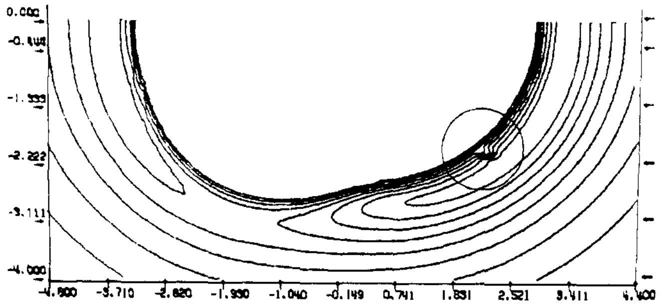

Figure 5. Isoenergy contour map of orientationally optimized formaldehyde water pairwise interactions analogous to Figure 2 but based on the (12-1) HPF. The minimum energy contour is −5.7079 kcal/mol with successive lines spaced at an interval of 0.6 kcal/mol.

sources: magnitudes of the statistics, stability of the statistics, and direct examination of results produced by the function.

VI. Summary and Conclusions

A heuristic method has been described for the determination of intermolecular potential functions from quantum mechanical calculations and applied to the formaldehyde-water system. The stability of statistical indices of the function and the reasonable computed energy grids indicate that the procedure works satisfactorily and within acceptable tolerance. The fact that satisfactory numerical results were obtained for a relatively small data base with respect to the positional and orientational degrees of freedom in the problem indicates that the heuristic potential function approach can be a viable means of generating intermolecular potential functions for larger polyatomic moieties and thus provide a basis for computer simulation studies of molecular assemblies of chemical and biochemical interest.

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Ground States of Molecules. 44.[1]
MINDO/3 Calculations of Absolute Heat Capacities and Entropies of Molecules without Internal Rotations

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Abstract: MINDO/3 calculations of $S°$ and $C_p°$ are reported for 27 molecules in which internal rotations are absent. Agreement between these data and corresponding quantities calculated from spectral data is excellent, being in almost every case within one entropy unit at 298.15 K. Entropies of activation for six reactions are calculated and found to be in good agreement with experiment. These results suggest that such calculations may assist in studies of reaction mechanisms and equilibria involving species whole vibrational frequencies cannot easily be determined by experiment.

Introduction

Thermodynamic quantities are now routinely calculated from vibrational frequencies and moments of inertia when these are know from experiment.[3] Indeed the success of such calculations has led almost to the extinction of thermochemical measurements in this connection. Similar calculations could of course also be carried out using vibration frequencies determined by quantum mechanical methods. The results of such treatments are, however, in general both less reliable and less accurate than those given by experiment. Nevertheless there are important situations where such experimental data are lacking and where theoretical estimates of vibration frequencies could be very useful, faute de mieux. Three obvious examples are entropies of activation, equilibria involving transient species at high temperatures, and the thermodynamic properties of large molecules. The vibrational frequencies of transition states cannot in principle be measured experimentally, while technical difficulties often prevent such information being obtained for transient intermediates. In the case of large molecules it is again very difficult to determine vibrational frequencies from IR/Raman spectra, both because of their large number and the complexities which arise from the numerous combination and overtone bands possible in these systems.

Calculations of entropies of activation could provide an extremely useful criterion of reaction mechanisms since they depend critically upon the geometry of the transition state and the strength and type of bonding in it. Equilibria depend on the free energies of the species involved. It is often quite easy to estimate the corresponding heats of reaction at room temperature from heats of formation, estimated if necessary by empirical procedures, but to extrapolate them to higher temperatures involves a knowledge of specific heats. The specific heats and entropies of some such transient species are not always easy to estimate. And finally, lack of thermodynamic data greatly limits the possibility of calculating equilibria in systems involving larger molecules.

Work in these laboratories led some years ago to the development of a semiempirical SCF MO method (MINDO/3[4]) which gave surprisingly good estimates of the heats of formation and geometries of a wide variety of organic compounds. Subsequent studies showed that it could also reproduce a wide range of other ground state properties[5] including molecular vibration frequencies.[6] Since MINDO/3 calculations can be carried out expeditiously for quite large molecules, it seemed to us that it might also prove useful in the connections indicated above. We have therefore used it to calculate absolute entropies and heat capacities of a number of molecules where these properties are known experimentally, to determine whether MINDO/3 could achieve a degree of accuracy that might be of practical value in such cases. We have also used MINDO/3 to calculate entropies of activation for a number of reactions where reliable kinetic data seemed to be available for comparison.

It should be noted that kinetic isotope effects can also be derived rigorously from the vibrational frequencies of the reactants and transition states for a reaction and we have found that they too can be estimated satisfactorily by MINDO/3.[7,8] Here, however, we will be concerned only with the results for thermodynamic properties.

In this paper we restrict ourselves to the case of molecules in which internal rotations are absent since here the rigid rotor harmonic oscillator (RRHO) approximation applies. In later papers we extend the treatment to flexible molecules. We begin by calculating absolute entropies and heat capacities for 27 molecules of this type for which we have previously published vibrational frequencies from MINDO/3 calculations and for which reliable spectroscopic data are available for comparison.[6]

Computational Procedure

Neglecting the effects of rotation-vibration coupling, anharmonicity, and centrifugal distortion, the absolute entropy and heat capacity of an arbitrary molecule without internal rotations are given by the standard formulas of statistical mechanics[3] as the sum of translational, rotational, and vibrational contributions.

$$S^\circ = (S^\circ)_{\text{tr}} + (S^\circ)_{\text{rot}} + (S^\circ)_{\text{vib}} \qquad (1)$$

$$C_p{}^\circ = (C_p{}^\circ)_{\text{tr}} + (C_p{}^\circ)_{\text{rot}} + (C_p{}^\circ)_{\text{vib}} \qquad (2)$$

$$S_{\text{tr}}{}^\circ = {}^5\!/_2 R \ln T + {}^3\!/_2 R \ln m + R \ln \left[\left(\frac{2\pi}{N} \right)^{3/2} \frac{k^{5/2}}{h^3} \right] + {}^5\!/_2 R - R \ln p \qquad (3)$$

