a probe of the influence of other substances in replacing it in the interfacial region. Further, elucidation of the kinetics and mechanism of extraction of metal chelates of higher molecular weight extractants absolutely requires the fundamental information obtained by such studies. Work addressing these opportunities is now underway in our laboratory.

Acknowledgment. The project was supported by a grant from the National Science Foundation.

Registry No. Dz, 60-10-6; MeDz, 16026-13-4; EtDz, 83454-27-7; BuDz, 65388-10-5; HexDz, 70857-97-5; $CHCl_3$, 67-66-3; CCl_4, 56-23-5; benzene, 71-43-2; *n*-hexane, 110-54-3.

The Dimers of Carbon Monoxide and Carbon Monosulfide. Chemically Bound Triplet Electronic Ground States

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Abstract: The $^3\Sigma_g^-$ electronic ground states of OCCO and SCCS have been studied by using nonempirical molecular electronic structure theory. Reasonably large double-ζ plus polarization (DZ + P) basis sets have been used throughout and are designated C,O(9s5p1d/4s2p1d), S(11s7p1d/6s4p1d). Geometrical structures and vibrational frequencies were determined at the self-consistent-field level of theory and relative energies from explicitly correlated wave functions. The structures of $^3\Sigma_g^-$ ethylenedione and ethylenedithione lead one to anticipate strong chemical bonds. The predicted vibrational frequencies also support this general view. For both C_2O_2 and C_2S_2, the $^3\Sigma_g^-$ electronic states are minima on their respective potential energy hypersurfaces. In each case the $^3\Sigma_g^-$ state lies below the lowest spin-allowed dissociation limit, $X^1\Sigma^+ + a^3\Pi$: for C_2O_2 the predicted dissociation energy is 74 kcal and for C_2S_2, 119 kcal. Furthermore, triplet ethylenedithione is predicted to be the absolute minimum on the C_2S_2 energy surface, lying 39 kcal below $X^1\Sigma^+$ CS + $X^1\Sigma^+$ CS.

Introduction and Qualitative Analysis

It has long been appreciated[1] that it is possible to write down a plausible valence structure for the carbon monoxide dimer $(CO)_2$. The chemical name ethylenedione is readily seen to be applicable to structure **1**. The existence of valence structure **1** suggests a

$$\underset{\mathbf{1}}{O{=}C{=}C{=}O}$$

close-shell singlet electronic ground state, and this arises from the electronic configuration

$$^1\Sigma_g^+ \qquad \underset{\mathbf{2}}{1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 3\sigma_u^2 4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 1\pi_u^4 1\pi_g^4 5\sigma_u^2}$$

Nevertheless, all efforts, beginning as early as 1913, to prepare a chemically bound C_2O_2 species have proven unsuccessful.[2-7] $(CO)_2$ does of course exist as a van der Waals molecule, but its dissociation energy appears to be less than 1 kcal/mol.[8] The cation $(CO)_2^+$ is reasonably well characterized experimentally and has a dissociation energy D_0 (OC–CO$^+$) = 22 ± 1 kcal,[9] indicative of considerably less than a true carbon–carbon single bond.

Theoretical studies have shown[1,10-14] that the ground-state electron configuration of C_2O_2 is not **2** but rather

$$^3\Sigma_g^-\ {}^1\Delta_g,{}^1\Sigma_g^+$$
$$\underset{\mathbf{3}}{1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 3\sigma_u^2 4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 1\pi_u^4 1\pi_g^4 2\pi_u^2}$$

Hund's rules then require the lowest electronic state of the open-shell configuation **3** to be the $^3\Sigma_g^-$ state. Moreover, a triplet ground state of C_2O_2 might be more difficult to detect experimentally than an ordinary closed-shell singlet (note of course that ESR experiments would be more suitable for a triplet ground state). However, a point that does not appear to have be given proper emphasis is the fact that $^3\Sigma_g^-$ C_2O_2 is a genuine chemically bound system. In the absence of spin–orbit coupling (which should be small for a molecule as light as ethylenedione), the ground triplet state is forbidden by spin conservation to dissociate to two ground-state carbon monoxide molecules:

$$^3\Sigma_g^-\ C_2O_2 \rightarrow {}^1\Sigma^+\ CO + {}^1\Sigma^+\ CO \qquad (1)$$

