the spectra of the cis isomer. The strong band at 1160 cm^{-1} remains unshifted while the band at 1530 cm^{-1} shifts to 1540 cm^{-1} in the cis isomer. Rimai et al.[34,35] have investigated the Raman spectra of a series of isomers of retinal. They found that the most prominent changes in the spectra occurred in the 1100–1400-cm^{-1} region. In particular, the various cis isomers are characterized by specific new bands in this spectral region as compared to the all-trans isomer.

Taking these observations into account, we believe that the observed changes in the Raman spectra in going from the parent ground-state compound to the lowest excited triplet state indicate substantial C=C bond twisting in the equilibrium conformation of the triplet state. In particular, the new feature at 1236 cm^{-1} in the triplet spectrum suggests that the bond twisting of the triplet excited β-carotene is localized at the 15,15′ double bond.

The interpretation of the triplet Raman spectrum suggested here is qualitatively supported by the similarity between the triplet–triplet absorption spectra of *all-trans-β*-carotene and 15,15′-*cis-β*-carotene[4,5] and by theoretical predictions based on molecular orbital calculations.[36,37] As far as the present discussion is concerned, these calculations predicted double bond twisting of the polyenes in their excited states. Twisting of the inner double bonds was preferred energetically as compared with twisting of outer double bonds.

The remaining band at 1496 cm^{-1} in the triplet spectrum can be correlated with the ground-state band at 1520 cm^{-1}, resulting in a shift of 24 cm^{-1}. As the ground-state band at 1520 cm^{-1} is probably due to in-phase C=C stretching vibrations, the observed shift upon excitation can be explained qualitatively by the decreased π-bond order in the excited state which has been predicted.[36,37]

Lutz et al.[33] reported that the strong C=C band of *all-trans-β*-carotene at 1530 cm^{-1} in their spectra shifted to 1540 cm^{-1} in the spectrum of 15,15′-*cis-β*-carotene. Assuming that our interpretation of the triplet spectrum of *all-trans-β*-carotene given above is adequate, we may notice that two opposing effects are operating. One is the electronic effect caused by the electronic excitation and the other the conformational effect due to the change in equilibrium geometry. Thus the shift due to the electronic excitation alone should be greater than 24 cm^{-1}.

Having discussed the frequency shift of the 1520-cm^{-1} ground-state band in terms of the decreased π-bond order of the excited state, the 32-cm^{-1} downward shift of the 1157-cm^{-1} ground-state band remains to be explained. Although the 1157-cm^{-1} mode contains a minor contribution from C=C stretching according to Rimai et al.[8] the shift can hardly be explained by the theoretically predicted decrease in π-bond order upon excitation, as this decrease should be accompanied by a bond order increase in the single bond regions. Twisting of the 15,15′ bond in the excited state cannot explain the shift either, as Lutz et al.[33] reported the strong band at 1160 cm^{-1} in both isomers. On the basis of their resonance Raman spectrum of the triplet β-carotene, Dallinger et al.[24] proposed that the 1005-cm^{-1} band might be due to the C—C stretching mode, as they observed a minor upward frequency shift for this band. Our measurements do not support this assignment as the shift from 1005 to 1009 cm^{-1} is insignificant; thus they agree with the assignment of this band to the C–CH$_3$ stretching mode. In conclusion we must leave the question open and note, as Dallinger et al. did, that these resonance Raman data may indicate that the force constants in the C–C stretching region are not changing in the predicted manner. Studies on related structures might help in resolving this problem.

Conclusions

The resonance Raman spectrum of the lowest excited triplet state of *all-trans-β*-carotene has been obtained and the assignment of the transient bands supported by investigating the dose and time dependence of the Raman intensity. The frequency and intenisty changes observed in going from the ground-state molecule to the triplet excited molecule suggest that the *all-trans-β*-carotene in its lowest excited triplet state is twisted, presumably about the 15,15′ bond. The shift observed for the ground-state band at 1157 cm^{-1}, however, cannot be qualitatively explained in terms of the suggested geometry changes.