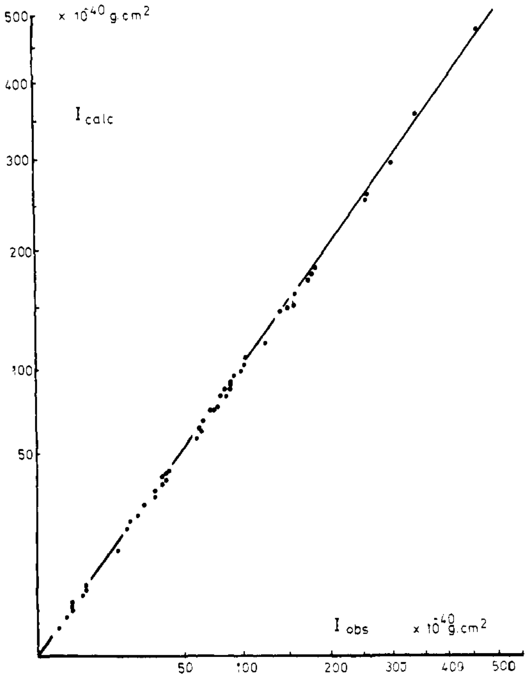


Figure 1. Calculated (MINDO/3) and observed principal moments of inertia.

$$S_{\text{rot}}{}^\circ = \begin{cases} R/2(3 \ln T - \ln ABC - 2 \ln \sigma + \ln \left[\pi \left(\frac{k}{hc} \right)^3 \right] \\ \quad + 3) \qquad \text{(nonlinear)} & (4a) \\ R(\ln T + \ln \frac{k}{hc} - \ln B - \ln \sigma + 1) \\ \quad \text{(linear)} & (4b) \end{cases}$$

$$S_{\text{vib}}{}^\circ = R \sum_i g_i \ln (1 - e^{-\omega_i hc/kT}) + \frac{Rhc}{kT} \sum_i \frac{g_i \omega_i e^{-\omega_i hc/kT}}{1 - e^{-\omega_i hc/kT}} \qquad (5)$$

$$(C_p{}^\circ)_{\text{tr}} = {}^5\!/_2 R \qquad (6)$$

$$(C_p{}^\circ)_{\text{rot}} = \begin{cases} {}^3\!/_2 R & \text{(nonlinear)} \qquad (7a) \\ R & \text{(linear)} \qquad (7b) \end{cases}$$

$$(C_p{}^\circ)_{\text{vib}} = R \left(\frac{hc}{kT} \right)^2 \sum_i \frac{g_i \omega_i{}^2 e^{-\omega_i hc/kT}}{(1 - e^{-\omega_i hc/kT})^2} \qquad (8)$$

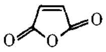
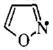
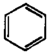
In these formulas the pressure p is taken to be 1 atm. The symmetry number σ has its usual significance and the rotational constants A, B, and C are calculated from the corresponding moments of inertia through the relation $A = h/8\pi^2 c I_A$, etc. The terms ω_i and g_i are the vibrational frequencies in cm^{-1} and their degeneracies, respectively.

Results

The moments of inertia appearing in the expression for $(S^\circ)_{\text{rot}}$ were calculated from the previously published[4,9] MINDO/3 geometries. These results are compared with those deduced from recent IR, Raman, and microwave spectral studies in Table I and presented graphically in Figure 1.

The accuracy of these calculations is clearly very high indeed. The slope of the regression line through the 65 points is 1.018 ± 0.004 (99% confidence limit). The average difference between the observed and calculated moments of inertia is 2.5% with over half the values agreeing to within 2%. Since the moments of inertia appear in the expression for $(S^\circ)_{\text{rot}}$ as a logarithmic term together with other terms involving only

Table I. Moments of Inertia from MINDO/3 Geometries

	$I_A \times 10^{-40}$, g cm^2		$I_B \times 10^{-40}$, g cm^2		$I_C \times 10^{-40}$, g cm^2	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
H_2O	1.004[a]	1.016	1.928[a]	1.808	3.015[a]	2.884
H_2S	2.701[b]	2.345	3.104[b]	3.488	5.915[b]	5.833
NH_3	4.645[c]	4.431	2.814[d]	2.960		
CO_2			71.72[e]	73.92		
CS_2			256.5[f]	253.0		
HCN			18.93[g]	18.97		
H_2CO	2.975[h]	2.722	21.60[h]	21.52	24.67[h]	24.24
$H_2C\overset{+}{N}\overset{-}{N}$	3.011[i]	2.878	74.21[j]	72.30	77.35[j]	75.17
CH_3Cl	5.433[k]	5.454	63.12[k]	60.72		
CH_4			5.340[l]	5.418		
$CH\equiv CH$			23.78[m]	23.56		
$CH_2{=}C{=}O$	2.974[n]	2.851	81.50[n]	82.41	84.61[n]	85.27
CH_3CN	5.351[o]	5.270	91.21[p]	91.58		
$CH_2{=}CHCl$	14.78[q]	13.72	142.1[q]	144.1	157.1[q]	157.8
$CH_2{=}CH_2$	5.751[r]	5.478	27.95[r]	28.20	33.78[r]	33.67
	32.92[s]	30.73	37.92[s]	38.34	59.50[s]	58.29
	38.18[s]	36.70	77.50[s]	76.30	104.5[s]	102.3
	36.90[t]	36.30	39.59[t]	39.74	62.69[t]	62.92
$CH_2{=}C{=}CH_2$	5.817[u]	5.537	94.45[v]	95.39		
$CH_3C\equiv CH$	5.384[w]	5.277	98.18[x]	97.31		
	66.58[y]	67.52	41.76[z]	41.77		
	125.0[aa]	118.7	338.4[aa]	354.7	463.4[aa]	473.5
	88.81[bb]	89.09	90.73[bb]	90.30	179.6[bb]	179.4
	104.3[cc]	111.4	154.8[cc]	151.1	259.3[cc]	262.5
	91.89[dd]	92.86	93.20[dd]	93.43	185.1[dd]	186.2
	85.73[ee]	84.80	87.62[ee]	87.96	173.5[ee]	172.8
	259.1[ff]	299.9	147.6[gg]	150.00		

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fundamental constants, the agreement between the $(S°)_{rot}$ contributions obtained from the two sets of data is considerably better than this, being on average less than 1% at 298.15 K.