The lowest energy dissociation limit available for C–C bond rupture involves the lowest triplet state of CO, and inspection of (2) shows that this dissociative channel is symmetrically allowed

$$^3\Sigma_g^-\ C_2O_2 \rightarrow {}^1\Sigma^+\ CO + {}^3\Pi\ CO \qquad (2)$$

only for nonlinear pathways. Since the $a^3\Pi$ state of CO lies 48 687 cm^{-1} = 139 kcal[15] above the $X^1\Sigma^+$ ground state, it is implicit in earlier theoretical studies that the $^3\Sigma_g^-$ ground state of C_2O_2 could be quite stable with respect to C–C dissociation. One can, however, envision a predissociative mechanism that might yield a relatively short lifetime for $^3\Sigma_g^-$ C_2O_2. The spin–orbit coupling might be large enough if a potential curve crossing occurs not too far from the minimum in the $^3\Sigma_g^-$ state (e.g., by a $^1\Sigma^+$ state

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repulsive with respect to carbon–carbon stretch).

The failure of ethylenedione to display a ground electronic state significantly bound compared to two ground-state carbon monoxide molecules may reasonably be attributed to the exceptional stability of the isolated CO molecule. With a dissociation energy of 11.1 eV = 256 kcal, C≡O incorporates the strongest known chemical bond.[15] In the formation of C_2O_2,

$$C{\equiv}O + C{\equiv}O \rightarrow O{=}C{=}C{=}O \qquad (3)$$

one loses the second π bond in each CO molecule and gains the double bond between the two carbon atoms. If we ascribe the standard values[16] of 77 kcal to the third bond in CO and 146 kcal for the C=C double bond in ethylenedione, it is readily seen that reaction 3 is endothermic by 8 kcal. Although this crude estimate is certainly reliable to no better than ±10 kcal, one nevertheless concludes that breaking the third bond in C≡O is sufficiently costly in energetic terms that C_2O_2 cannot be a terribly stable molecule.

Several years ago it occurred to us that the analogous carbon monosulfide dimerization

$$C{\equiv}S + C{\equiv}S \rightarrow S{=}C{=}C{=}S \qquad (4)$$

might be more favorable energetically. Specifically, the C≡S bond energy (170 kcal)[15] is much weaker than that in carbon monoxide, and the C=S double-bond energy (128 kcal)[16] is not comparably reduced relative to the standard C=O bond energy (179 kcal). Thus the energy of the third bond in C≡S is only about (170 − 128) = 42 kcal, making the formation of ethylenedithione exothermic by roughly (146 − (2 × 42)) = 62 kcal. Again, one does not want to take such a crude estimate too seriously, but this simple bond-energy argument does encourage one to pursue quantitative theoretical studies.

The goals of the present theoretical study were then twofold: first, to examine the $(CS)_2$ system in the anticipation that it might have an enthalpic stability not present for the analogous CO dimer; and secondly to carry out a detailed theoretical study of the $^3\Sigma_g^-$ ground state of $(CO)_2$. The most reliable previous investigation of ethylenedione is that of Haddon, Poppinger, and Radom,[14] and these authors (HPR) concentrated on the lowest singlet electronic state of C_2O_2. Another unique aspect of the present research is the detailed prediction of vibrational frequencies, inasmuch as one of the most likely means of experimental detection of chemically bound C_2O_2 or C_2S_2 is matrix-isolation infrared spectroscopy.[17]

Theoretical Approach

Since the ethylenedithione molecule had not been the subject of previous theoretical studies, preliminary explorations were carried out at relatively crude levels of theory. Specifically, the STO-3G minimal basis and the 4-31G extended basis sets of Pople and co-workers[18] were used in conjunction with self-consistent-field (SCF) theory to predict the structure of $^3\Sigma_g^-$ C_2S_2. It should also be noted that with these smaller basis sets, the unrestricted SCF procedure of Pople and Nesbet[19] was employed.

