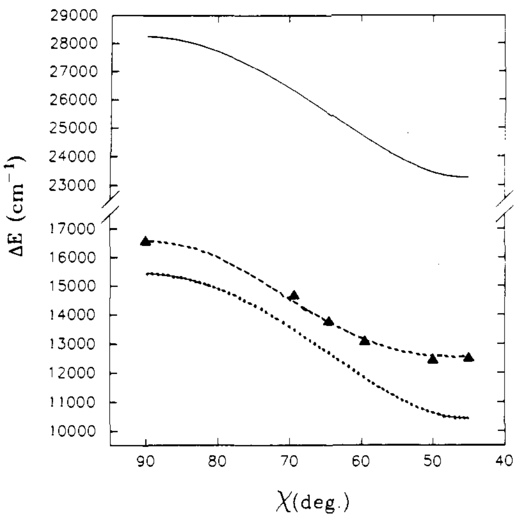

Figure 7. Comparison of the singlet δ–δ^* transition energies as a function of the internal rotation angles: (—) calculated results for $Mo_2Cl_4(PH_3)_4$; (- - -) from a non-linear least-square fitting of the measured results (▲) for molecules of the $Mo_2Cl_4(PP)_2$ type; (···) corrected results by subtracting 1.59 eV from the calculated results.

The nature of this error has been recognized by Hay[9] in his calculation of the same transition energy in $[Re_2Cl_8]^{2-}$ by the GVB method. It is well-known that, as in the valence-bond treatment, the $^1\delta\delta^*$ state can be shown by conventional LCAO MO theory to be a purely ionic state in which an atomic d orbital on one of the metal centers would be found to be doubly occupied. Very strong electron correlation is then associated with such a double occupation.[21] There is good reason[21,22] to expect that such an atomic intrapair correlation energy could be at least 1 eV in the second transition series. The CASSCF wave function employed in our present study is, however, not capable of treating this type of correlation properly, although it gives a good description of electron correlation in the ground state which is predominantly covalent. Absence of the atomic intrapair correlation energy in the $^1\delta\delta^*$ state in our calculations, therefore, leads to a high energy for the state.

There have been some attempts[23] to calculate the atomic intrapair correlation energy for pairs of 3d electrons. The correlation energy may also be estimated empirically or semiempirically as in an MGVB study on the Cr_2 and Mo_2 molecules by Goodgame and Goddard.[22] These authors corrected the correlation error that primarily arises from the negative ionic terms by decreasing the values of the one-center self-Coulomb integrals. The correction to the atomic self-Coulomb energy for a 4d pair in Mo atoms was given to be 1.59 eV. Simply accepting this value (1.59 eV) as the atomic intrapair correlation energy in our case may not be justified but, certainly, a good estimation of the correlation energy should not be very different from this value. As such, we then simply subtracted 1.59 eV from our calculated singlet δ–δ^* transition energies and plotted the results in Figure 7. As shown in the figure by the dotted curve, the final results have indeed improved dramatically and agree satisfactorily (ca. 1000 cm^{-1}) with the measured results.

Acknowledgment. We thank the National Science Foundation for support. We are grateful to Professor M. B. Hall and Dr. Z. Lin for helpful discussions and for access to their GAMESS program package. Texas A&M University Supercomputer Center is also thanked for granting computer time.

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Solvent Effects. 4. Effect of Solvent on the *E*/*Z* Energy Difference for Methyl Formate and Methyl Acetate

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Abstract: The effect of solvent on the difference in energy between the *E* and *Z* rotamers of methyl formate and methyl acetate has been studied using reaction field theory and the spherical cavity approximation. The calculated free energy difference for methyl formate was reduced from 5.2 kcal/mol in the gas phase to 1.6 kcal/mol for ϵ = 35.9 (acetonitrile). Similarly, with methyl acetate the difference was reduced from 8.5 to 5.2 kcal/mol. The changes in geometry, dipole moments, charge distributions, and vibrational frequencies on going from ϵ = 1 to 35.9 also were calculated and are in accord with increasing polar character of the carbonyl group in the more polar solvent. The change in *E*/*Z* energy difference for methyl formate was in very good agreement with that found previously using a more detailed treatment of the solvent interaction, and the change in energy difference for methyl acetate was also in good agreement with that calculated by statistical mechanics simulation. The change in equilibrium constant as a function of temperature in acetonitrile was calculated for methyl formate, and it was found that the change in dielectric constant of the solvent with temperature led to a much smaller than expected change in equilibrium constant with temperature. It is likely that the ΔH° and $\Delta H^\ddagger$ values derived by measuring equilibrium or rate constants as a function of temperature in polar solvents will often be considerably in error because of the change in solvent dielectric constant with temperature.

1. Introduction

The difference in properties between *Z*- and *E*-ester rotamers has been the subject of a number of experimental and theoretical studies. The *Z* rotamer of methyl formate has been found to be 4.8 kcal/mol more stable than the *E* form, and with methyl acetate the energy difference was found to increase to 8.5 ± 1 kcal/mol.[1] The barrier to rotation about the C–O bond for methyl acetate was 10–15 kcal/mol. The experimental results have been re-

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0002-7863/93/1515-1078$04.00/0

produced by extended basis set ab initio calculations including correction for electron correlation.[2]

The *E* rotamer of methyl acetate has been calculated to be significantly more acidic than the *Z* form, and this has been related to the observed unusually high acidity of Meldrum's acid.[3,4] The *E* rotamers of esters have been calculated to be significantly more basic than the *Z* forms, and this corresponds to the experimental observation that lactones having the *E*-ester conformation are considerably more basic toward methyl cation than are the larger ring lactones having the *Z*-ester conformation.[5]

The infrared spectra of both forms of methyl formate[6] and methyl acetate[7] have been determined via matrix isolation, and the spectra in the gas and liquid phases also have been studied. Some significant frequency shifts have been noted on going from one phase to another.

