Experimental and Theoretical Identification of C₃O₂···H₂O and C₃O₂···NH₃ Complexes: Pre-reactive Intermediates of a 1,4 Nucleophilic Addition

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Abstract: The structure and energy properties of the H_2O/C_3O_2 (D_2O/C_3O_2) and NH_3/C_3O_2 ($^{15}NH_3/C_3O_2$) 1:1 complexes have been investigated in solid argon matrices with FT-infrared spectroscopy and ab initio calculations at the MP2/6-31G** level. These complexes trapped in argon matrices are characterized by a large shift of the ν_{CCO} stretching modes to lower frequencies. Predicted frequency shifts for the T_{Nu} shaped structure were found to be in good agreement with the observed complex vibrational frequency shifts. These complexes are indicative of a nucleophilic attack of the oxygen (or nitrogen) atom on the C4 atom of the C_3O_2 moiety. At the same time, we observe very short intermolecular distances between the O1 oxygen atom of the suboxide subunit and the hydrogen atom of H_2O (D_2O), or NH_3 ($^{15}NH_3$), lying in the C_3O_2 plane (2.77 and 2.96 Å for H_2O (D_2O) and NH_3 ($^{15}NH_3$), respectively). These values are indicative of a hydrogen bond between these atoms. Examination of the T_{Nu} complex structures shows for the C_3O_2 subunit the pinching of the CCC ($-22°$ and $-26°$ for H_2O and NH_3, respectively) and the CCO valence bond angles ($-3°$ for H_2O and NH_3). The geometries of the complexes and the structural modifications of the complex's suboxide moiety suggest pre-reactive intermediates of an 1,4 nucleophilic addition.

Introduction

The study of van der Waals complexes by experimental as well as theoretical approaches continues to be an interesting area of physicochemical research, resulting in a better understanding of the nature of intermolecular forces.[1−3] Complexes in which the components interact through a hydrogen bond have attracted special interest, especially those complexes between water and a large variety of molecules including carbon oxide derivatives such as CO_2[2] and CO.[3] One of the reasons for investigating the hydrogen bond is the central role played by this weak interaction in biological structures and processes, in the chemistry of aqueous solutions, and of course in determining the properties of water.

The susceptibility to nucleophilic attack is one of the most characteristic properties of ketenes. These compounds are usually trapped by H_2O or amines to produce acids or amides, respectively. However, while the structure, the energy properties, and the reactivity of the 1:1 complex formed between C_3O_2 (the first bisketene) and HCl have been previously described in our laboratory,[4] its reactivity toward H_2O remains of interest.[4d,5] Carbon suboxide is known to react with liquid water to form malonic acid, and the addition of H_2O to C_3O_2 could occur by 1,2 or 1,4 addition, but the structures of the probable intermediates remain unknown. From kinetic experiments and theoretical calculations, Allen et al.[5] suggest an initial step involving 1,2 addition to the C=O bond, but the transition states could not be successfully calculated.

The matrix isolation experiments were developed for the study of highly reactive species, and it is a powerfull technique for observing pre-reactive intermediates.[4a] So a large part of the work on complexes has focused on the development of cryogenic techniques for production and on the determination of their high-resolution infrared spectra.

The purpose of the present work is 3-fold: (1) obtain direct and accurate experimental results for the $C_3O_2···H_2O$ ($C_3O_2···D_2O$) and $C_3O_2···NH_3$ ($C_3O_2···^{15}NH_3$) 1/1 complexes trapped in cryogenic matrixes, (2) compare the distances and bonding energies for the H_2O complexes with those obtained for

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Table 1. Experimental (exp) and Calculated (cal) Frequency Shifts for the $\mathbf{T_{Nu}}$ and $\mathbf{L}$ C_3O_2:H_2O Complexes ($\Delta\nu = \nu$ monomer $- \nu$ complex)^a