In the later stages of this study, both C_2O_2 and C_2S_2 were examined by using standard double-ζ plus polarization (DZ + P) basis sets of contracted Gaussian functions. For carbon and oxygen, the (9s5p) sets of Huzinaga[20] were contracted to (4s2p) following Dunning.[21] For sulfur, Huzinaga's (11s7p) primitive basis was contracted to (6s4p) in the manner of Dunning and Hay.[22] To each atom was appended a set of six d-like functions (xx, yy, zz, xy, xz, yz multiplied times ($e^{-\alpha r^2}$) with orbital exponents α = 0.8 (oxygen), 0.75 (carbon), and 0.6 (sulfur). Thus the complete DZ + P basis set has the designation C,O(9s5p1d/4s2p1d), S(11s7p1d/6s4p1d).

Table I. Comparison between Theory and Experiment for the Diatomic Molecules CO and CS[a]

		total energy, hartrees	bond distance r_e, Å	harmonic vibrational frequency, cm^{-1}
		CO		
$X^1\Sigma^+$	DZ + P SCF	−112.758 78	1.118	2372
	experiment		1.128	2170
$a^3\Pi$	DZ + P SCF	−112.560 11	1.185	1992
	experiment		1.206	1743
		CS		
$X^1\Sigma^+$	STO-3G SCF	−430.471 70	1.519	
	4-31G SCF	−434.776 20	1.555	
	DZ + P SCF	−435.307 06	1.520	1396
	experiment		1.535	1285
$a^3\Pi$	DZ + P SCF	−435.206 09	1.569	1204
	experiment		1.569	1135

[a] Experimental bond distances and vibrational frequencies are from ref 15.

With the DZ + P basis, the restricted Hartree–Fock method of Roothaan[23] was used to investigate C_2O_2 and C_2S_2. Both equilibrium geometries and quadradic force constants were determined by using analytic gradient techniques.[24] The Cartesian force constants were subsequently subjected to a standard analysis[25] to yield harmonic vibrational frequencies.

The effects of electron correlation were investigated variationally by using the method of configuration interaction (CI).[26] The CI procedure included all (within certain classes) configurations differing by one or two electrons from the Hartree–Fock reference configuration, either **2** or **3**. The core molecular orbitals $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, and $2\sigma_u$ (carbon and oxygen 1s-like orbitals) were held doubly occupied in all configurations, and the corresponding (in a DZ-type basis set) four highest lying virtual orbitals were deleted from the CI procedure. Furthermore, for the open-shell species, only the Hartree–Fock interacting space[27,28] (those configurations having nonzero matrix elements with the SCF reference configuration) was included. Finally, the actual calculations were carried out not in $D_{\infty h}$ but its subgroup D_{2h}. With these specifications, it may be stated that for C_2O_2 there are 17 415 configurations for the $^3\Sigma_g^-$ state (**3**), 35 538 configurations for the $^3\Pi$ dissociation limit, and 15 009 configurations for the closed-shell singlet state (**2**). Final estimates of energy differences were made by using Davidson's correction for higher excitations (unlinked clusters).[29]

The Diatomics CO and CS

Since no experiments have been successfully carried out for the chemically bound C_2O_2 and C_2S_2, the component diatomics provide the only mechanism whereby we may touch base with experiment. For this reason, such a comparison is made in Table I. In general, the agreement is reasonable and consistent with what one expects from SCF theory applied with good basis sets. For carbon monoxide, the ground and first excited state bond distances are shorter than experiment by 0.010 and 0.021 Å, respectively. For CS, the $X^1\Sigma^+$ internuclear separation is 0.015 Å less than experiment, while the $a^3\Pi$ bond distance is spot-on. For ground-state CS, the minimal (STO-3G) and extended (4-31G) basis sets also do a reasonable job on the bond distance, lying 0.016 Å too short and 0.020 Å too long, respectively.