One important difference between the ester rotamers is found in their dipole moments. Whereas the *Z* rotamers have relatively low dipole moments, those for the *E* forms, in which the C–O bond dipoles reinforce each other, are quite large. As a result, there should be a fairly large solvent effect on the *E*/*Z* energy difference. The estimation of the solvent effect via the use of reaction field theory[8] in the context of ab initio molecular orbital theory[9-12] is the subject of the present study. The effect of the solvent on the infrared spectrum and other properties also has been calculated.

2. Method of Calculation

There are two fundamentally different, but complementary, approaches to the nonempirical calculation of solvent effects. One approach explicitly represents the solvent molecules and samples their configurations about the solute through molecular dynamics or Monte Carlo statistical mechanics simulations.[13] Recently, such calculations have addressed the effect of going from the gas phase to acetonitrile as the solvent on the *E*/*Z* energy difference for methyl acetate.[14]

The alternative approach treats the solvent molecules as a continuous medium, characterized by the solvent's macroscopic dielectric properties. Onsager's reaction field model[8] as implemented in the context of ab initio molecular orbital theory represents one such approach. In its simplest form, the solute is taken as occupying a spherical cavity of radius a_0 in a medium which is represented as a continuous dielectric with a given dielectric constant (ϵ). If the solute has a permanent dipole moment, it will induce a reflection dipole in the medium. The interaction of the reflection dipole with the solute dipole leads to stabilization. The interaction is treated as a perturbation to the Hartree–Fock Hamiltonian, and the calculation is continued until self-consistency is achieved in the presence of the reaction field. This model has been applied to several conformational problems, leading to results that were in good agreement with experiment.[12] The model also may be used with procedures designed to correct for electron correlation, such as MP2, CISD, and QCI.[12] It is, of course, most applicable to solvents which do not have a specific association (such as hydrogen bonding) with the solute.

Other cavity shapes, such as an ellipsoid,[11] or an approximation to the van der Waals surface[10] have been used; the effect of higher moments also has been examined.[11] However, the simple model remains the only one for which analytical gradients and second derivatives are available.[15] They are needed for efficient geometry optimizations and calculations of vibrational frequencies in the presence of the reaction field. For small compact molecules such as methyl formate and methyl acetate, the use of a spherical cavity might be expected to be satisfactory. A related method that makes use of the calculated surface charge at the van der Waals surface to estimate the interaction with the solvent has been described by Tomasi et al. and has been applied to methyl formate.[16] It was of interest to see how well the two procedures agree for this case.

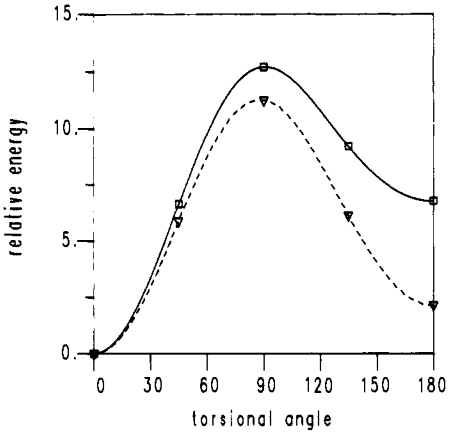

Figure 1. Rotational profile for methyl formate (kcal/mol). The solid line is for $\epsilon = 1$, and the dashed line is for $\epsilon = 36$.

In the molecular dynamics or Monte Carlo approach, one learns much about the effect of the solute on the solvent, but only limited information concerning the effect of solvent on the solute is obtained. Reaction field theory, on the other hand, gives detailed information on the effect of the solvent on the solute, but only limited information on the effect of the solute on the solvent. Therefore, the two approaches are complementary. Since Jorgensen et al. have studied the solvent effect on the *E*/*Z* energy difference for methyl acetate in this fashion,[14] the present investigation provides an opportunity to compare the results obtained via these two quite different methods of studying solvent effects.

The structures and energies of both rotamers of methyl formate and methyl acetate and of some structures along the path leading to rotamer interconversion have been calculated for the gas phase and for $\epsilon = 35.9$ (the observed value for acetonitrile).[17] A cavity radius of 3.4 Å was used with methyl formate, and 3.65 Å was used for methyl acetate. These cavity radii were based on the observed molecular volumes[18] plus an empirically determined additive factor of 0.5 Å to account for the nearest approach of solvent molecules.[12] The center of the spherical cavity was taken as the center of mass. The results are summarized in Table I for methyl formate and in Table II for methyl acetate. Some changes in geometry were found on going from the gas phase to solution, and they are summarized in Tables III and IV.