		experiment					calculation							
		monomer		complex			monomer		complex				$\Delta\nu_{cal}$	
		ν	I	ν	I	$\Delta\nu_{exp}$	ν	I	νT	I	νL	I	$\mathbf{T}$	$\mathbf{L}$
H_2O	ν_3	3736.0	2	3715.7	5.7	20.3	4030.7	43.5	4024.3	5.1	4024.6	2	6.4	6.1
	ν_1	3639.0	2	3632.7	3.6	6.3	3891.9	5.4	3886.9	45.7	3892.4	0.3	5	−0.5
	ν_2	1592.9	100	1570.2	1.3	22.7	1681.7	100	1672.0	2.7	1692.4	5.5	9.7	−10.7
C_3O_2	$\nu_2 + \nu_3$	3064.8	2.6	3075.7	3.7	−10.9	3258.4		3278.4		3271.6		−20	−13.2
	ν_3	2289.3	100.0	2241.0	100.0	48.3	2453.0	100	2378.8	100	2489.9	100	74.2	−36.9
	ν_1	2194.4	1.9	2193.0	11.1	1.4	2247.0	0.7	2249.8	0.	2260.9	3.0	−2.8	−13.9
	ν_4	1596.3	4.2	1564.2	2.7	32.1	1601	2.5	1556.6	3.7	1621.5	1.3	44.4	−20.5
	ν_5'	577	0.1	575.7	2.7	1.3	569.8	0.5	568.7	0.3	567.0	0.	1.1	2.81
	ν_6	538.5	0.2	545.6	2.7	−7.1	540.3	2.5	550.5	1.8	554.7	3.0	−10.2	−14.4
	ν_6'	532.8	2.7				531.8	2.5	547.1	2	552.5	2.5	−15.3	−20.7

^{a} I = intensity, $\mathbf{T_{Nu}}$ and $\mathbf{L}$ refer to the complex structures presented in Scheme 3.

complexes with NH_3 with the same partner molecule, and (3) answer the question "does water (or ammonia) act as a nucleophile or as a proton donor in carbon oxide derivative complexes". On the basis of these results we hope to describe the nature and the differences in the bonding between the H_2O complexes and those of NH_3.

Experiments were monitored by FT-IR spectroscopy. Quantum calculations were undertaken to compare the experimental IR spectra with the calculated ones and thus assign observed absorptions and furthermore to determine the complex structures.

Experimental Method

Pure C_3O_2 was synthesized by using the method described by Miller et al.[6] NH_3 was supplied by Air Liquide, and $^{15}NH_3$ was supplied by Aldrich and used without further purification. H_2O was doubly distilled before use and D_2O was supplied by SDS.

The apparatus and experimental techniques used to obtain argon matrices have been described elsewhere in the literature.[7] The relative concentrations Ar/C_3O_2/H_2O (6500/3/180), Ar/C_3O_2/NH_3 (6500/6.5/195), Ar/C_3O_2/D_2O (6500/3/178), and Ar/C_3O_2/$^{15}NH_3$ (6900/7/185), at room temperature, were adjusted by pressure measurements; reproducible solute partial pressures required the use of a Datametrics (Barocel, series 600) capacitance manometer. The mixture was deposited at 20 K on a CsBr window. The deposition rate (2 mmol/h) of gas mixtures was controlled with an Air Liquide microleak (V.P/RX). The thickness (250 μm) of the matrices was determined by counting transmission franges.

Results and Discussion

Argon matrices containing only C_3O_2, H_2O (D_2O), or NH_3 ($^{15}NH_3$) were prepared, yielding infrared absorption spectra that were similar to those previously reported. Table 1 summarizes the observed absorptions with spectral assignments based on the work of Pietri[4a,b] (C_3O_2), Ayers[8] (H_2O), Sefik and Nishiya[9] (NH_3), Ayers[8] and Redington[10] (D_2O), and Sefik[9a] ($^{15}NH_3$).

The H_2O/C_3O_2/Ar Matrix (Cf. Figure 1 and Table 1). The spectra recorded after co-deposition of H_2O/C_3O_2/Ar at 10 K show new absorption bands with respect to the spectra of pure H_2O[8] and pure C_3O_2[4a,b] trapped in the argon matrix (cf. Figure 1 and Table 1).

In the ν_{OH} region, between 3800 and 3600 cm^{-1} (cf. Figure 1A) we observe the characteristic absorption bands of free and

$(H_2O)_n$ polymers ($n = 2, 3, ...$).[8] The absorption band observed at 3715.7 cm^{-1}, lower than the value observed for the free ν_{OH} mode, is attributed to the 1/1 complex. The most intense band of the ν_3 mode of C_3O_2 trapped with H_2O appears at 2241 cm^{-1} (see Figure 1B). This value is shifted to the lower frequencies by 48.3 cm^{-1} with respect to the more intense ν_3 absorption band of the two characteristic site responses of pure C_3O_2 (2289.3 and 2272.4 cm^{-1}). The intensity of the 2193 cm^{-1} absorption band increases. Between 1620 and 1550 cm^{-1} in the $\nu_{CCO_{as}}$ C_3O_2 and δH_2O region, two new absorption bands appear; they are shifted to lower frequencies at 1564.2 and 1570.2 cm^{-1}, respectively.