The calculation of the translational contribution to $S°$, $(S°)_{tr}$, is of course trivial, depending only on the temperature, molecular weight, and a number of fundamental constants. On the other hand, calculation of the vibrational contributions depends critically on the accuracy of the lower vibrational frequencies. Fortunately these vibrations are manily bending and deformation modes which are among those most accurately calculated by the MINDO/3 procedure.[6] The low-frequency torsional vibrations are admittedly badly underestimated by the MINDO/3 procedure, but since we are considering only molecules without internal rotation, no problems arise from this source. Furthermore, since the vibrational contributions at moderate temperatures are relatively small (2-10% of $S°$ at 298 K for the molecules studied in this paper) any errors in $(S°)_{vib}$ are correspondingly reduced in importance in calculating the overall entropy, $S°$. Table II lists the vibrational contributions to $S°$ at 298.15 K calculated from both the MINDO/3[6] and experimental[6] frequencies. These results are presented graphically in Figure 2, the line here being the theoretical one of unit slope passing through the origin. The regression line through these points has a slope of 1.2, the calculated values of $(S°)_{vib}$ being overestimated by 10-30% or about 0.5 cal mol^{-1} deg^{-1}.

The final values of the entropies and heat capacities of these compounds in the ideal gaseous state of 298.15 K are given in

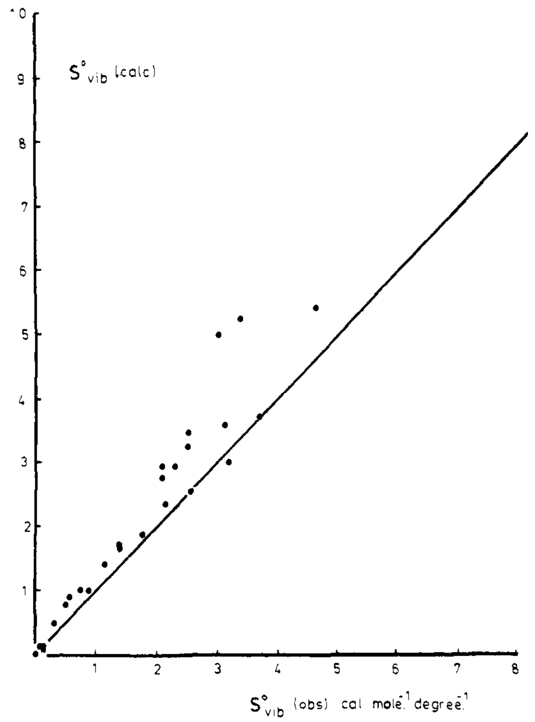
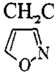
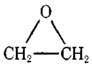
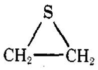
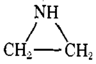
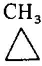
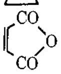
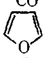
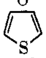
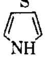


Figure 2. Calculated (MINDO/3) and observed vibrational contribution to the absolute entropy at 298.15 K.

Table II. Vibrational Contributions[a] to $S°$ at 298 K

Compd	S vib° obsd	S vib° calcd
H_2O	0.01	0.01
H_2S	0.04	0.14
NH_3	0.13	0.08
CO_2	0.72	1.01
CS_2	2.32	2.95
HCN	0.29	0.47
H_2CO	3.20	2.99
$CH_2{=}\overset{+}{N}{=}\overset{-}{N}$	2.47	3.24
CH_3Cl	0.50	0.74
CH_4	0.10	0.14
$CH{\equiv}CH$	1.41	1.69
$CH_2{=}C{=}O$	2.08	2.76
CH_3CN	2.56	2.51
CH_2CHCl	2.07	2.94
	2.10	2.33
	4.60	5.43
$CH_2{=}CH_2$	0.59	0.90
	0.90	1.00
	1.74	1.89
	1.14	1.41
$CH_2{=}C{=}CH_2$	3.09	3.58
$CH_3C{\equiv}CH$	3.66	3.68
	1.38	1.67
	7.60	9.42
	2.47	3.49
	3.53	5.23
	2.98	5.01

[a] Based on vibrational frequencies listed in Table I of ref 3.

Table III and compared graphically in Figures 3 and 4.

Table III and Figure 3 compare our calculated values of $S°$ with experiment. The average error is less than 1% or 0.5 cal mol^{-1} deg^{-1}. Only two of the compounds studied were in error by more than 1 cal mol^{-1} deg^{-1} at this temperature, i.e., furan and maleic anhydride (errors 1.01 and 1.84 cal mol^{-1} deg^{-1}, respectively). These errors are due largely to the presence of low-frequency vibrations which are underestimated by MINDO/3. Thus in the case of maleic anhydride, both the low-frequency carbonyl bending vibration (calcd, 111; obsd,[11] 173 cm^{-1}) and out of plane ring deformation (calcd, 226; obsd,[11] 275 cm^{-1}) are substantially underestimated, accounting for two-thirds of the total error (1.20 vs. 1.84 cal mol^{-1} deg^{-1}).