Calculations: The ab initio calculations were carried out using GAUSSIAN-91[23] and standard basis sets.[22] The charges were calculated

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Table I. Calculated Energies of Methyl Formate Rotamers[a]

a. Energies (H)

	6-31G*		6-31 + G**		MP2/6-31 + G**	
τ (deg)	ϵ = 1	ϵ = 35.9	ϵ = 1	ϵ = 35.9	ϵ = 1	ϵ = 35.9
0 (Z)	−227.789 42	−227.790 70	−227.802 50	−227.803 98	−228.456 26	−228.457 46
45	−227.779 22	−227.781 10	−227.791 90	−227.794 59		
90	−227.769 04	−227.772 29	−227.782 24	−227.786 03	−228.433 61	−228.436 68
135	−227.774 55	−227.780 15	−227.787 84	−227.794 22		
180 (E)	−227.779 45	−227.786 33	−227.792 73	−227.800 56	−228.446 62	−228.453 53

b. Relative Energies (ΔE, kcal/mol)

	6-31G*		6-31 + G**		MP2/6-31 + G**		MP2 + ZPE	
τ (deg)	ϵ = 1	ϵ = 35.9	ϵ = 1	ϵ = 35.9	ϵ = 1	ϵ = 35.9	ϵ = 1	ϵ = 35.9
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
45	6.40	6.02	6.65	5.89				
90	12.79	11.55	12.71	11.26	14.21	13.04	13.44	12.27
135	9.33	6.22	9.20	6.12				
180	6.25	2.74	6.76	2.14	6.05	2.47	5.57	2.05

c. Dipole Moments (D)

	6-31G*		6-31 + G**		MP2/6-31 + G**	
τ (deg)	ϵ = 1	ϵ = 35.9	ϵ = 1	ϵ = 35.9	ϵ = 1	ϵ = 35.9
0	1.99	2.31	2.08	2.45	1.90	2.27
45	2.42	2.78	2.52	2.94		
90	3.22	3.67	3.40	3.92	2.95	3.44
135	4.15	4.82	4.36	5.15		
180	4.59	5.36	4.81	5.72	4.31	5.21

d. Scaled Zero-Point Energies[a] (ZPE, kcal/mol), $H - H_0$ (kcal/mol), Entropy (S, cal/mol), and Relative Free Energies (ΔG, kcal/mol) at Room Temperature (298 K)[b]

	ZPE		$H - H_0$		S		ΔG^c	
τ (deg)	ϵ = 1	ϵ = 35.9	ϵ = 1	ϵ = 35.9	ϵ = 1	ϵ = 35.9	ϵ = 1	ϵ = 35.9
0	38.16	38.12	3.33	3.33	67.04	67.15	0.00	0.00
90	37.38	37.34	3.11	3.12	65.90	65.99	13.55	12.41
180	37.68	37.68	3.56	3.55	69.18	69.16	5.16	1.66

[a] Scaled by 0.9. [b] All energies were calculated using the HF/6-31G* optimized geometries. [c] The MP2/6-31+G** energies were used in deriving these free energies.

using PROAIM.[24]

3. Methyl Formate

Geometry optimization for methyl formate was carried out at the HF/6-31G* level for several O–C–O–CH_3 torsional angles from 0° (Z) to 180° (E) with both ϵ = 1.0 and ϵ = 35.9 (corresponding to acetonitrile). Energies were calculated using the 6-31+G** basis set, which should give improved relative energies. The energy changes for the gas phase and for the more polar medium are summarized in Figure 1. Correction for electron correlation also was carried out using second-order Møller–Plesset perturbation theory (MP2). At the highest level of theory used in this study, MP2/6-31+G**, the E/Z energy difference (ΔE) was 6.1 kcal/mol for the gas phase, and it dropped to 2.5 kcal/mol with ϵ = 35.9.

For a comparison with experimental data, it is important to correct for the difference in zero-point energy between the E and Z forms. The vibrational frequencies were calculated both in the presence[15] and in the absence of the reaction field (Tables V and VI). The difference in energy for the gas phase decreased to 5.6 kcal/mol. We have previously calculated the energy difference for the gas phase at a somewhat higher level of theory (MP3/6-311+G**) and found an energy difference of 5.6 kcal/mol. Correction for the difference in zero-point energy would reduce the calculated difference to 5.1 kcal/mol. This is in very good agreement with the experimental value (4.9 kcal/mol). In the solution phase, the correction for zero-point energy reduced the E/Z energy difference to 2.1 kcal/mol.

It is important to note that the perturbation due to the reaction field is a free energy term. It would therefore be appropriate to correct the calculated energy difference for the entropy term to give free energy differences (ΔG). Section d of Table I gives the zero-point energies for the gas phase and the solution, the corresponding enthalpy changes on going from 0 to 298 K, and the entropies at 298 K. The gas-phase entropies were calculated using the translational, rotational, and vibrational partition functions. In solution, translation becomes diffusion, and its partition function is not well defined. However, for rotamers of an ester the diffusion terms should be essentially the same and would cancel. Therefore, the entropy was calculated using the gas-phase partition functions for translation and rotation, but the vibrational terms wre calculated using the vibrational frequencies appropriate to the phase. The final calculated free energy differences are 5.2 kcal/mol for ϵ = 1.0 and 1.6 kcal/mol for ϵ = 35.9.

Tomasi et al calculated the energy difference using reaction field theory, but making use of the calculated surface charge rather than the molecular dipole.[16] With the 4-31G basis set they found an E/Z energy difference of 7.5 kcal/mol for ϵ = 1 and 3.6 kcal/mol for ϵ = 36. The smaller basis set and the lack of correction for electron correlation led to a less satisfactory energy difference for ϵ = 1, but the effect of the basis set on the difference between ϵ = 1 and ϵ = 36 should be small. This difference, 3.9 kcal/mol, is in very good agreement with the present result (3.6 kcal/mol). It remains to be seen if this good agreement will be found with other molecules.

The calculated changes in structure on going from the gas phase to solution are shown in Table III. With the higher energy E rotamer (which has the larger dipole moment), the central C–O bond becomes shorter and the other C–O bonds become longer. These are the expected changes corresponding to an increase in dipole moment (4.3 D at ϵ = 1.0; 5.2 D at ϵ = 35.9).