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Intermediate Molecular Species in the Oxidation of H_2S. An ab Initio Configuration Interaction Study

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Abstract: An ab initio configuration interaction method has been applied to the study of the intermediate products H_2SO, HSO, and HSOH of the oxidation reaction of H_2S in an argon matrix. The variation of energy with respect to SH asymmetric stretch is determined near the equilibrium geometry for H_2SO, and the SH bonding energy is estimated. HSOH is found to be more stable than H_2SO. A normal coordinate analysis of the former gives a frequency assignment in good agreement with matrix IR spectroscopy.

Introduction

The reaction between atomic oxygen, O(^{3}P), and hydrogen sulfide, H_2S, has been widely studied due to its occurrence in fuel combustion and in polluted earth atmosphere. In the earlier investigations[1–4] the temperature and pressure were varied over

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a large range, and different methods of detection of the reaction products were used to elucidate the mechanism of the oxidation (mass spectrometry, chemiluminescence, electron spin resonance).

There is a general agreement on the fact that SO radicals are produced, but the reaction is strongly dependent on conditions, and two mechanisms for the production of radicals have been proposed:

The three step reaction

$$O + H_2S \rightarrow OH + SH \quad (1)$$

$$O + SH \rightarrow SO + H \quad (2)$$

$$H + H_2S \rightarrow H_2 + SH \quad (3)$$

where reactions 2 and 3 constitute a chain mechanism, or a process involving a loose activated complex as invoked in the reaction of dimethyl sulfide with oxygen,[5]

$$O + H_2S \rightarrow [H_2S{=}O] \rightarrow HS{=}O + H \quad (4a)$$

More recently the oxidation reaction has been generated in an argon matrix at 8 K by flash photolysis of a mixture of $O_3 + H_2S$.[6] The products of the reaction have been identified by infrared spectroscopy of the matrix. Evidence was found for the existence of a new species HSOH in favor of reaction 4a, but probably with a small energy barrier and low frequency factor, so that at higher temperature reaction 1 could be predominant. The reaction mechanism in eq 4b was also proposed.

$$H_2S + O \rightarrow [H_2SO] \rightarrow H_2 + SO \quad (4b)$$

The goal of this work is to apply ab initio configuration interaction theory to a study of some molecular species which could be intermediates in the oxidation of H_2S, as suggested by reaction 4a.

Methods

The calculations are of restricted self-consistent-field (SCF) type using contracted basis sets of Gaussian lobe orbitals, followed by configuration interaction using the CI method of Whitten and Hackmeyer.[7] The problem being rather complex, we followed a simplified scheme. Starting with the compound H_2SO, we studied the stretching of one HS bond leading to dissociation into HSO + H; then a hydrogen is moved toward the O atom of HSO to form HSOH. Also the stretch of HS in the radical HSO is studied. Our investigation includes the determination of some geometrical parameters in H_2S, H_2SO, and HSOH as well as the electronic structure and energy of atomic and molecular species S, H, O, OH, SH, and SO.

The selection of the basis set and the development of the CI are the result of some preliminary calculations summarized in the next section.

Preliminary Calculations

The relevant atomic basis sets concern hydrogen, sulfur, and oxygen. Trial atomic basis sets on hydrogen and sulfur were first checked with respect to their ability to give the angular geometry of H_2S, keeping the bond length at its experimental value 2.524 au.[8] The following contracted Gaussian lobe orbitals were used.

Hydrogen: a five-term s orbital split into two components with scaled exponents (scaling factor $\eta^2 = 2.2$) as given by Petke and Whitten;[9] a one-component p orbital (exponent 0.65) and a one-component d orbital (exponent 0.55).

Sulfur: an atomic basis set reported by Petke et al.[10] augmented by a one-component d orbital (exponent 0.5, following Jafri et al.[11]).

Oxygen: an atomic basis set reported by Besnainou and Whitten[12] with the five-term p orbital split into two groups and the basis augmented by the two-term d orbital of Neumann and Moskowitz.[13]

The resulting initial bases for H_2S and H_2SO contain 32 and 46 contracted atomic orbitals, respectively (only one in plane d_{xy} orbital per hydrogen is included). The *y* axis bisects the HSH angle and the SO bond lies in the *yz* plane. Once the energy with respect to HSH angle variation was verified to be close to the experimental value of 92° (numerical comparisons are given in the next section), we then studied H_2SO by varying the HSO angle, fixing the HSH angle at 100° and the SO bond at 2.778 au by analogy with $(CH_3)_2SO$.[14] The HSO angle was calculated to be 107°, which is close to the CSO angle in $(CH_3)_2SO$.