The spectrum recorded after co-deposition of D_2O:C_3O_2:Ar at 10 K shows the caracteristic absorption band of D_2O, HOD, and H_2O species.[8] The ν_3 mode of C_3O_2 trapped with D_2O appears at 2453 cm^{-1} shifted to lower frequencies by 58.5 cm^1 with respect to the ν_3 absorption band of pure C_3O_2 (Table 4).

The NH_3/C_3O_2/Ar Matrix (Cf. Figure 2 and Table 2). As observed in the previous case, with NH_3 new weak absorption bands appear in the infrared spectra with respect to those of the pure compounds. In the area of 3500−3000 cm^{-1} a new absorption band is observed at 3078.5 cm^{-1}. This band, corresponding to the $(\nu_2 + \nu_3)_{C_3O_2}$ combination,[4a] is shifted to the higher frequencies by 13.7 cm^{-1} compared to the pure C_3O_2. At 2221.6 cm^{-1} a new absorption band appears at lower frequency, shifted by 67.7 cm^{-1} with respect to the more intense ν_3 absorption band of C_3O_2 (Cf. Figure 2A).

In the region of ^{14}NH deformations and C_3O_2 antisymmetric stretching, between 1700 and 1500 cm^{-1}, two new absorption bands, shifted to the lower frequencies by 5 and 50.8 cm^{-1} with respect to the NH_3[9] and C_3O_2 monomers, appear at 1633.5 and 1545.5 cm^{-1}, respectively. In the region characteristic of the symmetric deformation of NH, between 1100 and 900 cm^{-1}, a new band appears at 1006.5 cm^{-1} shifted to the higher frequencies by 32.1 cm^{-1} with respect to pure ammonia (cf. Figure 2B).

In the case of $^{15}NH_3$ experiments the complex is characterized by the shift of the ν_3 and ν_4 C_3O_2 absorption bands, which are shifted by 67.7 and 50 cm^{-1}, respectively (Table 4).

Ab Initio Computation: Computational Details. To establish the molecular structures of $C_3O_2\cdots H_2O$ (D_2O) and NH_3 ($^{15}NH_3$) complexes ab initio calculations were carried out with Gaussian 94[11] at the MP2/6-31G** level.[12]

Several geometric arrangements are possible in the H_2O (NH_3) and C_3O_2 subunits in the complexes. With respect to the resonance structures (see Scheme 1), water or ammonia are expected to attack the carbon suboxide on the C_α atom (nucleophilic attack) or on the C_β carbon or the oxygen (acid

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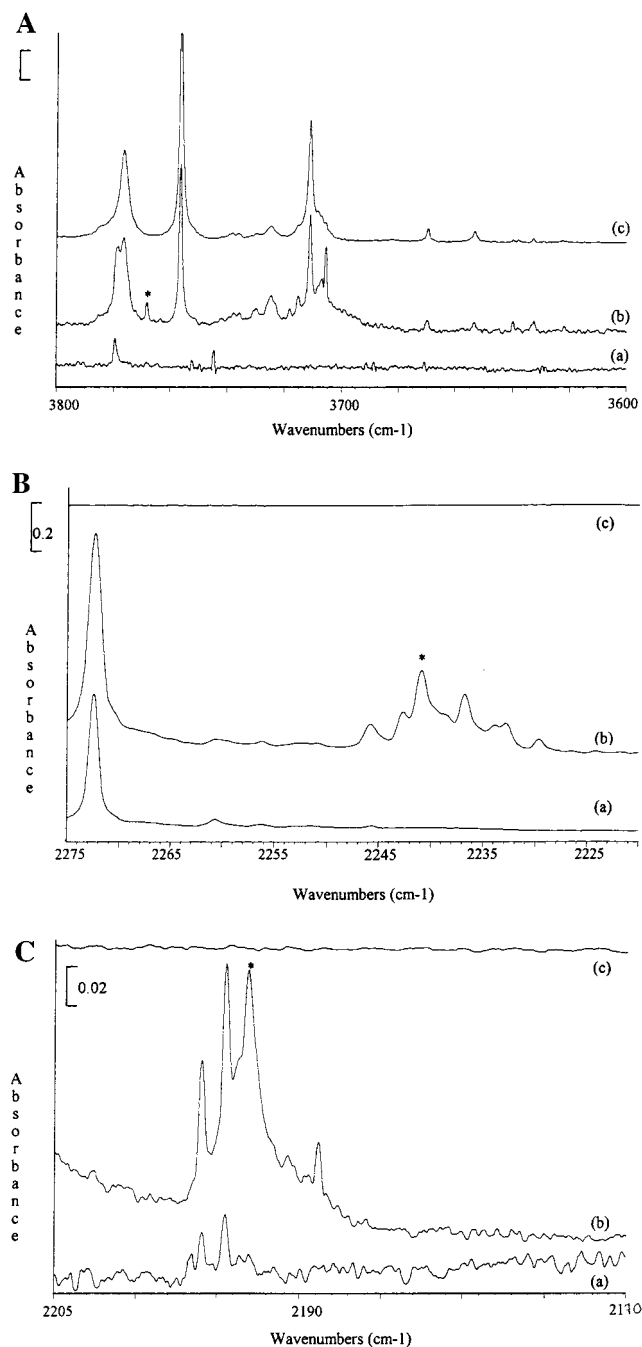(10) Redington, R. L.; Milligan, D. *J. Chem. Phys.* **1963**, *39*, 1276.