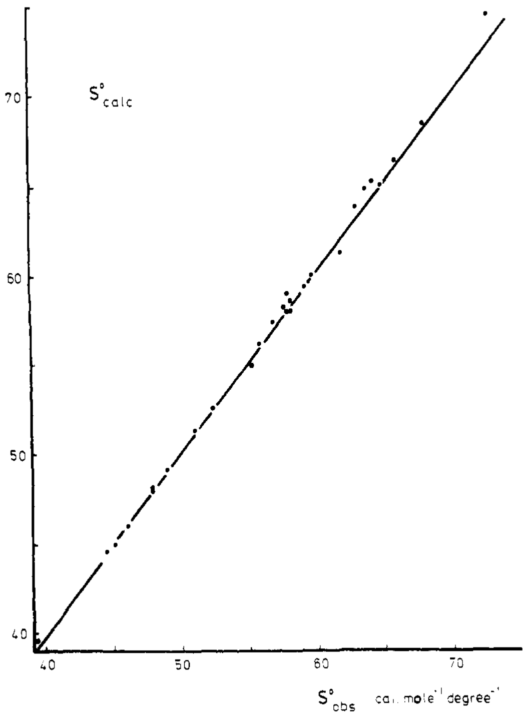


Figure 3. Calculated (MINDO/3) and observed entropies at 298.15 K.

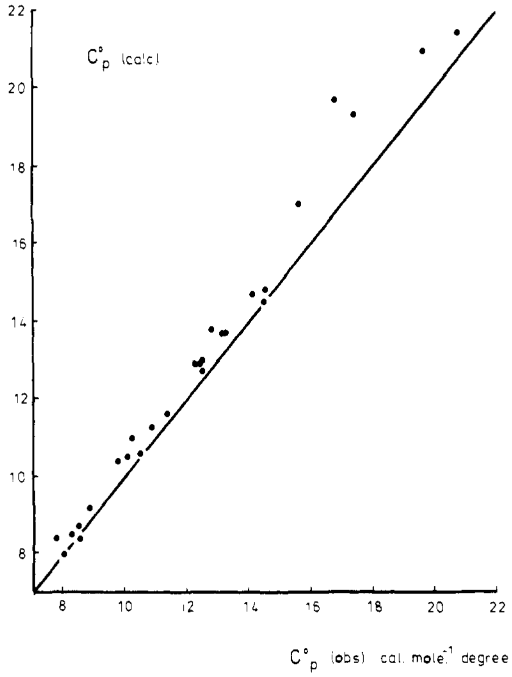
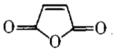
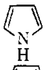
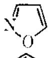


Figure 4. Calculated (MINDO/3) and observed heat capacities at 298.15 K. Since the only variables involved in this plot are the vibrational frequencies (cf. eq 6-8) this plot is, apart from a change of origin, identical with that of the calculated and observed vibrational contributions to $C_p°$ (not shown).

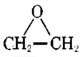
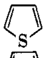
Table III and Figure 4 compare our calculated specific heats $C_p°$ with experiment. Here errors in the vibrational frequencies have a more serious effect than they do in the case of entropies. Nevertheless, the average error was only 0.63 cal mol^{-1} deg^{-1} (4.4%). At higher temperatures the agreement improves because better estimates of $(C_p°)_{vib}$ are obtained as more vibrational levels become populated. For example, at 600 K the average absolute error in $C_p°$ falls to 0.39 and at 900 K to 0.35

Table III. Calculated and Observed Entropies and Heat Capacities at 298 K[a]

	$S°$, cal mol^{-1} deg^{-1}			$C_p°$, cal mol^{-1} deg^{-1}		
Compd	Obsd	Calcd	Error	Obsd	Calcd	Error
H_2O	45.1	45.0	0.1	8.0	8.0	0.0
H_2S	49.1	49.2	−0.1	8.2	8.5	−0.3
NH_3	46.0	46.0	0.0	8.5	8.4	0.1
CO_2	51.1	51.4	−0.3	8.9	9.2	−0.3
CS_2	56.8	57.4	−0.6	10.9	11.3	−0.4
HCN	47.9	48.1	−0.2	7.8	8.4	−0.6
H_2CO	55.3	55.0	0.3	10.1	10.5	−0.4
CH_2N_2	58.0	58.7	−0.7	12.5	13.0	−0.5
CH_3Cl	55.9	56.1	−0.2	9.7	10.4	−0.7
CH_4	44.5	44.6	−0.1	8.5	8.7	−0.2
$CH{\equiv}CH$	48.0	48.3	−0.3	10.5	10.6	−0.1
$CH_2{=}C{=}O$	57.8	58.3	−0.5	12.4	12.9	−0.5
CH_3CN	58.1	58.1	0.0	12.5	12.7	−0.2
$CH_2{=}CHCl$	63.1	63.9	−0.8	12.8	13.8	−1.0
$CH_2{=}CH_2$	52.4	52.6	−0.2	10.2	11.0	−0.8
	58.0	58.0	0.0	11.4	11.6	−0.2
	61.9	61.3	0.6	13.3	13.7	−0.4
	59.8	60.0	−0.2	12.2	12.9	−0.7
$H_2C{=}C{=}CH_2$	58.2	58.6	−0.4	14.1	14.7	−0.6
$CH_3C{\equiv}CH$	59.3	59.3	0.0	14.5	14.5	0.0
	56.6	56.9	−0.3	13.1	13.7	−0.6
	72.6	74.5	−1.9	20.7	21.4	−0.7
	63.8	64.8	−1.0	15.6	17.0	−1.4
	67.9	68.3	−0.8	17.4	19.3	−1.9
	65.8	66.4	−0.6	16.8	19.7	−1.9
	64.8	65.0	0.0	14.5	14.8	−0.3
	64.3	65.2	−0.9	19.6	20.9	−1.3

[a] Calculated via eq 1–8, the experimental and MINDO/3 vibrational frequencies listed in Table I of ref 3, and moments of inertia in Table I (this paper).

