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Publication Date
1976-04-01

CHARGE TRANSFER COMPLEXES.
NH_3-O_3, NH_3-SO_2, AND $N(CH_3)_3-SO_2$

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April 1976

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Charge Transfer Complexes. NH_3-O_3, NH_3-SO_2, and $N(CH_3)_3$-SO_2[*]

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Abstract

The donor-acceptor complex between trimethylamine and sulfur dioxide is the strongest (in terms of its dissociation energy to $N(CH_3)_3$ plus SO_2) such complex yet to be studied experimentally in the gas phase. Ab initio self-consistent-field theory has been applied to this and two related complexes, NH_3-O_3 and NH_3-SO_2. Minimum basis sets were used for all three complexes, while for NH_3-SO_2 two considerably larger sets (double zeta and double zeta plus sulfur d functions) were employed. The equilibrium structure of these complexes was predicted by an investigation of many points on the respective potential energy surface. To a surprising degree, the O_3 or SO_2 molecule is found to lie in a plane nearly perpendicular to the amine C_{3v} axis. Further, the central atom in O_3 and SO_2 is predicted to lie only slightly off the amine C_{3v} axis. With these guidelines, the prediction of further structures of this type essentially reduces a one-dimensional search for the central atom-N distance. Using a minimum basis set, the three predicted binding energies are 2.24, 5.00, and 4.06 kcal/mole. Using the double zeta basis set the NH_3-SO_2 dissociation energy is increased to 10.40 kcal/mole. When a set of sulfer d functions is added to the latter set, the binding energy becomes 9.30 kcal/mole.
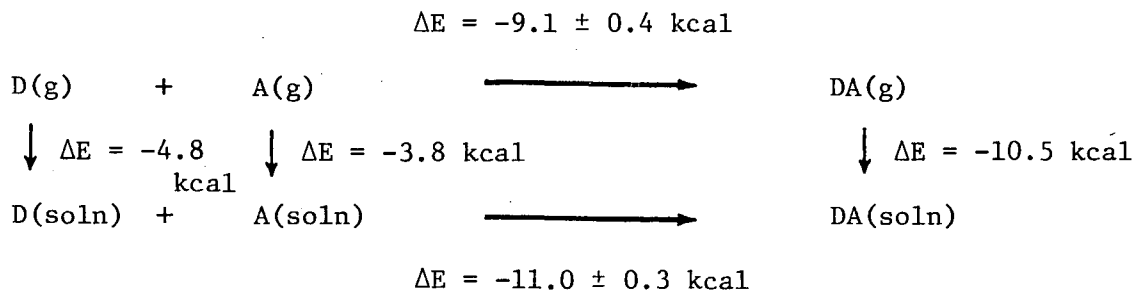
Introduction

Experimental[1-2] and theoretical[3-5] progress in the study of charge-transfer (or donor-acceptor, a term we use interchangeably) complexes has rapidly accelerated in recent years. The goal of most chemical research in this area is the elucidation of the structure, energetics (especially dissociation energies), and electronic spectroscopy of such species. As an example of the recent theoretical developments we note the ab initio study by Lathan, Pack, and Morokuma[4] of the carbonyl cyanide-benzene complex. In addition to carrying out self-consistent-field (SCF) calculations, they were able to estimate the dispersion energy or electron correlation contribution to the binding or dissociation energy. At the present time, theory appears particularly well suited to the study of charge transfer complexes, since experimental determinations of their equilibrium geometries are extremely difficult and hence quite rare.[6] The structures and energetics of these molecular complexes are very important to our understanding of molecular interactions, since they lie somewhere between van der Waals molecules[7] and chemically bound systems,[8] and are much less well understood than traditional hydrogen bonding situations.[9]

As pointed out clearly in the recent review of Tamres,[10] there exists at least one major roadblock to the fundamental understanding of charge-transfer complexes. This is the fact that while existing theoretical models[11,12] and detailed studies[3-5] are appropriate to gas phase situations, most experimental studies[1,2] have been made in solution. An example of this dilemma is given by our recent theoretical study[13] of the NH_3 and $N(CH_3)_3$ complexes with the halogens F_2, Cl_2, and ClF. While the theoretical

methods predict the ammonia complexes to be ∿ 30% stronger than those of trimethylamine, the opposite trend is well established in solution (usually n-heptane) by the experiments of Nagakura and co-workers.[14]