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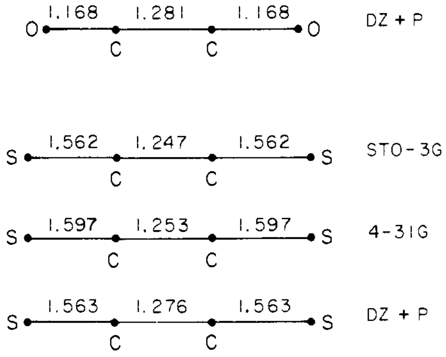


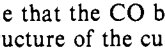
Figure 1. Predicted equilibrium geometries for the $^3\Sigma_g^-$ ground electronic states of C_2O_2 and C_2S_2.

The harmonic vibrational frequencies are too large by 9.3% for $X^1\Sigma^+$ CO, 14.3% for $a^3\Pi$ CO, 8.6% for $X^1\Sigma^+$ CS, and 6.1% for $a^3\Pi$ CS. Thus, on balance, it would appear that the DZ + P SCF level of theory does a bit better for CS than for CO. For the $X^1\Sigma^+ - a^3\Pi$ separation, the Hartree–Fock approximation inherently predicts a separation less than experiment, since the triplet state is treated better by a single-configuration wave function than is the closed-shell singlet ground state. With DZ + P SCF, the CO separation is 124.7 kcal (experiment 139.2 kcal[15]) and the CS X − a energy difference is 63.4 kcal (experiment 79.1). In both cases the error in the SCF singlet–triplet separation with respect to experiment is ~15 kcal.

Since vibrational frequencies for C_2O_2 and C_2S_2 were subsequently predicted only at the DZ + P SCF level of theory, the above results suggest that errors of the order of +10% should be expected there. However, the relative energies of C_2O_2 and C_2S_2 were also predicted by using correlated wave functions (see previous section for description), and accordingly smaller errors were anticipated. This notion is supported by the comparison of results obtained for the dissociation limits $X^1\Sigma^+$ CO + $X^1\Sigma^+$ CO and $X^1\Sigma^+$ CO + $a^3\Pi$ CO. As just noted, the DZ + P SCF value of this $X^1\Sigma^+ - a^3\Pi$ separation is 124.7 kcal. However, the DZ + P CI and cluster-corrected[29] DZ + P CI methods predict 134.8 and 136.3 kcal, respectively, for the same energy difference. The latter result is only 2.9 kcal less than the experimental value[15] (139.2 kcal), and this error may be considered representative of the reliability expected for other energy differences predicted in the same way.

Geometrical Structures of Ethylenedione and Ethylenedithione

The predicted $D_{\infty h}$ stationary point geometries of the $^3\Sigma_g^-$ electronic ground sates of C_2O_2 and C_2S_2 are illustrated in Figure 1. For C_2O_2, comparison with the earlier predictions of HPR[14] show qualitative agreement. Their STO-3G (1.256 Å) and 4-31G (1.261 Å) values of the C–C bond distance are slightly less than the present DZ + P SCF value of 1.281 Å. All three levels of theory concur that the bond order of the C–C bond in ethylenedione is about 2.5. Somewhat in contrast, the DZ + P SCF C–O bond distance is 1.168 Å, a bit shorter than HPR values 1.214 Å (STO-3G) and 1.186 Å (4-31G). The DZ + P SCF theoretical value of 1.168 Å places the C—O distance in C_2O_2 just about halfway between the formaldehyde C═O double bond (1.203 Å)[30] and the carbon monoxide C≡O triple bond (1.128 Å).[15] On this basis one would conclude that the CO bond order is about 2.5 and sketch a valence structure of the curious form:



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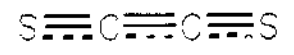
This structure, among other problems, has a bond order of *five* about each carbon atom and should not be taken too seriously. Nevertheless, the short carbon–carbon distance is very different from that expected for a van der Waals molecule[8,9] and obviously indicative of genuine chemical bonding.