Table IV. Comparison of Absolute Entropies Determined Calorimetrically from Spectroscopic Data and by MINDO/3

Compd	Temp, K	$S°$ exp[a]	$S°$ spec[b]	$S°$ MINDO[c]
NH_3	239.68	44.13 ± 0.10[d]	44.22	44.25
CH_3Cl	248.96	54.27 ± 0.15[e]	54.24	54.33
CH_3CN	298.15	58.67 ± 0.20[f]	58.15	58.09
$CH_2{=}CH_2$	169.40	47.36 ± 0.10[g]	47.33	47.32
	283.66	57.38[h]	57.45	57.46
	298.15	63.86 ± 0.10[i]	63.83	64.84
	357.32	70.40 ± 0.20[j]	71.40	72.10
	362.11	68.38 ± 0.15[k]	69.41	70.63

[a] Correction to hypothetical ideal gas state has been made by the original workers in each case. [b] Calculated via eq 1, 3, 5, experimental frequencies collected in Table I of ref 3, and moments of inertia from Table I (this paper). [c] Calculated via eq 1, 3-5, MINDO/3 vibrational frequencies collected in Table I of ref 3, and moments of inertia from Table I (this paper). [d] R. Overstreet and W. F. Giauque, *J. Am. Chem. Soc.*, 59, 254 (1937). [e] G. H. Messerley and J. G. Aston, *ibid.*, **62**, 886 (1940). [f] W. E. Putnam, D. M. McEachern, Jr., and J. E. Kilpatrick, *J. Chem. Phys.*, 42, 749 (1965). [g] C. J. Egan and J. D. Kemp, *J. Am. Chem. Soc.*, 59, 1264 (1937). [h] W. F. Giauque and J. Gordon, *ibid.*, 71, 2176 (1949). [i] G. B. Guthrie, Jr., D. W. Scott, W. N. Hubbard, C. Katz, J. P. McCollough, M. E. Cross, K. D. Williamson, and G. Waddington, *ibid.*, 74, 4662 (1952). [j] G. Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver, S. S. Todd, W. N. Hubbard, J. C. Smith, and H. M. Huffman, *ibid.*, 71, 797 (1949). [k] D. W. Scott, W. T. Berg, I. A. Hossenlopp, W. N. Hubbard, J. F. Messerley, S. S. Todd, D. R. Douslin, J. P. McCullough, and G. Waddington, *J. Phys. Chem.*, 71, 2263 (1967).

cal mol^{-1} deg^{-1} (1.69%). Naturally at higher temperatures the limitations of the RRHO approximation become more severe. For example, the inclusion of anharmonicity,[12] centrifugal distortion,[13] and rotation-vibration[14] corrections for methane[15] accounts for 0.2, 0.5, 1.4, and 11.6% of $C_p°$ at 298.15, 600, 1000, and 5000 K, respectively, although the corrections to the other thermodynamic functions are smaller.[15]

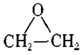
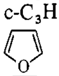
In a number of cases it is possible to compare the theoretical values of $S°$ and $C_p°$ with those determined calorimetrically. For this comparison to be meaningful, the experimental values should be corrected for gas imperfections, often the greatest source of uncertainty in these data. Nevertheless, inspection of Tables IV and V reveals that values of both $S°$ and $C_p°$ determined calorimetrically (including corrections for gas imperfections), spectroscopically, and by MINDO/3 are in excellent agreement. The only exceptions are the MINDO/3 results for the five-membered ring heterocycles which were discussed above.

Applications

Activation Entropies. The computational procedure was identical with that described above except that only $3n - 7$ vibrations in the transition state were considered, the imaginary frequency corresponding to translation along the reaction coordinate being excluded from the summation of eq 5. Results for six reactions that have been studied in these laboratories recently[7,8,16] are given in Table VI. Unfortunately the restriction to rigid systems was particularly severe in this connection. While none of these systems are entirely rigid, reactions 2-4 are essentially so and show small positive values of $\Delta S^{\ddagger}$ consistent with a slight "loosening" of the reactant molecule in the transition state. However, since the absolute magnitudes of $\Delta S^{\ddagger}$ are small it is difficult to make a more detailed comparison in these cases as the experimental uncertainties are so large. Indeed the quoted uncertainties were often somewhat on the optimistic side. For example, the discrepancy between the calculated and experimental values of $\Delta S^{\ddagger}$ for reaction 3 was rather disturbing, particularly as this kinetic study[17] appeared to be one of the more detailed we had considered. However, upon reanalysis of the published data[17] according to the Eyring equation in a least-squares procedure and calculating the error limits according to the Student's *t* distribution for the appropriate number of degrees of freedom we found for the 95% confidence limit $\Delta S^{\ddagger} = 4.27 \pm 2.06$ cal mol^{-1} deg^{-1} and at the 99% confidence limit $\Delta S^{\ddagger} = 4.27 \pm 2.97$ cal mol^{-1} deg^{-1}. By way of illustration we have also included three reactions which definitely involve nonrigid species. In spite of this, reaction 1[8] (Table VI), the retro-Diels-Alder decomposition of cyclohexene, seems to be well calculated. On the other hand, the several low frequencies exhibited by the reactants in 5 and 6 (Table VI) are probably responsible for the calculated values of $\Delta S^{\ddagger}$ being slightly too negative. Nevertheless, the present method is evidently capable of giving reasonable approximations to $\Delta S^{\ddagger}$ even when some nonrigidity is present, as the contributions from these sources largely cancel.