The most striking exception to the above dichotomy is the $N(CH_3)_3-SO_2$ complex. Due to the beautiful work of Grundnes and Christian,[15,16] this complex has been carefully studied in both the gas phase and in heptane. As pointed out by Tamres,[10] the trimethylamine-sulfur dioxide complex is the only one to date for which all steps in the thermodynamic cycle

$$\Delta E = -9.1 \pm 0.4 \text{ kcal}$$

$$D(g) \quad + \quad A(g) \quad \xrightarrow{\hspace{3cm}} \quad DA(g)$$

$$\downarrow \Delta E = -4.8 \text{ kcal} \qquad \downarrow \Delta E = -3.8 \text{ kcal} \qquad \qquad \downarrow \Delta E = -10.5 \text{ kcal}$$

$$D(soln) \quad + \quad A(soln) \quad \xrightarrow{\hspace{3cm}} \quad DA(soln)$$

$$\Delta E = -11.0 \pm 0.3 \text{ kcal}$$

have been evaluated, where D is the donor $N(CH_3)_3$ and A the acceptor SO_2. Note that the solvation energy in going from the gaseous to solution complex is comparable to the dissociation energies of 9.1 kcal (vapor) and 11.0 kcal (solution). The former figure of 9.1 kcal makes $N(CH_3)_3-SO_2$ the strongest complex yet studied in the gas phase. However, in spite of this wealth of thermodynamic information, the equilibrium geometry of this complex has not been determined experimentally.

The goal of the present theoretical study is the prediction of the structure and energetics of the $N(CH_3)_3-SO_2$ complex and two related systems, NH_3-SO_2 and NH_3-O_3. The existing experimental thermodynamic information will allow us to test the reliability of various levels of theory. And the reliability of _ab initio_ structural predictions[3-5,17-19] should allow us

to make some fairly definitive statements concerning the equilibrium

geometries of these fascinating complexes.

Theoretical Details

All the research reported here was carried out using single determinant self-consistent-field (SCF) theory and the programs GAUSSIAN 70[20] and POLYATOM.[21] Minimum basis sets were used for all systems studied, with each Slater function being expanded as a linear combination of three gaussians, following the precise prescriptions of the Pople group.[22,23]

For the NH_3-SO_2 system, a much more thorough study of basis set dependence was completed. Following the minimum basis studies, a basis twice as large (double zeta) was adopted. We accepted Dunning's recommendations[24] in contracting Huzinaga's H(4s/2s), N(9s 5p/4s 2p), and O(9s 5p/4s 2p) primitive basis sets.[25] For the sulfur atom, Veillard's (12s 9p) primitive set[26] was contracted to (7s 5p) so as to provide maximum flexibility[24,27] in the valence region, i.e., 6111111 for s functions and 51111 for p functions. After the equilibrium structure was determined, two final computations (one at the equilibrium and one for the separated molecules) were carried out in which the double zeta set was augmented by a set of six d-like functions (with gaussian orbital exponent $\alpha = 0.6$) on the S atom.

The most exhaustive geometry searches were carried out for the NH_3-SO_2 system. For the other two systems NH_3-O_3 and $N(CH_3)_3$-SO_2, the structures were to some degree assumed, based on the NH_3-SO_2 explorations using two different basis sets. In all calculations, the geometries of NH_3, $N(CH_3)_3$, O_3, and SO_2 were frozen at their experimental equilibrium values.[28,29] For NH_3 the NH bond distance was 1.0124 Å and the H-N-H bond angle 106.67°. For trimethylamine the microwave structure of Wollrab and Laurie[29] was adopted. For O_3, the bond angle and bond distance were 116.8° and 1.278 Å, while for SO_2 r_e(S-O) = 1.4321 Å and θ_e = 119.5°.