We were interested in seeing if the predicted small E/Z energy difference in solution could be examined experimentally. If the equilibrium constant changed significantly with temperature, and

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Table II. Calculated Energies of Methyl Acetate Rotamers[a]

a. Energies (*H*)

	6-31G*		6-31 + G**		MP2/6-31+G**	
τ (deg)	$\epsilon = 1$	$\epsilon = 35.9$	$\epsilon = 1$	$\epsilon = 35.9$	$\epsilon = 1$	$\epsilon = 35.9$
0 (*Z*)	−266.836 83	−266.837 85	−266.853 35	−266.854 53	−267.655 93	−267.656 82
45	−266.817 14	−266.828 70	−266.843 80	−266.845 59		
90	−266.816 41	−266.819 40	−266.832 96	−266.836 83	−267.634 14	−267.648 53
135	−266.818 31	−266.832 34	−266.834 83	−266.840 59		
180 (*E*)	−266.821 84	−266.828 00	−266.838 34	−266.845 37	−267.642 23	−267.636 98

b. Relative Energies (ΔE, kcal/mol)

	6-31G*		6-31 + G**		MP2/6-31 + G**		MP2 + ZPE	
τ (deg)	$\epsilon = 1$	$\epsilon = 35.9$	$\epsilon = 1$	$\epsilon = 35.9$	$\epsilon = 1$	$\epsilon = 35.9$	$\epsilon = 1$	$\epsilon = 35.9$
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
45	6.08	5.47	5.99	5.60				
90	12.81	11.58	12.79	11.39	13.67	12.45	13.13	11.90
135	11.62	9.11	11.62	8.75				
180	9.41	6.48	9.42	5.75	8.60	5.20	8.53	5.17

c. Dipole Moments (D)

	6-31G*		6-31 + G**		MP2/6-31 + G**	
τ (deg)	$\epsilon = 1$	$\epsilon = 35.9$	$\epsilon = 1$	$\epsilon = 35.9$	$\epsilon = 1$	$\epsilon = 35.9$
0	1.99	2.27	2.09	2.42	1.82	3.15
45	2.31	2.81	2.59	2.99		
90	3.41	3.87	3.60	4.15	3.14	3.65
135	4.53	5.06	4.64	5.42		
180	4.85	5.61	5.11	6.00	4.61	5.47

d. Scaled Zero-Point Energies[a] (ZPE, kcal/mol), $H - H_0$ (kcal/mol), Entropy (*S*, cal/mol), and Relative Free Energy (ΔG, kcal/mol) at Room Temperature (298 K)[b]

	ZPE		$H - H_0$		*S*		ΔG[c]	
τ (deg)	$\epsilon = 1$	$\epsilon = 35.9$	$\epsilon = 1$	$\epsilon = 35.9$	$\epsilon = 1$	$\epsilon = 35.9$	$\epsilon = 1$	$\epsilon = 35.9$
0	54.81	54.77	4.26	4.26	75.62	75.62	0.00	0.00
90	54.27	54.23	3.89	3.90	73.02	73.09	13.55	13.32
180	54.74	54.75	4.23	4.20	75.58	75.22	8.51	5.24

[a] Scaled by 0.9. [b] All energies were calculated using the HF/6-31G* optimized geometries. [c] The MP2/6-31 + G** energies were used in deriving these free energies.

Table III. Effect of Solvent on Structures of Methyl Formate Rotamers (HF/6-31G*)

	0° (*Z*)			90°			180° (*E*)		
param[a]	$\epsilon = 1$	$\epsilon = 35.9$	diff	$\epsilon = 1$	$\epsilon = 35.9$	diff	$\epsilon = 1$	$\epsilon = 35.9$	diff
r(C=O)	1.184	1.186	0.002	1.177	1.180	0.003	1.177	1.184	0.007
r(C–O)	1.317	1.312	−0.005	1.342	1.336	−0.006	1.323	1.314	−0.009
r(C–H)	1.085	1.085	0.000	1.088	1.088	0.000	1.091	1.090	−0.001
r(O–C)	1.419	1.420	0.001	1.415	1.421	0.006	1.411	1.423	0.012
r(C–H_a)	1.078	1.077	0.001	1.078	1.077	−0.001	1.078	1.077	−0.001
r(C–H_b)	1.080	1.080	0.000	1.082	1.082	0.000	1.084	1.082	−0.002
∠O-C=O	125.73	126.08	0.36	124.26	124.33	0.08	123.23	123.13	−0.10
∠O=C–H	124.20	123.93	−0.27	122.87	122.60	−0.27	123.00	122.68	−0.32
∠C–O–C	116.85	117.43	0.58	116.08	116.65	0.57	117.67	117.98	0.31
∠O–C–H_a	105.96	105.81	−0.05	106.47	110.26	−0.21	106.33	106.20	−0.13
∠O–C–H_b	110.41	110.31	−0.10	110.95	110.80	−0.15	111.10	111.73	0.63

[a] H_a and H_b, respectively, denote the unique and nonunique hydrogens of the methyl group.

if there were a difference in chemical shifts between the rotamers, it might be possible to study the equilibrium via NMR. The free energy change was calculated as a function of temperature including the effect of temperature on the dielectric constant of acetonitrile.[17] Table VII gives the experimental dielectric constant of acetonitrile at several temperatures, the calculated *E*/*Z* energy differences for each of the values of ϵ, and the terms needed to calculate ΔG. It also gives the calculated equilibrium constants and the mole fractions of the *E* rotamer. The change in the mole fraction of the *E* rotamer was found to be very small, which is a consequence of the relatively large change in ϵ with temperature that largely cancels the normally expected increase in the minor rotamer with increasing temperature.