A

B

C

Figure 1. Infrared spectra of C_3O_2, H_2O, and the C_3O_2:H_2O complex, isolated in argon cryogenic matrix at TS = 10 K in the $\nu(OH)$ region (A), $\nu(C=C=O)$ asymmetric region (B), and $\nu(C=C=O)$ symmetric region (C): (a) C_3O_2/Ar in the ratio 1/1320, (b) C_3O_2/H_2O/Ar in the ratio 3/180/6500, and (c) H_2O/Ar in the ratio 1/50.

attack). Three kinds of complexes are thus considered for optimization and vibrational frequency calculations (cf. Scheme 2). The **L** form, which involves a hydrogen bonding with the terminal oxygen of carbon suboxide, and the **T** forms for which there occurs (a) a hydrogen bonding with the C_β carbon atom (**T$_{Ac}$** form) or (b) a nucleophilic attack on the C_α carbon atom (**T$_{Nu}$** form) (cf. Scheme 2).

To determine the geometry of the complexes, ground-state potential energy surfaces were explored by using the same method as for the HCl complexes.[4a] The three independent variables R, α, and β (cf. Scheme 2) are respectively the distance between the interacting atom of H_2O (NH_3) and an X atom (carbon or oxygen) of the C_3O_2 moiety, the intermolecular angle

between R and the CCO moiety of the carbon suboxide, and the angle between R and the OH (NH) bond. Owing to computational constraints, it was not possible to optimize all the geometrical parameters for all points of the ground state. Thus, we worked on two approximations: (i) the dihedral angle ϕ was assumed to be 180°, and (ii) for the different values of R, the intermolecular angles α and β were varied while all the other intramolecular parameters were held constant at their MP2/6.31G** equilibrium values.

For the **L** form α and β parameters ranged from 90° to 270° in 30° steps. For the **T** forms α ranged from 60° to 90° and β from 60° to 180° in 30° steps. This type of surface is very flat but, except for the NH_3 **L** shaped structure, the minimum energy was determined for each 4-D surface corresponding to the complex.

The stabilization energy of the complex AB under study is evaluated as follows, $\Delta E = E(AB) - E^{BSSE}(A) - E^{BSSE}(B)$, where $E^{BSSE}(A)$ and $E^{BSSE}(B)$ are the respective energies of the A and B moieties corrected from the basis set superposition error (BSSE) by the usual counterpoise method.[13]

Starting from these initial approximations, all the geometrical parameters were fully optimized (using the Berny optimization procedure). The harmonic vibrational frequencies were determined at the stationary points and compared to experimental data.

