Electronic States of Organic Molecules. 2. Vibrational Intensities for Ethylene[1]

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Received January 26, 1976

Abstract: Dipole moment derivatives have been calculated for ethylene using STO-3G, 4-31G, and 4-31G plus bonding function basis sets. It is found that the use of bonding functions is necessary to satisfactorily reproduce experimental out-of-plane values, while the 4-31G basis is adequate for in-plane values. Calculated charge shifts as a function of vibrational displacement are presented, and the accompanying dipole moment derivatives are analyzed in terms of rehybridization arguments. It is found from calculated charge shifts that the out-of-plane intensity is purely geometrical in nature, while the in-plane mode involves considerable rehybridization.

It is now clear that the equilibrium geometry and dipole moments of many organic molecules may be satisfactorily calculated using a variety of molecular orbital methods.[2] It is not equally well determined whether or not properties of slightly deformed species may be calculated in a satisfactory fashion. Such calculations would provide additional tests for the adequacy of a given level of approximation.

Two properties of interest are force constants and infrared intensities. Both may be calculated for many molecules of chemical interest and then compared with the experimentally observed values. Such comparisons can be useful in deciding which of several possible experimental force fields is correct, as was done by Pulay[3a] in the case of ethylene. In addition, since many experimental vibrational assignments are not entirely certain, the requirement that the observed intensities be reproduced as part of a normal coordinate analysis would be a valuable additional constraint.

We have therefore initiated calculations of force constants and infrared intensities for a number of molecules, and we now report the results obtained for ethylene. This is a useful test case since it is a small molecule but still has five infrared active modes. Of these five modes, the three bending modes have significantly different intensities, a fact which previous analysis has not been able to explain.[3b,4-6] Pulay's extended basis ab initio calculations[3b] agree well with experiment. However, these results offer no interpretation for the difference in bending mode intensities, nor do they consider the effect of basis set size on the calculated intensities.

Theory

The absolute intensity of the ith infrared band is related to experiment through the equation:[7]

$$A_i = \int \alpha_\nu \, d\nu = \frac{1}{Nl} \int \ln (I_0/I) \, d\nu \qquad (1)$$

where α_ν is the experimentally derived absorption coefficient, N is the concentration, and l is the cell path length. I_0 and I are the incident and transmitted intensities, respectively, at frequency ν. The experimental intensity is related to the calculated quantities by the equation:[7]

$$A_i = \frac{N\pi}{3c^2} \sum_{g=x,y,z} \left| \left(\frac{\partial \mu_g}{\partial Q_i} \right) \right|^2 \qquad (2)$$

in which $\partial \mu_g / \partial Q_i$ is the derivative of the gth component of the molecule fixed axis with respect to the ith normal coordinate Q_i, and c is the velocity of light. Using eq 2, magnitudes of $\partial \mu / \partial Q_i$ may be obtained from experimental absorption spectra.

Calculated dipole moment derivatives and force constants are most easily analyzed in terms of derivatives with respect to symmetry coordinates, S_i. The $\partial \mu_g / \partial Q_i$ are related to the $\partial \mu_g / \partial S_j$ as[8]

$$\left(\frac{\partial \mu_g}{\partial S_j} \right) = \sum_i (L^{-1})_{ij} \left(\frac{\partial \mu_g}{\partial Q_i} \right) \qquad (3)$$

where $(L^{-1})_{ij}$ is the i,jth component of the usual $\mathbf{L}^{-1}$ matrix.[7]

Use of eq 3 presents a difficulty in that we obtain only the magnitudes of $(\partial \mu / \partial Q_i)$ from experiment.[9] There are two possible ways to handle this problem. First, if the spectra for various deuterated isotopes of the compound of interest can be obtained, all permutations of signs for $(\partial \mu_g / \partial Q_i)$ can be tried until a set is found which gives the same values to $(\partial \mu_g / \partial S_j)$ for each isotope.[10] This method may often depend on having very accurate values of $\partial \mu_g / \partial Q_k$, and even then it still may not be possible to unambiguously choose one set of sign combinations.