The other requirement for an NMR experiment is that there is a significant difference in the ^{13}C chemical shifts of the methyl groups of the two rotamers. The chemical shifts were estimated using IGLO[19] and the MP2/6-31G* geometries and are summarized in Table VIII. It can be seen that the expected difference in chemical shift is not found in these calculations. Only the carbonyl oxygen appears to have a significantly different chemical shift for the two rotamers. In an experimental study, the chemical shift of the methoxy carbon was found to change by only a small amount with temperature (a few tenths of a part per million), which was similar to that of the reference compounds that were included in the sample.

4. Methyl Acetate

Methyl acetate was studied in the same fashion, and the results are summarized in Tables II and IV. The relative energies calculated at the 6-31+G*//6-31G* level are summarized in Figure 2. A significant change in the *E*/*Z* energy was calculated, but here the ΔG values (8.5 kcal/mol at $\epsilon = 1$; 5.2 kcal/mol at $\epsilon = 35.9$) are so large (Table II, d section) that no significant amount of the *E* form would be present at equilibrium. Whereas the zero-point energy change on going from the gas phase to solution was fairly large for methyl formate, it was negligible for

Table IV. Effect of Solvent on Structures of Methyl Acetate Rotamers (HF/6-31G*)

	0° (*Z*)			90°			180° (*E*)		
param[a]	$\epsilon = 1$	$\epsilon = 35.9$	diff	$\epsilon = 1$	$\epsilon = 35.9$	diff	$\epsilon = 1$	$\epsilon = 35.9$	diff
r(C=O)	1.188	1.190	0.002	1.181	1.184	0.003	1.183	1.189	0.006
r(C–O)	1.327	1.323	–0.003	1.354	1.350	–0.004	1.335	1.328	–0.007
r(C–C)	1.504	1.504	0.000	1.506	1.505	–0.001	1.512	1.511	–0.001
r(O–C)	1.416	1.416	0.000	1.412	1.416	0.004	1.407	1.417	0.010
r(C–H$_a$)	1.080	1.080	0.000	1.080	1.080	0.000	1.079	1.079	0.000
r(C–H$_b$)	1.084	1.084	0.000	1.085	1.085	0.000	1.084	1.084	0.000
r(C–H$_c$)	1.079	1.078	–0.001	1.079	1.078	–0.001	1.079	1.078	–0.001
r(C–H$_d$)	1.081	1.081	0.000	1.083	1.083	0.000	1.083	1.082	–0.001
∠O–C=O	123.38	123.52	0.14	121.82	121.73	–0.09	119.22	119.08	–0.14
∠O=C–C	125.20	125.17	–0.03	124.59	124.61	0.22	122.67	122.66	–0.01
∠C–O–C	116.94	117.38	0.44	116.71	117.04	0.33	122.82	122.73	–0.81
∠C–C–H$_a$	109.61	109.70	0.09	110.19	110.32	0.33	107.95	108.18	0.23
∠C–C–H$_b$	109.72	109.71	–0.01	108.85	109.03	0.18	111.23	111.28	0.05
∠O–C–H$_c$	105.87	105.86	–0.01	106.58	106.48	–0.10	105.78	105.64	–0.14
∠O–C–H$_d$	110.57	110.51	–0.05	110.63	110.50	–0.13	111.71	111.46	–0.25

[a] H$_a$ and H$_b$ denote the unique and nonunique hydrogens of the C(Me) group, and H$_c$ and H$_d$ denote the unique and nonunique hydrogens of the O(Me) group.

Table V. Vibrational Spectrum of Methyl Formate[a]

	Z conformer						*E* conformer					
											$\Delta\nu(E-Z)$[f]	
mode	calcd- ($\epsilon = 1$)	calcd- ($\epsilon = 36$)	$\Delta\nu$[b]	obsd- (g)[c]	obsd- (soln)[d]	obsd- (matrix)[e]	calcd- ($\epsilon = 36$)	calcd- ($\epsilon = 36$)	$\Delta\nu$[b]	obsd- (matrix)[e]	calcd	obsd
A′ 1	3055 (22)	3065 (18)	10	3045	3032	3035	3053 (18)	3071 (12)	18	3004	6	–31
2	3015 (52)	3011 (67)	–4	2969	2954	2964	2943 (93)	2958 (77)	15	2955	–53	–9
3	2961 (35)	2961 (42)	0	2943	2934	2939	2928 (14)	2947 (16)	19	2889	–14	–50
4	1746 (455)	1722 (500)	–24	1754	1734	1746	1785 (577)	1794 (819)	9	1777	72	31
5	1446 (10)	1444 (14)	–2	1465	1455	1447	1448 (20)	1443 (30)	–5	1483	–1	36
6	1428 (3)	1427 (5)	–1	1445	1433	1435	1437 (4)	1437 (5)	0	1465	10	30
7	1356 (4)	1359 (7)	3	1371	1375	1373	1380 (3)	1380 (1)	0		31	
8	1223 (407)	1220 (531)	–3	1207	1203	1206	1224 (319)	1220 (450)	–4	1240	0	34
9	1159 (75)	1158 (91)	–1	1168	1156	1163	1115 (162)	1106 (224)	–9	1099	–52	–64
10	907 (37)	902 (48)	–5	925	913	922	1011 (80)	996 (105)	–15	1017	94	95
11	743 (11)	743 (15)	0	767	767	767	604 (14)	599 (35)	–5	635	–143	–132
12	283 (18)	275 (27)	–6	325	335	307	323 (1)	321 (2)	–2	373	46	66
A″ 13	3034 (27)	3035 (34)	1	3012	3005	3014	2997 (42)	3026 (28)	29	2999	–9	–15
14	1441 (7)	1441 (9)	0	1454	1446	1460	1449 (7)	1447 (12)	–2	1468	6	8
15	1140 (4)	1140 (5)	0	1168	1156	1158	1136 (4)	1131 (7)	–5		–9	
16	1040 (4)	1043 (5)	3	1032	1021		1036 (5)	1046 (6)	10	1032	3	
17	305 (41)	300 (48)	–5	341		337	153 (1)	167 (3)		224	–133	–113
18	148 (0)	144 (0)	–4	130			76 (14)	69 (16)	–10		–75	