Geometries of the Complexes. (Cf. Table 3). $H_2O\cdots C_3O_2$ Complexes. For the $C_3O_2\cdots H_2O$ complexes, calculations give only two local minima. The first, with the values $\phi = 180°$, $R = 2.209$ Å, $\alpha = 172.5°$, and $\beta = 130.5°$, corresponds to an **L** shaped structure. The second corresponds to a **T$_{Nu}$** shaped form ($\phi = 180°$, $R = 3.291$ Å, $\alpha = 123.6°$, and $\beta = 78.8°$). The geometries of these two complexes (cf. Scheme 3) are totally different. The C_3O_2 moiety is linear in the **L** form and bent in the **T$_{Nu}$** form. For this last complex, we observe, with respect to the bent monomer, a pinching of the valence bond angles ($\Delta CCC \approx -22°$ and $\Delta CCO \approx -3°$), a slight shortening of the C=O bond ($\Delta r = -0.003$ Å), and a lengthening of the C=C bond ($\Delta r = 0.012$ Å) (cf. Table 2). The H_2O and C_3O_2 moieties are coplanar. For the **L** complex the C=C bond is slightly shortened ($\Delta l = -0.003$ Å) but the C=O bond is unchanged with respect to the linear monomer structure (cf. Table 1). The **T$_{Ac}$** shaped form does not display a local minimum.

The **T$_{Nu}$** complex is slightly more stable than the **L** complex, but the energy difference (0.57 kcal mol^{-1}) is not very significant at this level of theory in determining clearly the structure present in cryogenic matrices. As a matter of fact, the stabilizing effect of the matrix cage is not accounted for in our calculation of a 1/1 complex. These results are similar to those obtained for the $H_2O\cdots CO_2$ complex.[2] In this case, in an oxygen matrix,[2e] the unstable **L** $H_2O\cdots CO_2$ form is observed. On energetics grounds alone, the **T$_{Nu}$** complex appears to be favored although some of the other structures may be observed, but at significantly lower concentration.

After BSSE correction had been carried out, using the counterpoise procedure,[13] the **T$_{Nu}$** and **L** complexes were

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Table 2. Experimental (exp) and Calculated (cal) Frequency Shifts for the T_{Nu} C_3O_2:$^{14}NH_3$ Complex ($\Delta\nu = \nu$ monomer $- \nu$ complex)

| | | experiment | | | | | calculation | | | | |
| | | monomer | | complex | | | monomer | | complex | | |
		ν	I	ν	I	$\Delta\nu_{exp}$	ν	I	ν	I	$\Delta\nu_{cal}$
$^{14}NH_3$	ν_3	3447.3	1.0				3716.8	0.2	3709.7	0.2	7.1
									3709.1	0.1	7.7
	ν_1	3345.4	0.				3560.5	0.2	3555.1	0.	5.4
									1723.5	0.9	1.8
	ν_4	1638.5	4.5	1633.5	0.9	5	1725.3	9.3	1721.6	1.2	3.7
	ν_2	974.4	100	1006.5	3.7	−32.1	1122.9	100.0	1139.9	8.6	−17.0
C_3O_2	$\nu_2 + \nu_3$	3064.8	2.6	3078.5	4.1	−13.7	3258.4		3282.0		−23.6
	ν_3	2289.3	100.0	2221.6	100.0	67.7	2453.0	100.0	2357.7	100.0	95.3
	ν_1	2194.4	1.9	2191.3	18	3.1	2247.0	0.7	2249.9	4	−2.9
	ν_4	1596.3	4.2	1545.5	2.7	50.8	1601.0	2.5	1540.7	0.8	60.3
	ν_5'	577	0.1	571.2	2.3	5.8	569.8	0.5	561.0	0.6	8.8
	ν_6	538.5	0.2	556.3	3	−17.8	540.3	2.5	558.5	3	−18.2
	ν_6'	532.8	2.7	551.2	4.5	−18.4	531.8	2.5	550.3	2.7	−18.5

^{a} I = intensity, T_{Nu} refers to the complex structure presented in Scheme 3.

Table 3. Monomer and Complex Geometrical Parameters (lengths in Å, angle in deg)^a

| | | | | C_3O_2:H_2O | | C_3O_2:NH_3 |
	C_3O_2	H_2O	NH_3	L	T	T
rC_2O_1	1.182			1.182	1.181	1.179
rC_2C_3	1.284			1.277	1.295	1.3
$\angle$OCC	177.3			179.9	174.9	173.1
$\angle$CCC	160.0			179.2	138.3	133.4
r		0.961	1.010	0.962	0.962	1.013
α				172.5	123.6	127.0
β				130.5	78.8	89.0
R				2.209	3.291	3.160
E	−264.0060082	−76.2197857	−56.3832170	−340.230069	−340.2309806	−320.395293
rel energies				0.57	0	

^{a} Energies (E) are given in hartrees and relative energy ($E_L - E_T$) for the C_3O_2:H_2O complex is given in kcal/mol.