Finally the basis set was made more flexible by splitting the long-range p orbital on sulfur into two groups, but the number of d orbitals was reduced to four ($d_{y^2-z^2}$, d_{xy}, d_{yz}, d_{xz}) based on an examination of the H_2SO results. Also only three d orbitals were kept on oxygen ($d_{y^2-z^2}$, d_{xy}, d_{xz}), while d's were eliminated entirely from hydrogen, retaining on H the two-component s orbital and a p_σ orbital directed along the SH bond. The total number of basis orbitals for H_2SO is now 40, giving a total energy lower by 0.0236 au than the energy of the 46 orbital basis set without splitting on the long-range p orbital on sulfur. Similarly the basis set on H_2S was reduced to 28 orbitals; for an apex angle of 100° the energy was nearly the same as the energy of the 32-orbital basis set.

The CI method is described in detail in ref 7, and here we give only a brief outline of the procedure. Configurations for a given state are constructed from an orthogonal basis of molecular orbitals obtained from ground-state SCF computations. An invariant core consisting of the set of lowest energy molecular orbitals is designated and configurations are generated by allowing variable occupancy of the remaining molecular orbitals. The generation scheme is based on an initial approximation Ψ_0 of the state of interest which is obtained from a small-scale CI treatment. Single and multiple excitations from the major contributing configurations in Ψ_0 are performed, and those resulting configurations Ψ_k with a sufficiently large interaction with Ψ_0

$$\frac{|\langle\Psi_k|H|\Psi_0\rangle|^2}{\langle\Psi_k|H|\Psi_k\rangle - \langle\Psi_0|H|\Psi_0\rangle} > \delta$$

are retained in the CI expansion. In the present work Ψ_0 is the ground-state configuration so that mainly double excitations appear in the CI wave function.

We have not attempted to generate extremely large CI expansions but the thresholds δ are sufficiently small ($\approx 10^{-5}$ au) to give the major energetic effects at distances near equilibrium and for the dissociated fragments. In general, a maximum of 18 valence electrons distributed over 26 occupied and virtual molecular orbitals were included, giving typically 1000 configuration expansions.

Results and Discussions

In the following we analyze in the first part the results obtained for the atomic species H, S, and O, the diatomic radicals OH, SH, and SO, and the molecule H_2S as a check of the reliability

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of the basis set chosen. In the second part we examine and discuss calculated structural and energetic properties of H_2SO, HSO, and HSOH.

I. Atoms, Diatomic Radicals, H_2S. (a) The hydrogen energy is essentially exact, −0.4998 vs. −0.5 au; using an atomic scaling factor appropriate for H_2S the H atom energy is 0.008 au higher. The energies of sulfur (−397.4894 au) and oxygen (−74.7921 au) are fairly close to the Hartree–Fock[15] values. Using the split basis set for the OH and SH radicals gives energies at ≈0.04 au higher than the Hartree–Fock results.[16,17] The energy of the SO radical, −472.3017 au, is higher by 0.1 au than the value computed by Green,[18] who employs a superior atomic basis.

Thus we conclude that the basis sets are of reasonable accuracy energetically at the SCF level for the atoms and diatomic radicals. For H_2S, keeping the SH bond length at the experimental value (2.524 au) and using the 32 orbital basis set, from which the 28 orbital set has been generated, we have calculated the energy as a function of the bond angle. The minimum energy is found at $\theta = 93° 42'$, close to the experimental value of 92°.[8] The bending force constant is 0.5 mdyn/Å, rather close to the experimental value of 0.43 mdyn/Å.[19]

To determine the possible existence of the remaining molecules with small binding energies, it may be necessary to go to the CI level.

(b) In the CI calculations on sulfur and oxygen all electrons are included and have been allowed to occupy all available SCF orbitals, but since only one higher angular momentum d orbital is included, only 16% of the correlation energy is obtained. (The correlation energies of sulfur and oxygen have been estimated[20] as 0.640 and 0.258 au, respectively.)