[a] The calculated (HF/6-31G*) frequencies (cm^{-1}) have been scaled by 0.91 if over 2050 cm^{-1} and by 0.88 if under 2050 cm^{-1}. The calculated intensities (km/mol) are given in parentheses. [b] Frequency shifts (cm^{-1}) on going from the gas phase to acetonitrile solution. [c] Reference 6b. [d] Reference 6c. [e] Reference 6a. [f] *E*/*Z* frequency shifts in solution.

methyl acetate. This is likely to be the case for most esters. The large energy difference calculated for the solution provides additional evidence for a steric interaction between the two methyl groups in the *E* rotamer.

Jorgensen et al. calculated the *E*/*Z* energy difference for acetonitrile using Monte Carlo simulations[14] and found the change in free energy (ΔG) on going from the gas phase to acetonitrile to be 2.7 ± 0.1 kcal/mol. This is in good agreement with the results of the present investigation (3.3 kcal/mol).

5. Effect of Solvent on Charge Distribution

In earlier studies, we found that charge distributions for a dipolar compound often were significantly affected by going from the gas phase to solution.[12] In view of the large C=O bond dipole, it might be anticipated that the C=O bond would become more polar on going from the gas phase to a solution. We have examined the charge distributions using Bader's theory of atoms in molecules,[20] in which the charge density for a given atom is integrated over a well-defined volume element. The results of this study, which made use of 6-31+G** wave functions, are given in Table IX.

It can be seen that the electron populations at the carbonyl oxygens of the methyl formate rotamers do increase on going from the gas phase to solution, and as expected, the effect is larger for the more polar *E* rotamers. However, in the latter, the change at oxygen does not come from the carbonyl carbon; rather, there is a general decrease in electron population at the hydrogens. The methyl carbon also experiences an increase in electron population. The same trends are found with the methyl acetate rotamers.

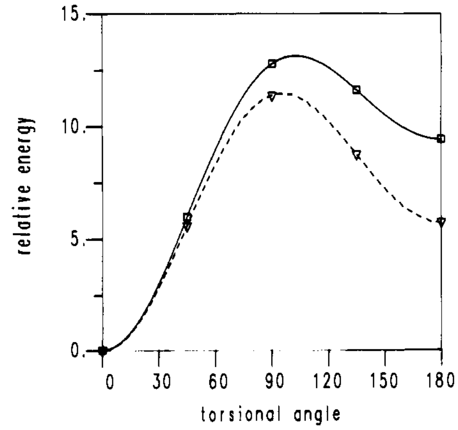

Figure 2. Rotational profile for methyl acetate (kcal/mol). The solid line is for $\epsilon = 1$, and the dashed line is for $\epsilon = 36$.

6. Effect of Solvent on Vibrational Spectra

It is known that infrared bands often shift on going from the gas phase to solution. The *Z* rotamers of methyl formate and

Table VI. Vibrational Spectrum of Methyl Acetate[a]