Table II. Predicted Harmonic Vibrational Frequencies for the Linear $^3\Sigma_g^-$ Ground States of OCCO and SCCS[a]

normal-mode symmetry	C_2O_2	C_2S_2	description
Σ_g^+	2653 (2369)	2104 (1879)	C–C stretch
Σ_u^+	1954 (1745)	1262 (1127)	asym C–X stretch
Σ_g^+	1023 (913)	595 (531)	sym C–X stretch
Π_u	345 (308)	199 (178)	cis bend
Π_g	277 (247)	485 (434)	trans bend

[a] All entries are in cm^{-1} and determined at the DZ + P SCF level of theory. The equilibrium geometries about which the vibrational analyses were performed are seen in Figure 1. The frequencies in parentheses have been empirically reduced by 12% from the ab initio values.

For ethylenedithione, the three levels of theory are again in qualitative agreement. It is also apparent that the mechanism of bonding is the same as for $^3\Sigma_g^-$ C_2O_2. At the DZ + P SCF level, the C–C distance r_e is only 0.005 Å shorter in C_2S_2 than in C_2O_2 and both bond distances imply a C–C bond order of about 2.5. In C_2S_2, the C–S distance of 1.563 Å is actually a bit closer to the triple bond of C≡S (1.535 Å)[15] than the C═S double bond of thioformaldehyde (1.611 Å).[31] Thus for ethylenedithione, one is again faced (strictly on the basis of geometrical data) with a bizarre valence structure:



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incorporating three bonds of order 2.5.

In light of these remarkable geometries, it is important to point out that for unusual molecular species the correlation between bond distance and bond strength often breaks down. For example, the very weak (~3.3 kcal) bond in diatomic XeF is only ~20% longer[32] than that in XeF_2, for which the first XeF bond has a dissociation energy of ~60 kcal. A second example[33] is the short but rather weak bond in Cr_2. Still other examples of short but weak aluminum–carbon bonds are given in the recent theoretical study of Fox and co-workers.[34] Therefore, one need not necessarily assume that these carbon–carbon bonds (in $^3\Sigma_g^-$ C_2O_2 and C_2S_2), which are sufficiently short to be classified of bond order 2.5, are necessarily very strong bonds in the conventional thermochemical sense.

Vibrational Frequencies

The DZ + P SCF harmonic vibrational analyses for linear ethylenedione and ethylenedithione are summarized in Table II. There, it is seen first of all that both linear structures are true mimina on their respective potential energy hypersurfaces. This immediately rules out the possible cis and trans bent structures examined in some detail at lower levels of theory of HPR.[14] However, the low-frequency bending modes of both molecules suggest that the energy surfaces are rather flat in the vicinity of these linear minima.

It is generally accepted that vibrational frequencies provide a fingerprint by which to identify functional groups.[35] Thus, for example, characteristic frequencies for carbon–carbon single, double, and triple bonds are respectively of the order of 1100, 1600, and 2100 cm^{-1}. However, before comparing the theoretical predictions with these "standard" frequencies, it is well to note that DZ + P SCF harmonic frequencies are typically of the order of 12% greater than the observed stretching fundamentals. In

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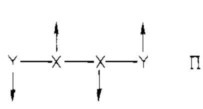
an ordinary case, this 12% difference might be due to a combination of the effects of anharmonicity (perhaps 4%) and neglect of electron correlation (perhap 8%).[36] For this reason, we now reduce the ab initio C=C stretching frequencies of Table II to 2369 cm^{-1} (C_2O_2) and 1879 cm^{-1} (C_2S_2) prior to comparison with experiment. Even so, both frequencies clearly fall within the sphere of carbon–carbon multiple bonding. It would, however, be a mistake to conclude that the high CC stretching frequency in C_2O_2 proves that a triple bond is present, since the proximity of the CC and CO stretching frequencies makes possible considerable mixing in the final vibrational analysis. In contrast, the lower frequency CS stretching (see Table I; ω_e = 2170 cm^{-1} for diatomic CO vs. 1285 cm^{-1} for diatomic CS) does not mix as effectively with the CC stretching in C_2S_2. We conclude that the predicted CC stretching frequency of 1879 cm^{-1} for C_2S_2 is more nearly isolated, and hence subject to standard group-frequency analysis,[35,37] than the predicted frequency at 2369 cm^{-1} for C_2O_2.