In the radicals the CI energy lowerings are substantial in view of the fact that most of the improvement is associated with the description of bonding. The binding energies have been calculated as the difference between the molecular energy and the sum of the ground-state atomic energies. They are for OH, 101 kcal/mol, and for SH, 62 kcal/mol, in fair agreement with experiment; 106.5 and 103 kcal/mol for OH; and 87 and 84 kcal/mol for SH, the former of each pair of experimental values corresponding to spectroscopy measurements[21] and the latter to a thermodynamic estimate.[22] For SO the calculated value, 43 kcal/mol, is much less than the thermodynamic evaluation of 124.7 kcal/mol.[22] The calculated SO binding energy is, however, rather close to values reported by Wallmeier and Kutzelnigg[23] for the SO bond in H_2SO.

Fixing the bond angle at 100° (with a bond angle of 100° the SCF energy is about 0.6 kcal/mol higher than the SCF minimum energy), the calculation on H_2S was repeated with the 28 orbital set, giving an average bond energy of 72 kcal/mol. The dissociation energy for one SH bond has been calculated by Benson[22] from thermodynamic data as 92 kcal/mol. One can see that the experimental ratio of the bond energies of SH and H_2S is correctly reproduced by the calculations.

In conclusion the above data suggest that it will be possible to draw reliable conclusions concerning the energetics of H_2SO, HSO, and HSOH.

II. H_2SO, HSO, and HSOH. The SH bond length and HSH angles being fixed at 2.524 au and 100° as described in the preliminary calculations, the HSO angle and the SO bond distance have been calculated from the corresponding SCF energy curves. We recall that with the 46 orbital basis set, keeping the SO bond at 2.778 au (1.47 Å), the minimum energy is found for HSO = 107°. The computed force constant is 1.62 mdyn/Å, corresponding to the symmetrical deformation of the HSO angles. Even if we subtract ≈0.1 mdyn/Å as a standard estimate for the interaction force constant between the two bending coordinates, what remains for the diagonal force constant is outside the expected range, between 0.4–0.9 mdyn/Å.[19] For comparison refer to the work on the HSO radical,[24] where the bending force constant computed at the CI level is 0.70 mdyn/Å.

When the HSO angle at 107° was kept and the other parameters were not varied, the SO bond was considered at three additional lengths, and the corresponding SCF energy computed with the 40 orbital basis set. The minimum energy is at $R_{SO} = 2.8724$ au (1.52 Å). The calculated force constant is 6.03 mdyn/Å, to be compared to earlier studies giving 4.11 mdyn/Å in HSO[24] and 3.08 mdyn/Å in SOH.[25]

To summarize, the calculated SCF geometry of H_2SO is rather similar to the experimental geometry of $(CH_3)_2SO$[14] with a slightly longer SO bond.

As a model of asymmetric stretch, one SH bond has been stretched with the other held constant in a series of calculations from $R = 2.524$ to 2.740 au. The energy curves are rather flat, particularly at the CI level of treatment.

The threshold of 70 μhartree should give the correct general shape, but the reliability of the curvature near the minimum which determines the force constant has not been carefully examined. The computed force constant is 4.01 mdyn/Å at the SCF level and 2.9 mdyn/Å at the CI level. The actual value is probably in between, which confirms the prediction of a slightly weaker SH bond in the hypothetical H_2SO. For comparison, the SH force constant of H_2S deduced from infrared spectroscopy is 4.14 mdyn/Å.[26] At the SCF level, a Mulliken population analysis for the symmetric case gives net charges of +0.57 on S, +0.05 on H, and −0.76 on O, showing, with respect to H_2S (net charge on S −0.32 and on H +0.16), a considerable change of the electronic distribution in the SH bonds. The hydrogen atoms gain some negative charge at the expense of the sulfur atom, which now becomes strongly positive due to the presence of the electron-attracting oxygen atom.

For this same geometry the binding energy calculated as the difference in energy between the molecular species and the sum of the atomic energies is 88 kcal/mol at the SCF level and nearly the same, 86 kcal/mol, at the CI level with a threshold of 25 μhartree. Compared to the sum of the binding energy of one SO bond and two SH bonds which is 167 kcal/mol at the CI level, H_2SO shows a decrease of 80 kcal/mol. This is in satisfactory agreement with Benson's[22] thermodynamic estimate of 110 kcal/mol, considering the poor description of the SO bond.