	Z conformer						*E* conformer					
											$\Delta\nu(F-Z)^e$	
mode	calcd- ($\epsilon = 1$)	calcd- ($\epsilon = 36$)	$\Delta\nu^b$	obsd- (g)[c]	obsd- (soln)[c]	obsd- (matrix)[d]	calcd- ($\epsilon = 1$)	calcd- ($\epsilon = 36$)	$\Delta\nu^b$	obsd- (matrix)[d]	calcd	obsd
A′ 1	3048 (26)	3054 (25)	6	3040	3020		3043 (8)	3057 (22)	14		3	
2	3036 (11)	3033 (19)	−3	3040	3020		3041 (26)	3042 (17)	1		9	
3	2959 (39)	2958 (48)	−1	2961	2955		2943 (47)	2956 (40)	13		−2	
4	2939 (5)	2940 (5)	1	2940			2933 (2)	2940 (0)	7		0	
5	1752 (387)	1732 (506)	−20	1771	1747	1761	1771 (517)	1728 (711)	−43	1774	−4	13
6	1447 (8)	1446 (9)	−1	1459	1455	1462	1451 (16)	1449 (25)	2		3	
7	1433 (21)	1433 (28)	0	1439	1438	1441	1442 (5)	1441 (4)	−1	1459	8	18
8	1416 (13)	1415 (21)	−1	1439	1438		1415 (13)	1413 (30)	−2		−2	
9	1372 (77)	1372 (91)	0	1378	1370		1372 (69)	1372 (85)	0		0	
10	1258 (449)	1253 (588)	−5	1244	1244	1246	1250 (421)	1247 (567)	−3	1255	−6	9
11	1175 (5)(	1174 (5)	−1	1194		1220	1152 (27)	1150 (23)	−2		−24	
12	1056 (80)	1054 (114)	−2	1058	1050	1057	1085 (89)	1066 (146)	−19	1116?	−12	
13	952 (8)	952 (11)	0	976	980		978 (40)	979 (55)	1		27	
14	833 (19)	835 (23)	2	842	845		759 (12)	759 (15)	0		−76	
15	611 (12)	610 (16)	−1	634	641	603	547 (21)	544 (36)	−3	509	−66	−94
16	399 (8)	398 (11)	−1	427	433	434	452 (2)	454 (4)	−2	509	56	75
17	265 (15)	261 (21)	−4	295			297 (0)	298 (0)	1		37	
A″ 18	3031 (30)	3029 (40)	−2	3000	3000		3004 (53)	3027 (36)	23		−2	
19	2996 (10)	2998 (10)	2	3000	3000		2988 (1)	2997 (4)	9		−1	
20	1441 (6)	1441 (8)	0	1467	1480		1457 (15)	1437 (21)	20		−4	
21	1423 (7)	1422 (8)	−1	1446		1447	1429 (5)	1427 (5)	−2	1459	5	12
22	1140 (4)	1140 (5)	0	1160			1133 (4)	1129 (5)	−4		−11	
23	1039 (9)	1038 (11)	−1	1058	1050		1032 (9)	1031 (12)	−1		−7	
24	591 (15)	591 (19)	0	603			562 (17)	566 (21)	4		−25	
25	170 (6)	168 (7)	−2	203			212 (2)	211 (2)	−1		43	
26	144 (4)	142 (4)	−2				124 (1)	133 (1)	9		−9	
27	78 (0)	80 (0)	−2				68 (0)	76 (0)	8		−4	

[a] The calculated (HF/6-31G*) frequencies (cm^{-1}) have been scaled by 0.91 if over 2050 cm^{-1} and by 0.88 if under 2050 cm^{-1}. The calculated intensities (km/mol) are given in parentheses. [b] Frequency shifts (cm^{-1}) on going from the gas phase to acetonitrile solution. [c] References 7a,b. [d] Reference 7c. [e] *E*/*Z* frequency shifts in solution.

Table VII. Calculated Free Energy Change for Methyl Formate as a Function of Temperature[a,b]

T (°C)	ϵ	ΔE	Δ(ZPE)	$\Delta(H-H_0)$	ΔS	ΔG	K^d	$x(E)^e$
−50	47.6	2.705	−0.425	−0.221	2.008	1.461	11.78	7.8
0	37.9	2.730	−0.425	−0.221	2.210	1.485	12.26	7.5
25	35.9	2.742	−0.425	−0.221	2.212	1.496	12.49	7.4
50	32.1	2.767	−0.425	−0.221	2.214	1.521	13.03	7.1

[a] HF/6-31G* energies calculated using the 6-31G* optimized geometries. [b] ΔE, scaled Δ(ZPE), $\Delta(H-H_0)$, and ΔG are in kcal mol^{-1}, and ΔS is in cal mol^{-1} K^{-1}. [c] Scaled by 0.9. [d] Equilibrium constants. [e] Mole fractions.

Table VIII. Calculated Chemical Shifts for Methyl Formate[a,b]

conformer	H	C	=O	-O-	C(Me)	H_a	H_b
Z	23.6	15.4	−151.8	143.4	139.8	28.1	28.0
	(7.4)	(177.3)	(457.5)	(162.4)	(52.9)	(2.9)	(3.0)
E	23.5	15.5	−184.7	146.4	139.0	27.8	28.1
	(7.5)	(177.2)	(490.5)	(159.4)	(53.7)	(3.2)	(2.9)

[a] The chemical shifts were calculated using basis set IV and the MP2/6-31G* geometries. Values are relative to bare nuclei. [b] Numbers in parentheses refer to values relative to TMS for carbons and hydrogens and to water for oxygens.

methyl acetate have been studied extensively, and information is available for these compounds in the gas phase, in solution, and in an argon matrix.[6,7] A mixture of *E* and *Z* rotamers which has been enriched in the former may be obtained by heating the esters along with argon in the gas phase and then rapidly cooling the mixture to give a matrix.[1] From these matrix-isolated spectra, the spectra of the *E* forms may be estimated.

The calculated spectral data for methyl formate in the gas phase and in a medium having $\epsilon = 36$ (corresponding to acetonitrile) are listed in Table V, and the available experimental data also are listed. Unfortunately, the experimental data were not obtained in order to determine the solution frequency shifts, and they were obtained in a relatively nonpolar solvent. The estimated uncertainties in band positions were generally ±2 cm^{-1}. Further, the CH modes are probably perturbed by Fermi resonance, and so the shifts may not be meaningful. Nevertheless, some useful comparisons may be made. Here, it might first be noted that the scaled[21] calculated gas-phase spectrum is in good agreement with the observed spectrum (rms error = 23 cm^{-1}), as is usually found to be the case.[22]

The largest predicted gas/solution shift for (*Z*)-methyl formate was found with the carbonyl stretching mode (ν_4), and here the observed shift is in very good agreement. This is generally the case with carbonyl groups.[15] With the *E* conformer, gas-phase and solution data are not available, and the only possible comparison is with the matrix-isolated spectra of the two rotamers. The observed A′ CH stretching shifts would give a good agreement between calculated and observed if modes 2 and 3 of the calculated spectra were reversed with respect to the observed. The calculated *E*/*Z* spectra shifts for the other bands are generally in good agreement with the observed shifts.

