3-pentanone and 5-nonanone have identical molar volumes and mean radii. Calculations of the intermolecular forces based on these mean radii predict equal interactions. Yet 5-nonanone is nearly 2.5 kcal/mol more solvated by benzene. A similar relationship exists for 2,2,4,4-tetramethylpentane and *n*-nonane. Calculation of dispersion interactions using any reasonable estimates of the ionization potentials suggests that the difference is no more than a few percent, yet the heats of vaporization differ by 1.9 kcal/mol (>20%). $\Delta H(\mathrm{v} \rightarrow \text{c-}C_6)$ and $\Delta H(\mathrm{v} \rightarrow n\text{-heptane})$ are respectively 10.63 and 11.06 for *n*-nonane and 9.14 and 9.16 kcal/mol for 2,2,4,4-tetramethylpentane.[8] Thus the dispersion interactions of the two C_9H_{20} isomers with a given solvent differ substantially, and are unequally affected by a change to another nonpolar solvent.

A problem associated with the calculation of intermolecular interaction energies by the traditional equations is properly defining the mean distance between interacting centers, *r*. Since results are dependent on r^{-6}, the choice is quite critical. But *r* is typically calculated from the apparent molar volume $[r = (\text{wt per mol/density} \times 6.03 \times 10^{23})^{1/3}]$ and assumes spherical molecules. This is usually a poor approximation, and the resulting interaction energies calculated may be quite far from reality. A similar problem may arise from the use of mean polarizabilities, α, in calculations on nonspherical molecules for which the polarizability is directionally dependent. We have previously noted that $\Delta H(\mathrm{v} \rightarrow \text{c-}C_6)$ (ketone) − $\Delta H(\mathrm{v} \rightarrow \text{c-}C_6)$ (hydrocarbon) decreases with increasing carbon number. The effect is quite large. For the symmetrical ketones, in going from C_5 to C_{11} half of the ketone–hydrocarbon difference is lost. In the other three solvents the change is only about 20%, but in all four solvents the $C_5 \rightarrow C_{11}$ change amounts to ~0.6–0.8 kcal/mol. On the other hand, the ketone–hydrocarbon difference is unaffected by increased steric hindrance at the carbonyl group (2,2,4,4-tetramethyl-3-pentanone). These observations are inconsistent with Meyer's model,[13] but we cannot at this time provide a satisfactory rationalization. It is likely that the interactions of ketones with cyclohexane are partially induction forces, although predominantly dispersion forces.

Methanol and DMF are the most structured of the four solvents studied, with the largest cavity-formation energies and the smallest methylene increments. Although the most exothermic values of $\Delta H(\mathrm{v} \rightarrow \mathrm{S})$ are generally those for benzene, the largest $\Delta H(\mathrm{v} \rightarrow \mathrm{S})(\text{ketone}) - \Delta H(\mathrm{v} \rightarrow \mathrm{S})(\text{hydrocarbon})$ differences are observed for DMF (3.7–4.7 kcal/mol for all ketones but the most highly hindered). This is indicative of strong polar (dipole–dipole) solute–solvent interactions. The ketone–hydrocarbon difference in DMF decreases with increasing size, and for a given carbon number decreases in the order cyclic ketones > 2-ketones > symmetrical ketones. ΔH(v → Bz) and ΔH(v → MeOH) become less exothermic in this same order. One might be tempted to attribute the large ΔH(v → S) of cycloalkanones to the smaller molar volumes (by 17–23 mL), but this would not account for the large cycloalkanone–cycloalkane differences, since the cycloalkanes also have smaller volumes than open-chain analogues by about the same amount. However, cycloalkanones have significantly larger dipole moments.[24] ΔH(v → MeOH) for cyclohexanone is at least 0.5 kcal/mol more exothermic than expected, probably because of partial conversion to the hemiacetal. This is reasonable in view of the much greater reactivity of cyclohexanone (compared with acetone, cyclopentanone, and cycloheptanone) in nucleophilic addition reactions[25] and the greater stability of the resulting addition products.[26] A similar effect has been noted for benzaldehydes with electron-withdrawing substituents.[27] It has also been suggested that the degree of keto–enol tautomerism in various solvents may affect the experimental heats of solution.[14]

While polar interactions of ketones account for the difference in solvation behavior compared with hydrocarbons in MeOH, DMF, and Bz, only for the two simplest ketones do polar interactions contribute more to ΔH(v → S) than do dispersion forces.

It is interesting to note in Table II that ΔH_s for the ketones in nonpolar DC-200 silicone fluid (measured in connection with GC–calorimetry determinations of ΔH_v) rather closely parallel ΔH_s values in c-C_6, although the values in DC-200 are less endothermic. ΔH(v → DC-200) values are correspondingly more exothermic than ΔH(v → c-C_6), but less so than for the other solvents.

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Structures and Energies of Cumulene Carbenes

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Abstract: Ab initio calculations have been used to predict structures and relative energies of propadienylidene, propargylene, butatrienylidene, ethynylvinylidene, transoid bivinylidene, and diacetylene. Some understanding of the accuracy of the predictions is obtained from extensive SCF and correlated calculations on vinylidene and acetylene. The energies of H_2C_2, H_2C_3, and H_2C_4 cumulene carbenes compared to methylene-like or stable rearrangement structures differ significantly. However, the energies of two different cumulene carbene structures of H_2C_4, butatrienylidene and ethynylvinylidene, are essentially the same. Electron correlation effects on the relative energies were found to be important, but do not change the qualitative predictions from uncorrelated treatments. The method of self-consistent electron pairs (SCEP) was used to determine correlation energies for these large systems and the largest wave function variationally included 120 499 symmetry-adapted configurations.

A recent study of the vinylidene–acetylene rearrangement[1] predicted a rearrangement barrier of 8.6 kcal and an energy difference between vinylidene and acetylene of 40 kcal. For carbenes with cumulene bond systems beyond $H_2C{=}C\colon$, rearrangement products may be stable molecules and also may be other carbenes. If rearrangement barriers for H_2C_3, H_2C_4, etc., are no higher than for vinylidene, these other carbenes may be competitive in radical reaction systems, especially if they are energetically as stable as the cumulene carbene. For a number of reactions involving H_2C_3, it is not clear whether the intermediate carbene is propargylene or propadienylidene.[2] Of the systems in this series of carbenes, vinylidene has been studied the most extensively by ab initio techniques.[1,3–5] Thus, this work was undertaken to determine reasonable structures

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