A second way of overcoming the problem of sign ambiguity would be to theoretically calculate the $(\partial \mu_g / \partial S_i)$ and use the equation

$$\left(\frac{\partial \mu_g}{\partial Q_i} \right) = \sum_j (L)_{ji} \left(\frac{\partial \mu_g}{\partial S_j} \right) \qquad (4)$$

to predict $\partial \mu_g / \partial Q_i$. Once the signs of $(\partial \mu_g / \partial Q_i)$ have been established, eq 3 can be used to obtain experimental $(\partial \mu_g / \partial S_j)$.

The symmetry coordinates used in these calculations, defined in Figure 1 and Table I, are similar to those of Fletcher and Thompson.[11] While a nonredundant set of coordinates would have been preferable, there are at least five existing sets in the literature, and the introduction of another set would be even more confusing.

Comparisons among different sets of coordinates are complicated by the existence of three different definitions of the out-of-plane bend. The Wilson, Decius, and Cross (WDC) definition[12] uses the angle between the C=C bond and the bisector of the CH_2 group. Machida[13] uses the angle between the two C=CH planes. Fletcher and Thompson use the C=C-H angle. Our choice was that of WDC, as this seems to be the most common choice in calculations on many molecules.

All force constants and dipole moment derivatives quoted in later tables have been converted to the coordinates in Table I and Figure 1. The force constants have been defined by the relation

$$V = \tfrac{1}{2} \sum_{ij} F_{ij} S_i S_j \qquad (5)$$

where V is the vibrational potential energy and F_{ij} is the force constant.

Table I. Ethylene Symmetry Coordinates[a]

A_g	$S_1 = \frac{1}{2}(r_3 + r_4 + r_5 + r_6)$ $S_2 = R$ $S_3 = 1/\sqrt{12}(2\alpha_2 - \beta_5 - \beta_6 + 2\alpha_1 - \beta_3 - \beta_4)$
A_u	$S_4{}^b = \tau$
B_{1g}	$S_5 = \frac{1}{2}(r_5 - r_6 - r_3 + r_4)$ $S_6 = \frac{1}{2}(\beta_5 - \beta_6 - \beta_3 + \beta_4)$
B_{1u}	$S_7{}^c = 1\sqrt{2}(\delta_1 + \delta_2)$
B_{2g}	$S_8{}^c = 1\sqrt{2}(\delta_1 - \delta_2)$
B_{2u}	$S_9 = \frac{1}{2}(r_5 - r_6 + r_3 - r_4)$ $S_{10} = \frac{1}{2}(\beta_5 - \beta_6 + \beta_3 - \beta_4)$
B_{3u}	$S_{11} = \frac{1}{2}(r_5 + r_6 - r_3 - r_4)$ $S_{12} = 1/\sqrt{12}(2\alpha_2 - \beta_5 - \beta_6 - 2\alpha_1 + \beta_3 + \beta_4)$

[a] Internal coordinates are defined in Figure 1. Angle coordinates are assumed scaled by 1.00 Å. [b] τ is the cis HCCH torsional angle. [c] δ_i is the out-of-plane motion as defined by Wilson, Decius, and Cross (see text). δ_i is positive for H motion in the z direction.

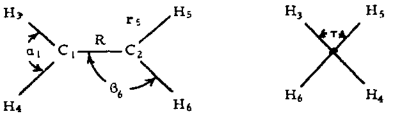

Figure 1. Ethylene internal coordinates.

Dipole moment derivatives and force constants were calculated numerically using angular displacements of 2 and 4° and stretches of 0.03 and 0.06 Å. Ab initio calculations were carried out at STO-3G[14] and 4-31G[15] levels using Pople's GAUSSIAN 70 program[16] and the numerically determined minimum energy geometries. The calculated charge shifts at both levels were essentially linear functions of the displacements.

Results and Discussion

The minimum energy geometry for ethylene was determined numerically at an STO-3G and a 4-31G level. The calculated geometries are compared with experiment[17] and Pulay's values[3] in Table II, along with the resultant energies. Agreement with Pulay's large basis set and experiment is reasonably good, with the 4-31G basis set giving better results than the STO-3G set.