Evidence for the formation of HSO in its $^2A''$ ground state as a reaction product on hydrogen abstraction has been inferred by analogy with the reaction products of the thermal oxidation of molecules similar to H_2S, like dimethyl sulfoxide in the gas phase. Although in the case of H_2S + O in an argon matrix, the analysis of the chemiluminescence spectrum generated by the warmup of the matrix does not exclude the possibility of HSO existing in the excited $^2A'$ state.[27]

The energy of HSO in its ground state ($R_{SH} = 2.524$ au, $R_{SO} = 2.835$ au, HSO = 107°) plus the energy of an H atom is higher by ≈0.052 au than the energy of H_2SO at the CI level. The SO bond is less polar. At the SCF level the net charges on sulfur, hydrogen, and oxygen are now +0.57, +0.05 and −0.62. The SH bond dissociation energy calculated as the difference in energy between H_2SO and HSO + H is 33 kcal/mol. The estimate by Benson[22] is 63 kcal/mol and by Smardzewski,[27] 28 kcal/mol. But the degree of accuracy of our calculations would rather favor the former value, whose strongest support is the character of self-consistency of the additivity rules[28] from which it is deduced.

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Table I. Main Force Constants of HSOH (mdyn/Å)

force constant	force field calculation	SCF calculated values
k_{SH}	4.0[a]	4.01 (in H_2SO)
k_{SO}	4.5[a]	6.03 (in H_2SO)
k_{OH}	6.71	6.23
$k_{\delta_{HSO}}$	0.18	1.52 (in H_2SO)
$K_{\delta_{SOH}}$		0.64
$k_{\tau_{HSOH}}$	0.08	
$k_{SO,OH}$	0.06[a]	

[a] Fixed force constants.

The refined calculation by Sannigrahi et al. on the HSO radical[24] in which all geometrical parameters were optimized shows the minimum energy at $R_{SH} = 2.55$ au, HSO = 100.6°, and $R_{SO} = 2.91$ au. Without changing the bond angle (107°) in our calculations but taking $R_{SO} = 2.91$ au, the energy was computed at two different distances, $R = 2.524$ au and $R = 2.929$ au, in a study of the SH stretch. The results are obtained using a relatively large threshold ($\delta = 100$ μhartree).

The lower energy of the two points is at $R_{SH} = 2.524$ au and the difference in energy between them, -0.012 au, is again suggestive of a rather shallow bonding energy curve, and a weak SH bond.

HSOH is considered geometrically similar to hydrogen persulfide where the HSS and SSH planes have been shown to be nearly orthogonal.[29] Assuming this for the HSO and SOH planes and keeping $R_{SH} = 2.524$ au, $R_{SO} = 2.91$ au, HSO = 107°, R_{OH} fixed at 1.984 au, the angle SOH was varied to determine its equilibrium value. Fitting the energy curve by a second order polynomial, the equilibrium bond angle and bonding force constant are found, respectively, equal to $\approx$113° and 0.64 mdyn/Å. Corresponding values calculated by Sannigrahi et al.[25] in the SOH radical at the CI level are 109° and 1 mdyn/Å.

Taking the SOH angle as 105°, which is the closest to the minimum energy calculated point, and keeping all other parameters unchanged the energy was computed for three more OH bond distances to determine the equilibrium OH bond distance. The equilibrium bond distance and the force constant have been computed from a polynomial fit, all points being taken into account. They are equal to 1.767 au and 6.23 mdyn/Å at the SCF level and 1.795 au and 5.33 mdyn/Å at the CI level. In the case of the SOH radical the following values have been reported previously,[25] $R_{OH} = 1.802$ au and $k_{OH} = 9.51$ mdyn/Å. For comparison, the normal OH bond length is $\approx$1.80 au and the corresponding force constant $\approx$7.7 mdyn/Å.[26] The energy of HSOH is lower than the energy of H_2SO by 34 kcal/mol (SCF) and 20 kcal/mol (CI), in good agreement with the thermodynamic estimate of 20 kcal/mol.[22]

As mentioned, HSOH has been identified by infrared spectroscopy of the products generated by the reaction $H_2S + O$ in an argon matrix. Using the experimental assignment[6] we have performed a force-field calculation of HSOH to determine if the results are consistent with the assumption of a molecular species. The force field is harmonic, and the force constants are adjusted to fit the frequencies of the molecules HSOH, DSOD, and $HSO^{18}H$; the geometrical parameters are $R_{SH} = 2.524$ au, $R_{SO} = 2.91$ au, $R_{OH} = 1.984$ au, HSO = 107°, and SOH = 105°, with the dihedral angle between the planes HSO and SOH equal to 90°. The calculation has been made by use of the program of Schachtshneider et al.[30] in whose work can be found a detailed description of the method. The number of observed frequencies is insufficient to determine all force constants; thus in the calculations certain values were fixed by trial calculations. Final results can be found in Table I in which the SCF computed values have also been reported.