With (*Z*)–methyl acetate, the only large predicted gas/solution shift was again found with the carbonyl stretching mode, and it agreed with the observed shift. The *E*/*Z* calculated and observed shifts are smaller than for methyl formate, and there are fewer data for comparison. The larger predicted shifts agree with the observed shifts. It might also be noted that the intensities of most of the infrared absorption bands were calculated to increase on going from the gas phase to a polar medium.

It can be seen that the reaction field calculations lead to a reasonable agreement between calculated and observed gas-phase to solution spectral shifts. Better data would be required in order to have a more detailed test of the calculations, and we plan to obtain such data.

Table IX. Calculated Electron Populations

	Z conformer			*E* conformer		
	$\epsilon = 1$	$\epsilon = 35.9$	Δ	$\epsilon = 1$	$\epsilon = 35.9$	Δ
			a. Methyl Formate			
C1	3.977	3.970	−0.007	3.963	3.968	+0.005
O2	9.391	9.401	0.010	9.368	9.397	+0.029
O3	9.352	9.352	0.000	9.340	9.346	+0.006
H4	0.975	0.978	+0.003	1.007	0.988	−0.019
C5	5.253	5.260	+0.007	5.240	5.283	+0.043
H6	1.021	1.004	−0.007	1.002	0.986	−0.016
H7	1.016	1.019	+0.003	1.041	1.018	−0.023
H8	1.016	1.019	+0.003	1.041	1.018	−0.023
sum	32.001	32.003		32.002	32.004	
			b. Methyl Acetate			
C1	4.101	4.101	0.000	4.091	4.102	+0.011
O2	9.406	9.415	+0.009	9.386	9.410	+0.024
O3	9.355	9.353	−0.002	9.343	9.348	+0.005
C4	5.769	5.768	−0.001	5.791	5.789	−0.002
C5	5.242	5.243	+0.001	5.219	5.252	+0.033
H6	1.017	1.026	+0.009	0.999	1.009	+0.010
H7	1.022	1.015	−0.007	1.035	1.017	−0.018
H8	1.022	1.015	−0.007	1.035	1.017	−0.018
H9	1.028	1.016	−0.012	1.008	1.002	−0.006
H10	1.020	1.024	+0.004	1.047	1.027	−0.020
H11	1.020	1.024	+0.004	1.047	1.027	−0.020
sum	40.000	39.999		39.999	39.999	

7. Conclusions

Polar solvents affect the energy of the *E* forms of esters considerably more than that of the *Z* rotamers, leading to smaller energy differences. With methyl formate, the change in *E*/*Z* relative energy on going from the gas phase to acetonitrile solution was in very good agreement with that calculated by making use of the surface charge.[16] In the case of methyl acetate, the change in relative energy derived via the reaction field model was in very good agreement with the results of Jorgensen and Houk derived via Monte Carlo simulations.[14] The effect of solvent on the position of the infrared bands of methyl formate and methyl acetate was calculated and was found to be in reasonable agreement with the experimental observations, especially for the C═O stretching mode. These results, along with the others that we have obtained,[12] suggest that the simple reaction field model used in this work will be generally useful, especially for relatively compact molecules that may reasonably be considered as being approximately spherical. Current studies are designed to test the generality of the model.

The effect of temperature on the *E*/*Z* equilibrium constant for methyl formate was calculated and was found to be quite small because of the change in dielectric constant of acetonitrile with temperature. It seems likely that this will have a major effect on the $\Delta H°$ and $\Delta H^‡$ values derived from temperature coefficients of equilibrium constants or rate constants for processes in which there is a significant change in dipole moment.

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Electronegativities in Situ, Bond Hardnesses, and Charge-Transfer Components of Bond Energies from the Topological Theory of Atoms in Molecules

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Abstract: Rigorous definitions for electronegativities of atoms and functional groups in molecules, bond hardnesses, and the charge-transfer components of the bond energies are proposed. The definitions rely upon values of total energies and their derivatives calculated for molecules composed of fragments with a controlled degree of charge transfer. Such calculations, in which the atomic or fragment charges are obtained with the help of the topological theory of atoms in molecules, are easily accomplished by adding appropriate Lagrange multiplier terms to the electronic Hamiltonian. Numerical examples that are given for 23 different systems indicate that the bond hardnesses are mostly transferable, but because of the electric field generated by the molecular environment the electronegativity differences are not.

Introduction

The concept of electronegativity[1] is central to understanding and explaining a multitude of chemical phenomena. As with any other quantity, in order to realize and harness its full predictive and explanatory potential, it is essential to replace the vague statement of electronegativity as "the power of an atom in a molecule to attract electrons to itself"[1a] by a rigorous definition. Over the last 50 years numerous quantitative definitions of electronegativity have appeared in the chemical literature. Although as early as in 1961 Iczkowski and Margrave related electronegativity to the linear coefficient in the *fitted* polynomial expansion for the total energy in terms of the total charge,[1b] it was not until 1978, when the connection between electronegativity, χ, and the first partial derivative of the total energy, E, with respect to the number of electrons, N (at a constant external potential, v),

$$\chi = -\left(\frac{\partial E}{\partial N}\right)_v \tag{1}$$

was made, that the full understanding of the concept of electronegativity was achieved.

As the derivative (1) is discontinuous at integer values of N, in practice the above definition is replaced by a finite-difference approximation, yielding

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[1] (a) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; and references cited therein. (b) Iczkowski, R. P.; Margrave, J. L. *J. Am. Chem. Soc.* **1961**, *83*, 3547.