Table 4. Experimental (exp) and Calculated (cal) Frequency Shifts in C_3O_2:H_2O, C_3O_2:D_2O, C_3O_2:HOD, C_3O_2:DOH, C_3O_2:$^{14}NH_3$, and C_3O_2:$^{15}NH_3$ for the C_3O_2 Subunit ($\Delta\nu = \nu$ monomer $- \nu$ complex)^a

| | C_3O_2:H_2O | | | C_3O_2:D_2O | | | C_3O_2:HOD | | | C_3O_2:DOH | | | C_3O_2:$14NH_3$ | | C_3O_2:$15NH_3$ | |
| | | $\Delta\nu_{cal}$ | | | $\Delta\nu_{cal}$ | | | $\Delta\nu_{cal}$ | | | $\Delta\nu_{cal}$ | | $\Delta\nu_{exp}$ | $\Delta\nu_{cal}$ | $\Delta\nu_{exp}$ | $\Delta\nu_{cal}$ |
	$\Delta\nu_{exp}$	T	L	$\Delta\nu_{exp}$	T	L	$\Delta\nu_{exp}$	T	L	$\Delta\nu_{exp}$	T	L				
$\nu_2 + \nu_3$	−10.9	−20.0	−13.2	−14.6	−19.8	−13.0	−14.6	−16.9	−13.2	−14.6	−19.8	−13.0	−13.7	−23.6	−15.4	−23.6
ν_3	48.3	74.2	−36.9	58.5	74.4	−36.7	58.5	77.3	−36.9	58.5	74.4	−36.7	67.7	95.3	67.7	95.3
ν_1	1.4	−2.8	−13.9	1.9	−2.7	−13.9	1.9	−2.7	−3.9	1.9	−2.7	−13.9	3.1	−2.9	2.9	−2.9
ν_4	32.1	44.4	−20.5	44.6	44.4	−20.6	44.6	44.2	−20.6	44.6	44.3	−20.6	50.8	60.3	50.0	60.4
ν_5'	1.3	1.1	2.8	1.6	1.3	2.9	1.6	1.2	2.9	1.6	1.2	2.9	5.8	8.8	-	8.8
ν_6'	−7.1	−10.2	−14.4	−18.4	−10.1	−14.3	−18.4	−10.2	−14.3	−18.4	−10.1	−14.3	−17.8	−18.2	−17.8	−18.2
ν_6		−15.3	−20.7	−16.5	−15.7	−20.6	−16.5	−15.8	−20.7	−16.5	−15.3	−20.6	−18.4	−18.5	−18.4	−18.5

^{a} C_3O_2:HOD, the hydrogen interact with the O_1 oxygen of C_3O_2. C_3O_2:DOH, the deuterium interact with the O_1 Oxygen of C_3O_2.

stabilized with regard to the monomer molecules by 2.31 and 1.55 kcal mol^{-1}, respectively.

(b) NH$_3$···C$_3$O$_2$ Complexes. For the C_3O_2···NH$_3$ complexes, calculations give only one local minimum for the values $\phi = 180°$, $R = 3.160$ Å, $\alpha = 127°$, and $\beta = 90°$, which corresponds to the T_{Nu} shaped structure (cf. scheme 3). The geometry of this form is similar to those of the corresponding H$_2$O complex with a pinching of −26° and −3° of the CCC and the CCO valence bond angles, respectively, and a lengthening of the C=C bond ($\Delta l = 0.015$ Å). The T_{Ac} and the L shaped structures do not display local minima.

Identification of the Complexes. The previous calculation provides valuable insight into the stability and the spectroscopic features of the complexes. First, the complexing effects can be observed on the geometry of the partner molecules and on their most significant stretching frequencies. To identify the form present in argon matrices, we must compare the ν_{CCO} vibrational

frequency shifts of the complexes with those calculated for the free C_3O_2 (cf. Tables 1, 2, and 4).