Table II. Observed and Calculated Frequencies (cm^{-1}) and Assignment in HSOH

compd	experimental frequency assignment	observed frequency	calculated frequency	theoretical frequency assignment[a]
HSOH	ν_{OH}	3425	3428	ν_{OH}
			2638	ν_{SH}
	δ_{SOH}	1177	1164	$\underline{\delta_{SOH}} + \nu_{SO}$
	ν_{SO}	763	815	$\underline{\nu_{SO}} + \delta_{SOH}$
	τ_{HSOH}	449	478	$\underline{\tau_{HSOH}} + \delta_{HSO}$
			434	$\underline{\delta_{HSO}} + \tau_{HSOH}$
DSOD	ν_{OD}	2661	2525	ν_{OD}
			1892	ν_{SD}
	δ_{SOD}	866.3	950	$\nu_{SO} + \underline{\delta_{SOD}}$
	$\nu_{SO} + \delta_{SOD}$	775	731	$\underline{\nu_{SO}} + \delta_{SOD}$
			355	$\delta_{DSO} + \underline{\tau_{DSOD}}$
	τ_{DSOD}	332	315	$\underline{\delta_{DSO}} + \tau_{DSOD}$
$HSO^{18}H$	ν_{OH}	3410	3457	ν_{OH}
			2636	ν_{SH}
	δ_{SOH}	1176	1152	$\underline{\delta_{SOH}} + \nu_{SO}$
	ν_{SO}	735	790	$\underline{\nu_{SO}} + \delta_{SOH}$
	τ_{HSOH}	443	477	$\underline{\tau_{HSOH}} + \delta_{HSO}$
		433		$\underline{\delta_{HSO}} + \tau_{HSOH}$

[a] When mixing occurs, the most important component is underlined.

As is well-known the force field is not unique, but the magnitude of the diagonal force constants remains approximately the same. In Table II can be found the experimental assignment and measured frequencies, together with the results of the calculation using the final force constants of Table I. There is generally good agreement between the observed and calculated assignment of frequencies, and in addition, the appearance of the torsional mode frequency in the expected frequency range for normal and isotopically substituted HSOH further supports the existence of this complex.

The somewhat lower than normal OH force constant is the consequence of the nonmixing of the OH mode with other modes and reflects the fact that the observed frequency is lower than normal (3425 cm^{-1} instead of $\approx$3600 cm^{-1}). The SH and SO bonds appear as nearly normal bonds. The striking features are the low value of the HSO bending force constant, the extremely small value of the torsional force constant, and the higher value of the SOH force constant, all of which suggest greater flexibility at the HSO end of the molecule.

The magnitude of the diagonal force constants obtained from the electronic calculations and from the vibrational analysis are comparable, except for the HSO bending force constant which differs markedly from the HSO force constant in the HSO radical. To elucidate this point it will be necessary to include other degrees of freedom in calculations on HSOH. Rearrangements can certainly be important as reaction 4a proceeds.

Conclusions

The calculations performed on the molecular species H_2SO, HSO, HSOH, and H_2S aid in the interpretation of the experiments on the oxidation of H_2S in an argon matrix. It is shown that H_2SO and HSOH can exist as stable species and that the electronic structure of the SH bond is greatly modified when going from H_2S to H_2SO, in which SO and SH bonds are much weaker than normal. The calculated dissociation energy of the SH bond in H_2SO is considerably less than the thermodynamic bond energy estimate and is approximately one-half of the calculated binding energy for the SH molecule. HSOH is found to be more stable than H_2SO, in good agreement with the thermodynamic estimate.

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A theoretical vibrational analysis confirms the IR spectroscopic identification of the HSOH complex.