The calculated force constants for ethylene are compared with experiment[11,18] and Pulay's large basis set values in Table III. The agreement with Pulay's values is quite good for the 4-31G basis. Since Pulay's basis is reasonably large, it is assumed that the 4-31G results approximately reflect the ability of restricted Hartree–Fock wave functions to predict force constants. As expected, Pulay's diagonal stretching constants are too large, since on dissociation the RHF wave function for the ground state correlates with a true excited state wave function (usually ionic in nature). The HF stretching potential will thus be steeper than the exact one. Agreement with experiment generally improves with the basis set, although variations in the off-diagonal terms for the STO-3G level are erratic. This behavior is to be expected, since each F_{ij} is proportional to $\Delta V - \frac{1}{2}(F_{ii}S_i{}^2 + F_{jj}S_j{}^2)$, where ΔV and $\frac{1}{2}(F_{ii}S_i{}^2 + F_{jj}S_j{}^2)$ are of the same magnitude. For STO-3G, the F_{ii} are far from the correct value, while the 4-31G values are much closer.

It should be noted that Pulay's values were calculated at the experimental equilibrium, following Schwendenman's suggestion.[19] This method generally yields better agreement with the experimental diagonal force fields than a corresponding calculation at the theoretical equilibrium. The effect of using the experimental equilibrium geometry on the calculated intensities is not clear, so the theoretical geometry has been used to provide a consistent framework on which to analyze our results.

Examination of Table III indicates that the only significant differences between the 4-31G results and those of Pulay are found in the C=C stretching values and the out-of-plane (B_{1u} and B_{2g}) modes. Calculations at the experimental geometry give F_{11} = 10.41 mdyn/Å but do not affect the out-of-plane modes. The inability of the 4-31G basis to predict the out-of-plane bending constants relative to Pulay's basis is most easily understood in terms of the participation of d functions, and will be considered later along with the out-of-plane dipole moment derivatives.

The infrared stretching and bending modes, along with the direction of the calculated dipole moments, are shown in Figure 2. The values of $\partial\mu/\partial S_i$ calculated using the STO-3G and 4-31G levels are compared with experiment[8] and Lewis and Levin's CNDO results[5] in Table IV. The values of $\partial\mu/\partial S_i$ are too large for the stretching modes, paralleling the results obtained for the diagonal stretching force constants. As in the case of the force constants, correlation of the RHF ground state wave function with ionic excited states will shift charge too rapidly toward hydrogen as the bond is stretched (since the correlation is with C^+H^-). The rehybridization charge shifts toward H will then be to large, thereby overly decreasing the magnitude of the C^-H^+ dipole. Larger basis sets, such as Pulay's, would not correct this problem because it is an error inherent to the restricted Hartree–Fock model. The values of $\partial\mu/\partial S_i$ in Table IV and the charge shifts in Table V are consistent with these arguments.

We now wish to compare the calculated values with those derived from experimental data. Since experiment can only give the magnitudes of $\partial\mu/\partial S_i$, two different sets of $\partial\mu/\partial S_i$ are possible for the B_{2u} and B_{3u} modes. Golike et al.[8] have calculated the appropriate $\partial\mu/\partial S_i$ for most of the deuterated ethylenes using an incorrect force field. These values have now been recalculated with Duncan's[18] force field. For the d_0 and d_4 isomers, the only major difference between the alternate sign combinations was found with S_{11}, which clearly indicates the +,+ combination in ν_{11},ν_{12}.

For the *trans*-$C_2D_2H_2$ ethylene, the dipole moment changes

Table II. Calculated Equilibrium Properties[a]

	STO-3G	4-31-G	4-31G + CH bonding functions[b]	Pulay[c]	Expt[d]
R	1.3061	1.3161		1.3148	1.330
r_i	1.0820	1.0729		1.0807	1.076
β_i	122.17	121.99		121.89	121.7
$-E$	77.073 955	77.922 157	77.932 648	78.048 408	78.617

[a] All lengths are in Å, angles in degrees, energies in hartrees. [b] Calculated at the experimental geometry. [c] Gaussian lobe results from ref 3. [d] Reference 17. Equilibrium values corresponding to the bottom of the potential well.