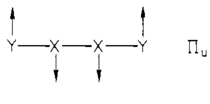
In like manner, the characteristic frequencies[37] of C–O single, double, and triple (diatomic CO of course is the only known example) bonds are 1050, 1700, and 2143 cm^{-1}. However, such a direct comparison with the theoretical values is not appropriate, since it is well-known that the presence of multiple bonds in close proximity gives rise to asymmetric and symmetric stretching frequencies separated by a considerable difference. For example, the CO_2 molecule clearly has two C=O double bonds, but the observed stretching frequencies,[40] at 2349 and 1388 cm^{-1}, are separated by 961 cm^{-1}. This is admittedly an extreme case, since the two C=O bonds are immediately adjacent, and, for the carbon suboxide molecule O=C=C=C=O, the observed C=O frequencies,[41] at 2258 cm^{-1} (Σ_g^+) and 2185 cm^{-1} (Σ_u^+) are separated by only 73 cm^{-1}. Clearly, the C_2O_2 molecule studied here, with predicted CO stretching frequencies of 1745 and 913 cm^{-1}, is closer to CO_2 than to C_3O_2. Furthermore, comparison of the present C_2O_2 frequencies (1745, 913 cm^{-1}) with those for CO_2 (2349, 1388 cm^{-1}) suggests somewhat *less* than CO double bond character for the CO bonds in C_2O_2.

For carbon–sulfur single bonds, a typical stretching frequency is 700 cm^{-1}, while in thioformaldehyde[31] the C=S mode lies at 1059 cm^{-1} and for diatomic C≡S, ν = 1273 cm^{-1}. Moreover, the adjacent C=S frequencies in CS_2 are 1533 and 658 cm^{-1}, while those separated by two bonds in C_3S_2 (carbon subsulfide) are 1663 and 485 cm^{-1}. In this light the theoretical CS stretching frequencies at 1127 and 531 cm^{-1} would appear to be characteristic of the system with two interacting *weak* C=S double bonds. In this sense the vibrational frequencies of the $^3\Sigma_g^-$ ground states of C_2O_2 and C_2S_2 are consistent in predicting CO and CS bond orders significantly less than the 2.5 suggested by the theoretical molecular structures.

An interesting prediction seen in Table II is that the Π_u bending frequency is the higher for C_2O_2, while the bending frequency of Π_g irreducible representation is significantly higher for C_2S_2. Note in this regard that these symmetry species correspond qualitatively to the following nuclear motions:



(5)



(6)

Table III. Relative Energies of the $^3\Sigma_g^-$ Ground Electronic States of C_2O_2 and C_2S_2 Relative to the Symmetry-Allowed $X^1\Sigma^+ + a^3\Pi$ Dissociation Limit and Relative to the Lowest Dissociation Limit $X^1\Sigma^+ + X^1\Sigma^+$[a]

O=C=C=O

method	absolute $^3\Sigma_g^-$ energy, hartrees	relative to $X^1\Sigma^+$ CO + $a^3\Pi$ CO, kcal	relative to $X^1\Sigma^+$CO + $X^1\Sigma^+$ CO, kcal
STO-3G UHF[b]	−222.37464	−91.8	47.9
4-31G UHF[b]	−225.03124	−93.1	46.1
DZ + P RHF	−225.39997	−65.4	73.8
DZ + P Cl	−225.90646	−73.7	65.5
Davidson corrected	(−225.97106)[c]	−74.2	65.0

S=C=C=S

method	absolute $^3\Sigma_g^-$ energy, hartrees	relative to $X^1\Sigma^+$ CS + $a^3\Pi$ CS, kcal	relative to $X^1\Sigma^+$ CS + $X^1\Sigma^+$ CS, kcal
STO-3G UHF	−861.05500	−149.2	−70.1
4-31G UHF	−869.67250	−154.5	−75.4
DZ + P RHF	−870.67470	−117.1	−38.0
DZ + P Cl	−871.11686	−120.8	−41.7
Davidson corrected	(−871.18209)[c]	−118.5	−39.4

[a] The experimental $X^1\Sigma^+$–$a^3\Pi$ separations[15] used here are 139.2 kcal (CO) and 79.1 kcal (CS). [b] Ref 14. [c] Not a variational result.