In the case of the C_3O_2···NH$_3$ complex, for which the T_{Nu} form is expected alone, we observe a good agreement between the experimental and calculated C_3O_2 mode frequency shifts (cf. Table 2). In the case of the C_3O_2···H$_2$O complex, the stretching suboxide mode frequency shifts of the T_{Nu} form are in better agreement than those of the L form. These results are compatible with a T_{Nu} shaped structure of the complex in the matrices and are indicative of a nucleophilic attack of the oxygen (or nitrogen) atom on the C4 atom of the C_3O_2 moiety. Observation of T_{Nu} complexes versus L ones agrees with the water and ammonia nucleophilicities, which are significantly larger than their electrophilicities. On the other hand, observation of a C···N distance shorter than the C···O distance ($R = 3.16$ and 3.291 Å, respectively) is in agreement with best nucleophilic character of ammonia.
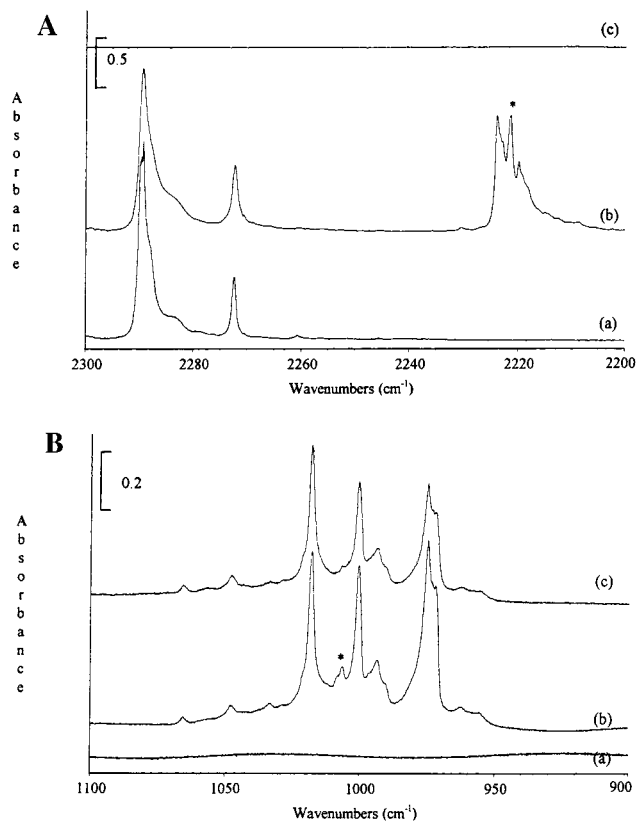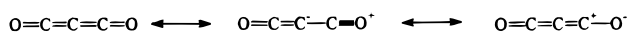
Figure 2. Infrared spectra of the $C_3O_2:NH_3$ complex, C_3O_2, and NH_3 isolated in argon cryogenic matrix at TS = 10 K in the ν(CCO) asymmetric region (A) and δ(NH) region (B): (a) C_3O_2/Ar in the ratio 1/1320, (b) C_3O_2/NH_3/Ar in the ratio 6,5/195/6500, and (c) NH_3/Ar in the ratio 11/333.

Scheme 1. Resonance Structures of Carbon Suboxide

**Scheme 2.** Three Kinds of Interaction Considered in Order To Obtain the T_{Ac}, T_{Nu}, and L Type Complex Geometry[a]
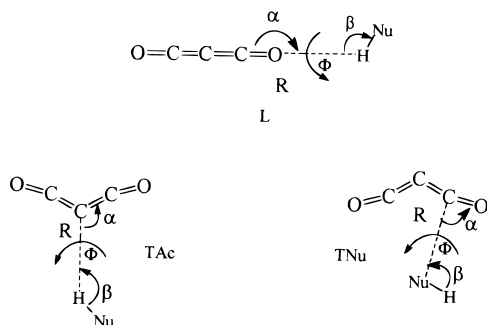
[a] The distance R and the angles α, β, and Φ used in the text to discuss the geometry are defined.

Examination of the complex structures in Scheme 3 shows, two types of modifications for the C_3O_2 subunit:

(1) The pinching of the CCC and the CCO valence bond angles, $-22°$ ($-26°$) and $-3°$, respectively, corresponds to an sp $\rightarrow$ sp^2 evolution of the hybridization of the carbon atoms. This angle modification agrees with the increasing intensity of the $\nu_{CCO_{as}}$ absorption band at 2193 cm^{-1} (2191.3 cm^{-1}).