Table III. Calculated Force Fields[a]

Symmetry species	F_{ij}	Exptl DMM[b]	Exptl FT[c]	STO-3G	4-31G	Pulay[d]	4-13G + CH[f] bond functions
A_g	1,1	5.638	5.124	7.54	6.23	5.950	
	1,2	0.365	0	+0.015	0.204	0.192	
	1,3	−0.056	0.1	−0.015	0.148	0.073	
	2,2	9.395	9.305	14.34	11.80 (10.41)[e]	9.939	
	2,3	−0.314	−0.315	−0.322	−0.317	−0.342	
	3,3	0.487	0.470	0.672	0.588	0.580	
A_u	4,4	0.297	0.262			0.357	
B_{1g}	5,5	5.657	5.180	7.714	6.130	5.854	
	5,6	0.396	0.185	0.19	0.25	0.226	
	6,6	0.659	0.633	0.843	0.773	0.732	
B_{1u}	7,7	0.298	0.307	0.463	0.415	0.374	0.399
B_{2g}	8,8	0.220	0.223		0.343	0.225	
B_{2u}	9,9	5.493	5.180	7.755	6.195	5.904	
	9,10	−0.175	0.185	0.060	0.106	0.095	
	10,10	0.486	0.441	0.601	0.576	0.524	0.567
B_{3u}	11,11	5.603	5.188	7.530	6.248	5.936	
	11,12	0.092	0.100	0.081	0.125	0.111	
	12,12	0.452	0.440	0.621	0.550	0.532	0.523

[a] Values in mdyn/Å. Bending modes are scaled by 1.0 Å. Our results are given for the calculated equilibrium geometry unless otherwise noted. [b] Reference 18. [c] Reference 11. [d] Reference 3. All values were calculated at the experimental geometry. [e] Values calculated at the experimental geometry. [f] One 1s GTO with $\alpha = 0.7$ centered on each CH bond.

Table IV. Calculated $\partial\mu/\partial S_i$[a]

	Exptl[b] +,+	Exptl[b] +,−	STO-3G	4-31G	CNDO[c]	4-31G + bond functions
B_{1u}: S_7	1.0497	1.0497	0.6438	1.3160	1.4565	1.1032[d] 0.9765[e]
B_{2u}: S_9	−0.7999	−0.7770		−0.9583	−0.845	
S_{10}	−0.0928	0.1255	−0.08835	−0.1748	−0.2106	
B_{3u}: S_{11}	0.6299	0.3069	−0.8873	−0.7371	−0.505	
S_{12}	0.3025	−0.2912	−0.3443	−0.2671	−0.103	

[a] All units are D/Å. [b] Reference 8. [c] Reference 5, converted to our symmetry coordinates. [d] One 1s GTO with $\alpha = 0.7$ centered on each CH bond. [e] One 1s GTO with $\alpha = 0.7$ on each CH bond and 2s and 2p functions with $\alpha = 0.2$ and $\alpha = 0.8$ centered on each CC bond.

for ν_9, ν_{10}, ν_{11}, and ν_{12} are all in the same symmetry class and will no longer take place along a single x or y axis. $|(\partial\mu/\partial Q_i)|^2$ will thus be the sum of x and y components, resulting in more unknowns than equations if eq 3 is used. To overcome this, values of $\partial\mu/\partial S_i$ from the d_0 and d_4 isomers were substituted in eq 4 and used to calculate $|(\partial\mu/\partial Q_j)|^2$. The calculated derivatives are not reported here, since they were essentially the same for all sign combinations.

The *cis*-$C_2D_2H_2$ dipole changes are along a single axis, but overlap of the ν_5,ν_9 bands prevents an accurate determination of $\partial\mu/\partial S_5$ and $\partial\mu/\partial S_9$.[8] For this reason *cis*-$C_2D_2H_2$ was treated in the same manner as *trans*-$C_2D_2H_2$ above. These results provide the same conclusions as derived from the d_0 and d_4 isomers.

The calculated results in Table IV indicate that the proper sign combination should be +,+ for the B_{2u} mode and −,− for the B_{3u} mode. This agrees with the experimental results. It should be pointed out that experiment cannot determine the absolute sign combination (−,−) in the B_{3u} mode. Knowledge of absolute signs is necessary, however, to explain dipole shifts in terms of hybridization arguments.