Displacement (5) is seen to lead to trans structures, while normal coordinate (6) moves the molecule into cis geometries. Thus it is seen that C_2O_2 is more favorable energetically toward cis bent structures, while C_2S_2 prefers trans distortions from equilibrium by a significant amount.

The known molecule most like C_2O_2 might appear to be cyanogen, C_2N_2, the vibrational frequencies of which are known.[41] However, the CC single-bond stretching frequency of C_2N_2 is only 851 cm^{-1}, much less than the 2369 cm^{-1} predicted here for C_2O_2. Note that this result is consistent with the former's longer C–C bond distance[42] (1.397 Å) compared with the 1.281-Å C–C distance predicted here for C_2O_2. Furthermore, the CN stretching frequencies (2330, 2158 cm^{-1}) appear to interact rather weakly compared to the separation of 832 cm^{-1} found for C_2O_2. Thus we conclude that the two CN fragments in C_2N_2 are much more weakly bound in this well-characterized molecule than for the experimentally unknown C_2O_2 $^3\Sigma_g^-$ electronic ground state. Hopefully this observation will encourage experimentalists to pursue the C_2O_2 species.

Relative Energies

The laboratory preparation of ethylenedione or ethylenedithione requires a measure of thermochemical stability. Should either C_2O_2 or C_2S_2 lie energetically below the respective ground-state dissociation limits CO + CO or CS + CS by more than a van der Waals dissociation energy, then a new absolute minimum for the energy hypersurface could be claimed. However, since the dimer electronic ground states are of $^3\Sigma_g^-$ symmetry, all that is required for thermochemical stability is a significant potential well relative to the separated diatomic dissociation limit $X^1\Sigma^+ + a^3\Pi$. In this light, we present in Table III a summary of the theoretical relative energies.

As noted earlier by HPR,[14] ethylenedione is not the absolute minimum on the C_2O_2 potential surface. However, every level of theory reported in Table III yields a $^3\Sigma_g^-$ ground state strongly bound relative to the lowest triplet CO + CO dissociation limit. Not anticipated from previous studies[13,14] of C_2O_2 is the fact that polarization basis functions (d functions on each atom) *decrease* the predicted dissociation energy from 93.1 kcal (4-31G basis) to 65.4 kcal (DZ + P basis). This is of course contrary to what

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is typically found[22] and is due to the fact that d functions are especially important in describing the triple bonds of the separated CO molecules. Electron correlation has a relatively small effect on the predicted value of D_e (OC – CO), which is increased by 8.3 kcal to 73.7 kcal (DZ + P CI). Finally, the Davidson correction for unlinked clusters[29] increases the predicted dissociation energy by 0.5 kcal to 74.2 kcal.

In contrast, $^3\Sigma_g^-$ ethylenedithione is the *absolute* minimum on the C_2S_2 energy hypersurface. This result is predicted at each of the five levels of theory considered here. As with C_2O_2, however, the predicted value of the dissociation energy is significantly reduced by the addition of d functions to the basis set. Relative to the lowest CS + CS triplet dissociation limit, the 4-31G and DZ + P SCF values of D_e (SC – CS) are 154.5 and 117.1 kcal, respectively. The dissociation energy relative to two ground-state CS molecules is similarly reduced from 75.4 kcal (4-31G) to only 38.0 kcal (DZ + P). These DZ + P SCF dissociation energies are, however, somewhat increased when the effects of electron correlation are variationally considered.