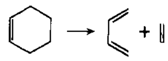
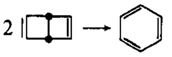
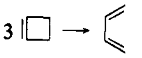
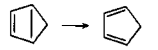
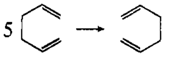
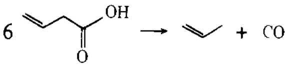
Equilibria at Elevated Temperatures. In order to test the MINDO/3 method adequately in this respect we have chosen six reactions of industrial importance for which we could make parallel calculations using conventional methods from accurately known spectroscopic data. The deficiencies of the

Table V. Comparison of Absolute Heat Capacities Determined Calorimetrically, from Spectroscopic Data, and by MINDO/3

Compd	Temp, K	$C_p°$ exp[a]	$C_p°$ spec[b]	$C_p°$ MINDO[c]
H_2O	381.20	8.112[d]	8.13	8.15
CO_2	300.06	8.903[e]	8.90	9.24
CS_2	325.65	11.175[f]	11.18	11.54
$CH\equiv CH$	291.15	10.46[g]	10.40	10.49
$CH_2=CH_2$	300.00	10.39[h]	10.29	11.05
	307.18	11.80[i]	11.90	11.68
$CH_2=C=CH_2$	300.00	14.18[j]	14.13	14.77
$CH_3C\equiv CH$	299.59	14.58[j]	14.56	14.57
c-C_3H_6	300.48	13.50[j]	13.20	13.81
	298.15	15.63[k]	15.64	17.04
	298.15	17.31[l]	17.39	19.28
	388.20	22.43[m]	22.33	25.08

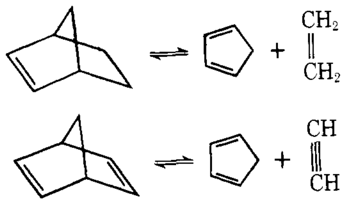
[a] Corrections to the hypothetical ideal gas state have been made by the original workers in each case. [b] Based on experimental vibrational frequencies (Table I, ref 3) and moments of inertia (Table I, this paper). [c] Based on MINDO/3 vibrational frequencies (Table I, ref 3) and moments of inertia (Table I, this paper). [d] J. P. McCullough, R. E. Pennington, and G. Waddington, *J. Am. Chem. Soc.*, 74, 4439 (1952). [e] G. B. Kistiakowsky and W. W. Rice, *J. Chem. Phys.*, 7, 281 (1939). [f] G. Waddington, J. C. Smith, K. D. Williamson, and D. W. Scott, *J. Phys. Chem.*, 66, 1074 (1962). [g] W. Heuse, *Ann. Phys. (Leipzig)*, 59, 86 (1919). [h] B. J. Burcik, E. H. Eyster, and D. M. Yost, *J. Chem. Phys.*, 9, 118 (1941). [i] G. B. Kistiakowsky and W. W. Rice, *ibid.*, 8, 618 (1940). [j] Reference 13. [k] G. B. Guthrie, Jr., D. W. Scott, W. N. Hubbard, C. Katz, J. P. McCullough, M. E. Gross, K. D. Williamson, and G. Waddington, *J. Am. Chem. Soc.*, 74, 4662 (1952). [l] G. Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver, S. S. Todd, W. N. Hubbard, J. C. Smith, and H. M. Huffman, *ibid.*, 71, 797 (1949). [m] D. W. Scott, W. T. Berg, I. A. Hossenlopp, W. N. Hubbard, J. F. Messerley, S. S. Todd, D. R. Douslin, J. P. McCullough, and G. Waddington, *J. Phys. Chem.*, 71, 2263 (1967).

Table VI. Comparison of Calculated and Observed Values of $\Delta S^{\ddagger}$ (cal mol^{-1} deg^{-1})

		Temp, K	$\Delta S^{\ddagger}$ (obsd)	$\Delta S^{\ddagger}$ (calcd)
1		600	8.05[a]	9.0[b,c]
2		321	-5.0 ± 7.0[d]	1.48[c]
3		423	0.1 ± 0.9[e]	0.76
4		350	4.4 ± 0.9[f]	1.60[c]
5		523	-13.8 ± 1.0[g]	-17.0[h]
6		650	-10.2 ± 2.5[i]	-13.9[j]

[a] M. Uchiyama, T. Tadas, and A. Amans, *J. Phys. Chem.*, 68, 1878 (1964). [b] Reference 8. [c] Since the transition state in these reactions had some biradical character we calculated the geometries and vibrational frequencies using a UHF version of our program. [d] Measurements in $CCl_2=CCl_2$ solution: R. Breslow, J. Napierski, and A. H. Schmidt, *J. Am. Chem. Soc.*, 94, 5096 (1972). [e] R. W. Carr, Jr., and W. D. Walters, *J. Phys. Chem.*, 69, 1073 (1965). [f] D. M. Golden and J. I. Brauman, *J. Am. Chem. Soc.*, 90, 1920 (1968); *Trans. Faraday Soc.*, 65, 464 (1969). [g] M. J. Goldstein and M. S. Benzon, *J. Am. Chem. Soc.*, 94, 5119, 7147 (1972). [h] Reference 16e. [i] G. G. Smith and S. E. Blau, *J. Phys. Chem.*, 68, 1231 (1964). [j] Reference 7.

Scheme I



RRHO approximation at higher temperatures have already been mentioned. In practice, however, except at very high temperatures, these corrections are small in comparison with the errors implicit in the use of vibrational frequencies derived from MO theory. Thus no attempt to incorporate them has been made, although in principle this is possible. Indeed, although we have not attempted to calculate anharmonicity constants to date, both Coriolis coupling constants and centrifugal distortion constants calculated from the MINDO/3 force fields agree to within about 10% of the experimental values for a variety of small molecules.[18]

Since energies calculated by MINDO/3 are not accurate enough for the present purpose, we had to use one experimental value, i.e., the heat of reaction (ΔH) at 25 °C (298.15 K).[19] We then calculated the values of ΔH at other temperatures, using our calculated specific heats ($C_p°$) to estimate the specific heat of reaction (ΔC_p) as a function of temperature together with Kirschoff's equation,

$$\Delta H^T = \Delta H^{298.15} + \int_{298.15}^{T} (\Delta C_p)\mathrm{d}T \qquad (9)$$