The calculated 4-31G values of $\partial\mu/\partial S_i$ for the bending modes agree very well with the experimental values, the only major exception being the out-of-plane B_{1u} mode. The physical interpretation derived from these results will be considered below.

In the three bending modes, two physical effects can be distinguished. One is the vector change in μ due to geometrical reorientation of the CH moments. The other is charge shift due to rehybridization effects. Assuming the same static μ_{CH} in all modes, geometrical changes alone predict $\partial\mu/\partial S_i$ for B_{1u}, B_{2u}, and B_{3u} to be $\sqrt{2}\,\mu_{CH}$, μ_{CH}, and μ_{CH}, respectively. However,

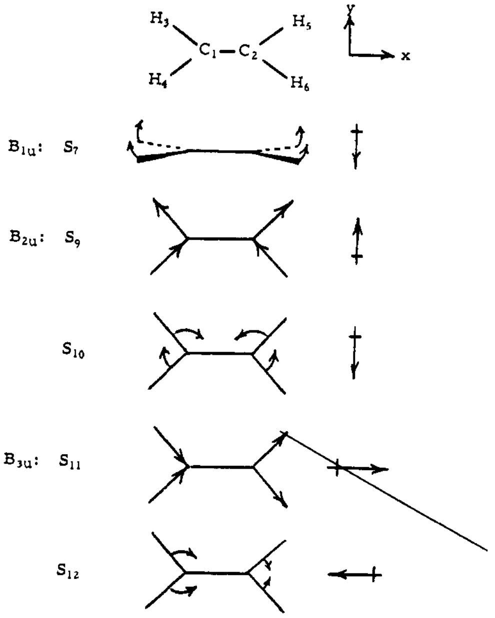

Figure 2. Calculated dipole moments.

Table V. Population Analysis Atomic Charge Shifts[a]

			Basis	
Symmetry	Mode	Atom	STO-3G	4-31G
B_{2u}	S_9	C_1	0.0003	−0.0013
		H_3	0.0038	0.0016
		H_4	−0.042	−0.0003
	S_{10}	C_1	0.0000	0.0002
		H_3	0.0006	0.0021
		H_4	−0.0005	−0.0022
B_{3u}	S_{11}	C_1	0.0199	−0.0066
		C_2	−0.0188	0.0042
		H_4	−0.0049	−0.0007
		H_6	0.0045	0.0017
	S_{12}	C_1	0.0035	0.0042
		C_2	−0.0029	−0.0025
		H_4	−0.0031	−0.0035
		H_6	0.0029	0.0027

[a] All bond stretches were 0.03 Å and all bends were 2°. Values are units of e. All B_{1u} charge shifts were on the order of 1×10^{-4} or less.

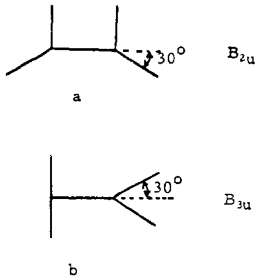

Figure 3. Rotational extrema for the B_{2u} and B_{3u} bending modes.

the rehybridization effects will not be the same for the out-of-plane and the two in-plane modes. For the latter modes, there are two rotational limits defined in Figure 3. In each of these limits, two of the four CH bonds are changing from sp^2 to sp type hybrids, thereby pushing the electrons toward H (due to greater p character). Since the calculated sense of μ_{CH} is C^-H^+, these CH bonds will have an effective μ_{CH} whose magnitude is smaller than the static μ_{CH}. For a finite B_{2u} displacement in the direction in Figure 2, the C_1H_3 and C_2H_5 bonds move toward the sp limit in Figure 3a and the C_1H_4 and C_2H_6 bonds move away from this limit. Thus the p character increases for the first two bonds and decreases for the last two, giving $\mu_{C_1H_3}, \mu_{C_2H_5} < \mu_{C_1H_4}, \mu_{C_2H_6}$. The resultant total dipole will then be less than its geometric values. Similarly, for the B_{3u} mode, we find $\mu_{C_2H_5}, \mu_{C_2H_6} < \mu_{C_1H_3}, \mu_{C_1H_4}$.