Concluding Remarks

A very simple and crude bond-energy argument presented in the introduction suggests that S=C=C=S might have a thermochemical stability (relative to the dissociation limit CS + CS) much greater than the analogous oxygen compound O=C=C=O, which lies energetically above two ground-state CO molecules. This seemingly naive suggestion has been confirmed in the present theoretical study, in the sense that the $^3\Sigma_g^-$ ground state of ethylenedithione is predicted to be the absolute minimum on the C_2S_2 potential energy hypersurface, lying 39 kcal below $X^1\Sigma^+$ CS + $X^1\Sigma^+$ CS. Therefore, we are convinced that C_2S_2 is a "makable" molecule and look forward to experimental efforts to this end. Since the monomer CS itself is not a very stable species, we appreciate that the production of gram quantities of C_2S_2 is unlikely. However, matrix-isolation infrared spectroscopy,[17] electron spin resonance techniques,[38] or molecular beam studies[39] would all appear to be viable approaches to the experimental identification of ethylenedithione. Although the $^3\Sigma_g^-$ state of C_2O_2 lies ~65 kcal above $X^1\Sigma^+$ CO + $X^1\Sigma^+$ CO, this metastable species nevertheless lies 74 kcal below its lowest spin-allowed dissociation limit and should also be detectable in a carefully designed experiment.

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Gas-Phase Nucleophilic Reactivities of Phenylnitrene ($PhN^{-}\cdot$) and Sulfur Anion Radicals ($S^{-}\cdot$) at sp^3 and Carbonyl Carbon[1]

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Abstract: The reactions of $PhN^{-}\cdot$ with a series of carbonyl-containing molecules (aldehydes, ketones, and esters) were shown to proceed via an addition/fragmentation mechanism, $PhN^{-}\cdot + R_2C{=}O \rightarrow [Ph\dot{N}C(O^-)R_2] \rightarrow PhN{=}C(O^-)R + \cdot R$, producing various acyl anilide anion products. In several cases, the tetrahedral intermediate anion radicals were observed as minor ions. The *intrinsic* reactivity of the carbonyl-containing molecules was aldehydes > ketones > esters, where similar R groups were involved. The overall exothermicities of these reactions did not appear to play the major role in determining the relative rates ($k_{rel}^{C=O}$) for these reactions. From the reaction of $PhN^{-}\cdot$ with cyclobutanone, a new type of anion radical, $PhN{=}C(O^-)CH_2\cdot$ (*m/z* 133) (+ C_2H_4), was produced; the loss of C_2H_4 was considered due to the ring strain in the ketone. With cyclopentanone, cyclohexanone, and cycloheptanone, the anion radicals $PhN{=}C(O^-)(CH_2)_n\cdot$ (n = 4–6) were the exclusive product ions. $PhN^{-}\cdot$ was shown to be a poor nucleophile in S_N2 displacement reactions with CH_3X molecules (X = Cl, Br, O_2CCF_3). $S^{-}\cdot$ was shown to exhibit modest S_N2 nucleophilicity with CH_3Cl and CH_3Br. The reactions of $S^{-}\cdot$ with CF_3CO_2R proceeded via both S_N2 displacement and carbonyl addition/fragmentation mechanisms: with R = CH_3, the anion products were 65% $CF_3CO_2^-$ and 35% CF_3COS^-; from R = C_2H_5, the product ions were 4% $CF_3CO_2^-$ and 96% CF_3COS^-. These data yield the ratio $k_{CH_3}/k_{C_2H_5} = 16$ for S_N2 displacement by $S^{-}\cdot$ at these alkyl groups. The reactions of $PhN^{-}\cdot$ with CO_2, COS, CS_2, and O_2 are also reported. The reaction of $PhN^{-}\cdot$ with CS_2 to produce $S^{-}\cdot$ as a major channel was used as the source of this atomic anion radical. In several reactions occurring at nearly the collison limit, selectivity was observed for (a) which of two reaction centers were attacked to give products and (b) which of two mechanisms would be dominant in the overall reaction.

Studies of S_N2 displacement reactions by closed-shell nucleophiles in the gas phase have been reported.[2-10] Predominant inversion of configuration was established in displacement of Br^- by Cl^- from an RBr molecule,[5] a relative kinetic nucleophilicity order was established,[6,7] and a double-minimum model for the potential surface of the gas-phase S_N2 mechanism was developed.[8,9]

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