We also calculated the entropies of reaction (ΔS) as a function of temperature from the corresponding MINDO/3 entropies ($S°$) of the reactants and products, and hence the free energy of reaction, ΔG:

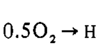
$$\Delta G^T = \Delta H^T - T\Delta S^T \qquad (10)$$

Table VII compares calculated and observed values of ΔG^T for the six reactions at 300, 900, and 1200 K. The errors in ΔG are nearly all less than 1 kcal mol^{-1}, the only exception being the fifth reaction (formation of HCN) where MINDO/3 would be expected to be less satisfactory in view of its known[4] weakness for molecules containing triple bonds. For the other five reactions the errors in ΔG correspond to an error of less than a factor of 1.5 in the equilibrium constant K, except for the third (formation of ethylene oxide) at 300 K where the calculated value is too small by a factor of 1.57. These results suggest that MINDO/3 may be of practical value in assessing the potential utility of possible reactions since it requires only a knowledge of the heats of formation of the reactants and products at one temperature (e.g., the standard values at 25 °C) to provide good estimates of equilibrium constants over a wide range of temperature.

Thermochemical Data for Large Molecules. As mentioned in the Introduction, unambiguous assignment of the fundamental vibrations of large molecules necessary for the calculation of the thermochemical properties may be difficult or impossible owing to the complex nature of the spectra. Reliable estimates of the moments of inertia from either microwave spectra or electron diffraction data may also be lacking.

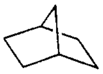
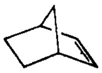
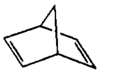
A case in point is norbornene (**1**). The available vibrational data[20] are incomplete and structural data[21] unsatisfactory.[22] Thus as examples of the present application we calculate the absolute entropies of **1** and the related molecules, norbornane (**2**) and norbornadiene (**3**). Accurate determinations of $S°$ from spectroscopic data are available for both **2**[23] and **3**.[23] The equilibria of Scheme I have been studied by Walsh and Wells[22,23] at several temperatures. Unfortunately the analysis of equilibrium data according to the usual van't Hoff plot, the method used in ref 22 and 23, leads to some uncertainty in the

Table VII. Free Energies of Reaction for Several Industrially Important Reactions Calculated from MINDO/3 Molecular Orbital Theory and Experimental Heats of Formation at 298 K

		Free energy of reaction:[b] ΔG, kcal/mol					
		300 K		900 K		1500 K	
Reaction	ΔH_{298}[a]	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
$N_2 + 3H_2 \rightarrow 2NH_3$	−21.94	−7.74	−7.82	24.24	24.15	58.36	57.55
$2CH_4 \rightarrow CH{\equiv}CH + 3H_2$	88.80	68.01	68.04	31.65	31.91	−7.43	−7.01
$CH_2{=}CH_2 + 0.5O_2 \rightarrow$  $\overset{O}{H_2C{-}CH_2}$	−25.12	−19.45	−19.72	−7.70	−8.07	3.88	5.00
$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$	39.45	27.07	27.03	−2.02	−1.80	−34.25	−33.72
$CH_4 + NH_3 + 1.5O_2 \rightarrow HCN + 3H_2O$	−112.33	−118.02	−119.02	−129.48	−133.81	−139.83	−143.43
$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$	−24.82	−25.64	−25.60	−27.48	27.52	−29.46	−29.78

[a] Reference 14. [b] Calculated for ideal gas state at 1 atm pressure.

Table VIII. Comparison of Calculated and Observed Values of $S°$ and $C_p°$ for Norbornene (1), Norbornane (**2**), and Norbornadiene (3)

	2 	1 		3 	
	298.15 K	298.15 K	560.0 K	298.15 K	600.0 K
Method			$S°$, mol^{-1} deg^{-1}		
Additivity[a] rules	75.7	75.1		72.6	
Spectroscopic	74.33[b]	~76.3[c] ~74.3[c,d]	~100.6[c,e] ~98.7[c,d,e]	71.75[b] 70.64[b,d]	97.29[b] 95.50[b,d]
Calorimetric	74.0 ± 0.6[f]				
Equilibria			97.95 ± 0.36[g]		96.69 ± 0.50[h]
MINDO/3	73.86	73.9	97.59	71.75	96.41
			$C_p°$, cal deg^{-1} mol^{-1}		
Additivity[a] rules	26.9	24.6		24.1	
Spectroscopic	28.70[b]	~27.4[c] ~26.9[c,d]		25.24[b] 23.94[b,d]	
MINDO/3	27.09	25.74		24.39	

[a] Reference 26. [b] Reference 23. [c] Approximate values from incomplete spectral data: see ref 22. [d] Duplicate values for alternate assignments. [e] From interpolation of data in ref 22. [f] Reference 25. [g] Calculated from data in ref 22, 24, and 19; see text. [h] Calculated from data in ref 23, 24, and 19; see text.

calculated values of ΔS owing to variation of the latter with temperature. For the equilibrium involving **1** which was studied[22] in the temperature range 531-589 K our calculations suggest a variation of 5.2 cal mol^{-1} deg^{-1} in ΔS. To circumvent this problem we have reanalyzed the data of Walsh and Wells[22] in the following way. Log K values were fitted to a polynomial (order 2) in $1/T$ and ΔH found by direct differentiation at the mean temperature of 560 K [$\Delta H(560) = -24.89$, lit.[22] −24.88]. From the value of ΔG calculated from the polynomial fit at 560 K and this value of ΔH, $\Delta S = 43.43 \pm 0.36$ was derived. The value obtained by Walsh and Wells[22] (45.46 ± 0.36) was somewhat higher owing to the curvature of the log K vs. $1/T$ plot. The absolute entropy of **1** was then obtained from ΔS together with values of $S°$ for cyclopentadiene and ethylene interpolated from published data[19,24] for 560 K. The analogous equilibrium involving **3** was studied by Walsh and Wells[23] at only three temperatures so here a similar analysis was not possible. However, our calculations indicate a rather smaller variation of ΔS (3.6 cal mol^{-1} deg^{-1}) in the temperature range studied. Only for **2** has a calorimetric determination of $S°$ been reported.[25] These results together with those of our MINDO/3 calculations are collected in Table VIII. Clearly the MINDO/3 results are in excellent agreement with experiment and superior to those from the additivity relationships of O'Neal and Benson.[26] The values of $S°$ for **1** deduced by Walsh and Wells[22] from the incomplete spectral data[20] and group vibrational frequencies are indeed too high as was noted by these authors. There seem to have been no calorimetric determinations of $C_p°$ for any of these systems. The MINDO/3 calculated values are, however, in good agreement with those from spectroscopic data,[22,23] although curiously in better agreement with the empirical values[26] in this case.