Matrix effects have not been taken into account in the present calculation, but they are expected to stabilize the complexes and shift slightly the infrared frequencies. The low temperature and the constraint of the matrix allowing only diffusion may inhibit the three-step mechanism and favor the process involving the complex [H_2SO].

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Preparation and Properties of Phosphine Complexes of Nickel-Containing Cyclic Amides and Esters $[(PR_3)_n\overline{NiCH_2CH(R^1)COZ}$ (Z = NR^2, O)]

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Abstract: Reactions of α,β-unsaturated amides, $CH_2{=}C(R^1)CONHR^2$ (R^1 = H, CH_3; R^2 = H, CH_3, C_6H_5), with bis(1,5-cyclooctadiene)nickel, $Ni(cod)_2$, in the presence of tricyclohexylphosphine, $P(c\text{-}Hx)_3$, or ethyldi-*tert*-butylphosphine, $PEt(t\text{-}Bu)_2$, give nickel-containing cyclic amide complexes formulated as $(PR_3)\overline{NiCH_2CH(R^1)CONR^2}$. Reactions of $(P(c\text{-}Hx)_3)\overline{NiCH_2CH(CH_3)CONH}$ with triethylphosphine (PEt_3) and 1,2-bis(diphenylphosphino)ethane (dpe) afford corresponding ligand-exchanged products, $(PEt_3)\overline{NiCH_2CH(CH_3)CONH}$ and $(dpe)\overline{NiCH_2CH(CH_3)CONH}$. The nickel-containing cyclic amide structure was confirmed by IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopy as well as by chemical reactivities of the complexes. The complex with the PEt_3 ligand forms a trinuclear complex whereas the complex with dpe has a monomeric structure. A similar reaction of acrylic acid with $Ni(cod)_2$ in the presence of $P(c\text{-}Hx)_3$ affords a nickel-containing cyclic ester complex, $(P(c\text{-}Hx)_3)\overline{NiCH_2CH_2COO}$. Reactions of nickel-containing cyclic amide and ester complexes with carbon monoxide yield succinimides and succinic anhydrides, respectively. Addition of sterically less demanding and/or less basic phosphine ligands other than $P(c\text{-}Hx)_3$ and $PEt(t\text{-}Bu)_2$ in the reaction of α,β-unsaturated amides with $Ni(cod)_2$ leads to the formation of normal π-type complexes formulated as $Ni(PR_3)_m(\alpha,\beta\text{-unsaturated amide})_n$. Reactions of the π-type complexes with CO lead to simple ligand-exchange reactions to liberate the α,β-unsaturated amide with the formation of $Ni(PR_3)_m(CO)_{4-m}$. $Ni(P(c\text{-}Hx)_3)(\pi\text{-acrylamide})_2$ is converted into the nickel-containing cyclic amide complex, $(P(c\text{-}Hx)_3)\overline{NiCH_2CH_2CONH}$, on heating the π-type complex in THF. Occurrence of a reverse type of conversion from the nickel-containing cyclic amide complex to the π-type complex is postulated in thermolysis of the nickel-containing cyclic amide complex, which liberates α,β-unsaturated amide on the thermolysis. An intramolecular Michael reaction type shift of H from NH or COOH to the α-carbon of α,b-unsaturated amide or acid in an intermediate π-type complex is proposed as the reaction pathway to lead to the formation of the nickel-containing cyclic complex. Effects of basicity and bulkiness of tertiary phosphines on the formation of the nickel-containing cyclic complex are discussed on the basis of the proposed reaction pathway.

Introduction

Preparation of transition metallacyclic complexes and utilization of the complexes for synthetic reactions are the subject of recent interest.[1-5] However, most of the transition metallacyclic compounds reported are ones in which the ring consists of only the transition metal and carbons, and only a few reports have been given concerning the isolation of a metallacyclic complex in which the ring contains other elements such as N and O.[6] We previously reported in preliminary form the preparation of a nickel-containing cyclic amide complex by the reaction of bis(1,5-cyclooctadiene)nickel, $Ni(cod)_2$, with methacrylamide in the presence of tricyclohexylphosphine $P(c\text{-}Hx)_3$, and conversion of the complex into 2-methylsuccinimide by the reaction with CO (eq 1).[7] As the extension of the work we have carried out similar reactions

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