(2) The r_{12} bonds between the O1 and C2 atoms are slightly perturbed for the T_{Nu} complex ($\Delta r \approx 0.001$ Å) and unperturbed for the L complex. On the other hand, the r_{23} bonds between C2 and C3 atoms are lengthened ($\Delta r \approx 0.014$ Å) and slightly

Scheme 3. Optimized Geometry for the T_{Nu} $C_3O_2:NH_3$ Complex (A), T_{Nu} $C_3O_2:H_2O$ Complex (B), and L $C_3O_2:H_2O$ Complex (C)
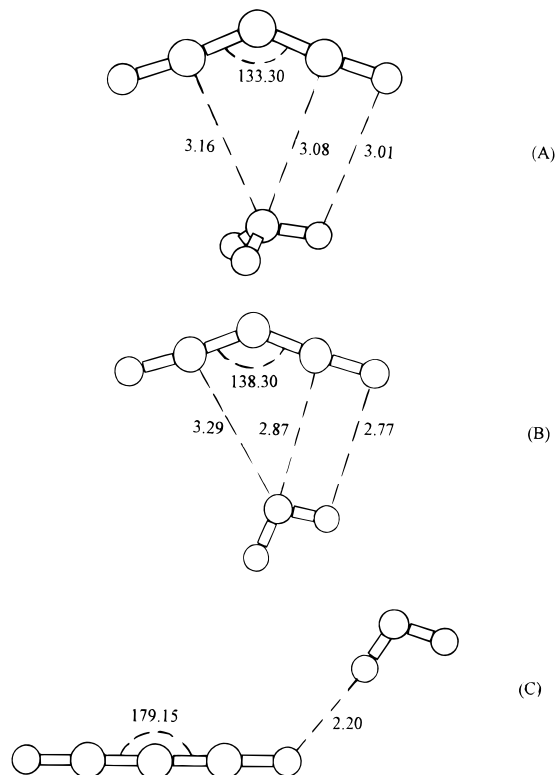
shortened ($\Delta r \approx 0.007$ Å) in the T_{Nu} and L complexes, respectively.

These modifications in the T_{Nu} complexes result from the strong interactions between the lone pairs of the nucleophile atom of H_2O, or NH_3, with the C4 atom of the carbon suboxide (these lone pairs are directed to the C4 atom). At the same time, we observe very short intermolecular distances between the O1 oxygen atom of the suboxide subunit and the hydrogen atom of H_2O, or NH_3, lying in the C_3O_2 plane (2.77 and 2.96 Å for H_2O and NH_3, respectively). These values are indicative of a hydrogen bond between these atoms. The geometries of the complexes and the structural modifications of the complex's suboxide moiety suggest a pre-reactive intermediate of a 1,4 nucleophilic different from the 1,2 addition mechanism proposed by Allen et al.[5] for the hydration of carbon suboxide.

Conclusion

The present study is devoted to the formation and the structural determination of 1:1 complexes of carbon suboxide with H_2O and NH_3. The results derived from theoretical calculations strongly suggest that the bimolecular reaction between the partners produces stable complexes. Distinct shifts were observed in the vibrational modes of both moieties in the complex. The magnitude of the C_3O_2 mode frequency shifts is characteristic of T_{Nu}. These complexes are indicative of a nucleophilic attack of the oxygen (or nitrogen) atom by the C4 carbon atom. They are stabilized by a hydrogen bonding with the O1 oxygen atom of carbon suboxide. The geometries of the complexes and the structural modifications of the complex's suboxide moiety suggest a pre-reactive intermediate of an 1,4 nucleophilic addition.

Supporting Information Available: Experimental and calculated frequencies and frequencies shifts in $C_3O_2···D_2O$, $C_3O_2···HOD$, $C_3O_2···DOH$, and $C_3O_2···^{15}NH_3$ complexes (Table 1 to 4); calculated frequencies in $^{13}C_3O_2···H_2O$ and $^{13}C_3O_2···NH_3$ (with carbon-13 in different positions) complexes (Tables 5 and 6); infrared spectra of $C_3O_2···H_2O$ and $C_3O_2···D_2O$ complexes isolated in argon cryogenic matrix at TS = 10 K in the $\nu(CCO)$ asymmetric region, (a) $C_3O_2/H_2O/Ar$ in the ratio 3/180/6500 and (b) $C_3O_2/D_2O/Ar$ in the ratio 3/178/6500 (Figure 1); and infrared spectra of $C_3O_2···NH_3$ and $C_3O_2···^{15}NH_3$ complexes isolated in argon cryogenic matrix at TS = 10 K in the $\nu(CCO)$ asymmetric region, (a) $C_3O_2/NH_3/Ar$ in the ratio 6,5/195/6500 and (b) $C_3O_2/^{15}NH_3/Ar$ in the ratio 7/170/6900 (Figure 2) (PDF). See any current masthead page for ordering information and Web access instructions.