On the basis of these arguments alone, the B_{2u} and B_{3u} modes would be predicted to have the same intensity. Account must be taken, however, of the loss of the CC reflection plane in the B_{3u} mode. This loss of symmetry permits the formation of a C=C dipole when the CH bonds rehybridize. A positive charge develops on C_2 while a negative charge develops on C_1. This $\mu_{C=C}$ reinforces the vector sum of the μ_{CH} making the B_{3u} mode more intense than the B_{2u} mode.

The calculated atomic population shifts in Table V support these rehybridization arguments. In particular, the large charge shift from C_2 to C_1 in the B_{3u} mode (largely through the $p_z(\pi)$ orbitals) confirms the importance of the temporary C=C bond dipole.

The agreement between experiment and the 4-31G values for $\partial\mu/\partial S_i$ is much poorer for the B_{1u} mode than for the B_{2u} and B_{3u} modes, paralleling the results obtained for the force constants. Both of these discrepancies arise because the 4-31G basis set is too rigid to allow charge to efficiently move into the bonding regions. To overcome this deficiency, the 4-31G basis set has been augmented by positioning bonding functions at the center of the CH bonds. The major effect of this basis was to move 0.13 electron from carbon onto the bonding function decreasing the magnitude of μ_{CH}. The augmented basis set gave $\partial\mu/\partial S_i = 1.1032$, in much better agreement with experiment (Table IV), while leaving the values for the in-plane modes essentially unchanged. This explanation is consistent with the population analysis which shows no charge shifts at any of the three basis set levels. The out-of-plane intensity is, therefore, largely geometric in nature. The STO-3G and 4-31G values of $\partial\mu/\partial S_i$ are incorrect because the magnitude of μ_{CH} is incorrect. For the in-plane modes, however, the 4-31G error in μ_{CH} is not as important because μ is the vector sum of opposing μ_{CH} dipoles, so that the error tends to cancel.

This "simply" augmented 4-31G basis set is not, of course, a very well optimized basis set, but it does point out the essential problem involved in calculating ethylene bending modes. The in-plane modes may be calculated at an ab initio 4-31G basis set level. However, the out-of-plane mode requires use of a basis which gives a very good description of bonding, either through the use of bonding functions or with polarization functions. Attempts to calculate this mode by semiempirical methods will generally fail, as these methods do not directly include polarization functions.

The above results are in contradiction with the usual rehybridization arguments used in explaining why the out-of-plane bending modes are more intense than the in-plane modes for benzene and ethylene.[6,20] Qualitatively, these arguments assume a value of 0.26 D for the effective value of μ_{CH}. As the methylene groups move out of the plane, the hybridization approaches sp^3, with a resulting flow of charge into the fourth sp^3 orbital. This orbital points in the opposite sense to the methylene motion, thus reinforcing the μ_{CH} moment and giving an effective CH moment of 0.742 D.

On the other hand, the augmented 4-31G results give $\mu_{CH} = 0.780$ D for the B_{1u} mode with no accompanying rehybridization. Further augmentation of the 4-31G basis with carbon-carbon bonding functions lowers $\partial\mu/\partial S_7$ to 0.9765 D/Å, with a resulting charge shift in the direction of the methylene motion and into the C=C π bonding orbital. Both of these results can be viewed as arising from the additional mixing in of the out-of-plane (d_{xz}, d_{yz}) polarization orbitals. This type of effect cannot be predicted with valence orbital rehybridization models: In fact, the above rehybridization model[6] is not even qualitatively correct. This is not surprising since the rotational limit for out-of-plane rehybridization is 90° away, much further than that of the in-plane modes. On this basis, more rehybridization would be expected for the in-plane modes, consistent with the ab initio results.

Also listed in Table IV are Lewis and Levin's CNDO values. For the in-plane bending modes in particular, CNDO reverses the relative intensities of the bands. This is consistent with CNDO for other molecules, where different parameterization schemes give different signs for the same mode.[5] Particularly, the best semiempirical results predict the wrong sign for CH_4, while ab initio results give the correct sign.[20]

Another reason to use caution in interpreting the CNDO results is, as stated above, the CNDO cannot directly include polarization functions. Subsequent empirical parameterization will artificially attempt to force polarization character into the parameters. This problem is reflected in the work of Orville-Thomas,[6] who finds using CNDO that the out-of-plane rehybridization moment is nearly twice that of the in-plane modes. This clearly contradicts the ab initio results.