Thus for compounds **1-3**, which admittedly are a rather favorable case being highly rigid hydrocarbons, MINDO/3 calculations are apparently capable of achieving an accuracy comparable with experiment.

Summary and Conclusions

The MINDO/3 molecular orbital technique is capable of yielding moments of inertia and molecular vibration frequencies of sufficient accuracy to enable absolute entropies and heat capacities to be calculated within the RRHO approximation with an accuracy in most cases of better than ±1 cal mol^{-1} deg^{-1}. In those cases where agreement falls outside this range, the errors may be attributed to the underestimation of the low-frequency vibration by the MINDO/3 procedure. This was the case for the five-membered ring heterocycles.

For the few reactions amenable to study by these methods the activation entropies were calculated to be small and positive and agree with the experimental determinations. Acceptable results were also obtained for several reactions involving nonrigid systems in which effective cancellation of errors was observed. The extension of the present methods to nonrigid systems is in hand.

Acknowledgments. This work was supported by the Air Force Office of Scientific Research (Grant AFOSR 75-2749) and the Robert A. Welch Foundation (Grant F-126). The calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computation Center.

Supplementary Material Available: Tables IX-XI, calculated Cartesian coordinates, moments of inertia, and vibrational frequencies of norbornene (**1**), norbornane (**2**), and norbornadiene (**3**) (6 pages). Ordering information is given on any current masthead page.

References and Notes

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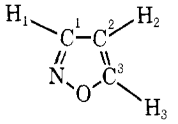
(9) MINDO/3 geometries for compounds not previously published follow: $CH_2{=}N^+{=}N^-$ NN = 1.113; CN = 1.274; CH = 1.113; HCH = 115.1; lit.[10] NN = 1.139; CN = 1.300; CH = 1.077; HCH = 126.1°.



NO = 1.368; NC^1 = 1.312; C^1C^2 = 1.445; C^2C^3 = 1.371; CO = 1.323; H^1C^1 = 1.106; H^2C^2 = 1.095; H^3C^3 = 1.106; C^3ON = 110.57°; ONC^1 = 106.71°; NC^1C^2 = 109.93°; $C^1C^2C^3$ = 107.44°; C^2C^3O = 105.35°; $H^1C^1C^2$ = 126.77°; $H^2C^2C^3$ = 128.83°; $H^3C^3C^2$ = 133.78.

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Dissociative Pathways and Molecular Vibrations. Compliance Constants and Minimum Energy Coordinates for BF_3 and SO_3

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Abstract: The minimum energy paths for unimolecular dissociation of SO_3 and BF_3 have been probed using vibrational spectroscopy and the semiempirical SCF-MO scheme MNDO. Minimum energy coordinates obtained from spectroscopic data show that initially the minimum energy pathway (MEP) is heterolytic in character, leading to BF_2^+ and SO_2^+ products. Since the thermodynamically favored products are radicals, this information suggests that the MEP must assume covalent character after the initial distortion. A constrained MEP for BF_3, as evaluated using the MNDO SCF-MO method, closely parallels the vibrational minimum energy coordinate out to 0.25 Å distortion of a B-F bond. At greater extensions, inclusion of configuration interaction in the MNDO calculations, or use of the UHF approach, reveals the increasing contribution of an excited covalent electronic configuration to the wave function. This avoided crossing eventually leads to homolytic bond cleavage. Implications concerning the use of minimum energy coordinates as a model of dissociative pathways are discussed.

Introduction

Chemists interested in studying bonding phenomena using vibrational spectroscopy generally model molecular vibrations in terms of displacement coordinates and the Wilson GF formalism.[1] In spite of the wide usage that the GF method has enjoyed, there are difficulties in using force constants as probes of interatomic forces. The value of a force constant is dependent on the coordinate set used to describe the molecule and the force matrix is indeterminant when there are redundancies among the internal coordinates.[2,3] While these mathematical difficulties do not interfere with many aspects of a vibrational study, they are troublesome when it comes to using force constants as bonding parameters. We have been interested in exploring the utility of the alternative compliance constant method,[2-4] which does not have these difficulties.

One of the appealing aspects of the compliant formalism is the direct connection between compliance constants and the reaction coordinate for unimolecular dissociation via minimum energy coordinates[5,6]

$$\mathcal{R}_i = \mathbf{r}_i + \sum_{\substack{j=1\\ \neq i}}^{n} (j)_i \mathbf{r}_j = \mathbf{r}_i + \sum_{\substack{j=1\\ \neq i}}^{n} (C_{ij}/C_{ii})\mathbf{r}_j \qquad (1)$$

Here $\{\mathbf{r}_i\}$ are unit vectors along the internal coordinate directions, $\{(j)_i\}$ are interaction displacement coordinates,[7] C_{ij} are valence compliance constants, and n gives the number of internal coordinates.

The interest in a tie between reaction pathways and potential functions is by no means new. Linnett and Wheatley[8] and Mills[9] had devised approximate force fields based on the apparent relationship between the signs of the interaction force constants and the geometry change expected upon dissociation.

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