References and Notes

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Heats of Formation of Disodium and Dipotassium Cyclooctatetraenide

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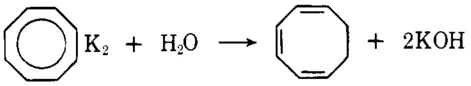
Received September 15, 1975

Abstract: Since the solid salts and solutions of the cyclooctatetraene (COT) dianion are known to be more stable and easier to form than those of other hydrocarbons, a determination of the thermodynamic heat of formation of M_2COT (where M is either sodium or potassium) has been carried out. This was done by measuring the enthalpy of the reaction between the dipotassium and disodium salts of COT with water to form cyclooctatriene and KOH_{aq} using calorimetric methods. A thermochemical series was utilized to obtain the heats of formation of these aromatic salts. It was found that the heat of reaction between COT and K^0 is about as exothermic as that between K^0 and water. Both salts (K_2COT and Na_2COT) were found to be more thermodynamically stable relative to the elements in their standard states than is benzene. This stability is attributed in part to the aromatic character of the ten π-electron dianions, but the majority of it is due to the large negative crystal lattice energy. The thermodynamic parameters controlling the stability of the COT dianion and anion radical are discussed for both the solution and solid state.

Probably the two most important quantities inherent in any compound are its energy and its structure. The entire concept of aromaticity simply comes from the fact that certain cyclic π-electron systems are of lower energy than would be expected without considering this concept (for example, the heat of formation of benzene is greater than that expected for the hypothetical cyclohexatriene). In the Hückel sense monocyclic π-electron systems with $(4n + 2)$ π electrons are aromatic. However, for the cases of [8]annulene (cyclooctatetraene),[1] [12]annulene,[2] and [16]annulene[3] the neutral molecules will react with alkali metals to form the corresponding aromatic dianions, each containing $(4n + 2)$ π electrons. To date there are no known heats of formation for any of these aromatic salts. Here we wish to report an experimental determination of the heat of formation of the aromatic dipotassium and disodium salts of cyclooctatetraene.

The most common method of obtaining the heat of formation of any compound involves the measurement of the heat of combustion.[4] This method requires very high precision in order to give useful results, and this high precision can only be obtained under very special conditions for organometallic compounds.[5] It would be much more feasible to measure a heat of reaction involving the alkali metal salts of the cyclooctatetraene.

Thielen and Anderson have observed that the addition of water to either the dianion or anion radical of cyclooctatetraene (COT) results in the formation of cyclooctatriene (H_2COT), eq. 1.[6] This reaction would be ideal for the proposed study, since the heat of hydrogenation of neutral COT is known.[7] However, it would first be necessary to eliminate the formation of hydrogen gas as a possible competing reaction (eq 2).



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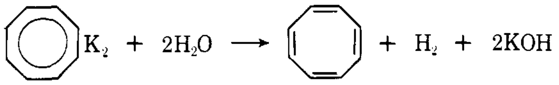

(2)

Solid crystalline alkali metal salts of COT can be obtained by crystallization from a saturated tetrahydrofuran (THF) solution.[8] In a similar manner yellow crystals of potassium 1,3,5,7-tetramethylcyclooctatetraenide were crystallized from diglyme for x-ray analysis.[9] In that study it was found that the crystal lattice had incorporated two molecules of the solvent (diglyme) for each molecule of tetramethylcyclooctatetraene. Since it is our intention to crystallize the dianion salts from THF, it is necessary that the number of THF molecules incorporated into the crystal lattice be determined prior to the thermodynamic study.

Results and Discussion

NMR analysis of the solution resulting from the addition of 1 ml of D_2O to 2 mmol of solid sodium or potassium salt did not show the presence of THF, indicating that the crystal lattices of neither Na_2COT nor K_2COT incorporate THF.

Allowing the noncondensable gases from the reaction of water with the solid salts of K_2COT and Na_2COT into the vacuum line connected with a Toepler Pump fitted with a gas

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