Results and Discussion

Given the constraint of rigid NH_3 and SO_2 structures, we made a serious attempt to locate the minimum on the NH_3-SO_2 potential energy surface. This general search was carried out using the minimum basis set described above. One of the more obvious possibilities is that the C_3 axis of NH_3 and C_2 axis of SO_2 be coincident:

$$
\begin{array}{cc}
H \diagdown & O \diagup \\
H - N \cdots\cdots\cdots S & \\
H \diagup & \diagdown O
\end{array}
\qquad (1)
$$
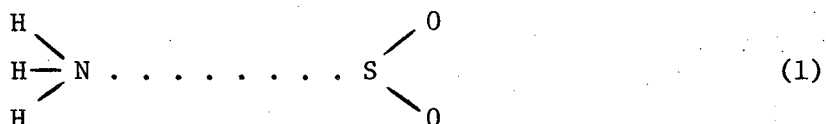
It is clear that this approach yields the largest classical attraction between the dipole moments of NH_3 and SO_2. This structure also has the obvious advantage that the geometry search is reduced to one dimension R, the N-S separation. Within the minimum basis set, R_e is predicted to be 3.54 Å and the dissociation energy 1.42 kcal. For completeness the same prediction was made with the double zeta basis, yielding R_e = 3.60 Å and 3.36 kcal/mole. The opposite geometrical configuration

$$
\begin{array}{cc}
O \diagup & H \diagdown \\
S \cdots\cdots\cdots H - N & \\
\diagdown O & H \diagup
\end{array}
\qquad (2)
$$
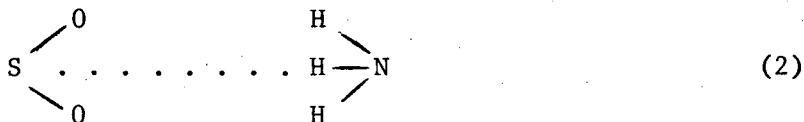
was also investigated, and, as expected classically, proved to be repulsive in nature.

Further explorations of the NH_3-SO_2 potential surface demonstrated conclusively that the plane of the SO_2 molecule prefers to be nearly perpendicular to the ammonia C_3 axis. The three most important degrees

of freedom R, α, and β are illustrated in the Figure. Thus we see, for

example, that structure (1) corresponds to both α and β being zero.

Within these three degrees of freedom, the NH_3-SO_2 structure was fully

optimized using both minimum and double zeta basis sets. The results

are summarized in Table I.

There it is seen by comparison with the results quoted above that there

is a tremendous change ($\sim$ 7 kcal in the double zeta calculations) in the bind-

ing energy as β goes from 0° to $\sim$ 90°. Perhaps the most surprising feature

of the predicted structure is the fact that it makes little classical "use"

of the rather large[30] (1.63 debye) dipole moment of SO_2. However, this

geometry does allow a sizeable attraction between the three "positively

charged" H atoms and two "negatively charged" O atoms. Another important

feature of the fully optimized equilibrium structure is that the N-S separation

R is a full 0.9 Å shorter than in the constrained (α = 0°, β = 0°) structure.

In this sense the tilting of the SO_2 group to β = 95.2° allows the two molecules

to approach each other much more closely. The minimum basis set geometry

prediction is in qualitative agreement with the more reliable double zeta

result. The angle α is nearly unchanged, differing by only 0.2° between the

two cases. The N-S separation decreases by 0.16 Å in going from the minimum

basis to the double zeta prediction, and the angle β increases by 8.4°. The

latter change means that in the double zeta case, together with the 8.2° value

for α, the SO_2 plane is tilting significantly away from the plane passing

through the S atom nucleus and perpendicular to the NH_3 C_3 axis.

As is often true in the much more thoroughly studied hydrogen bonding

situations,[5] we find for this charge transfer complex that the double zeta

basis yields a much stronger binding energy than the minimum basis. However,

for hydrogen bonds, the double zeta basis often yields dissociation energies

significantly greater than experiment (e.g., for the water dimer the double zeta binding energy is $\sim$ 8 kcal/mole,[31] while the experimental value is $\sim$ 5 kcal/mole). On the contrary, for the NH_3-SO_2 complex our double zeta prediction appears to be quite reasonable. The word "appears" is present in the previous sentence because the NH_3-SO_2 system has not been studied experimentally. However, as pointed out earlier, the $N(CH_3)_3$-SO_2 complex has a large gas-phase binding energy, 9.1 ± 0.4 kcal/mole. And our minimum basis comparisons suggest that NH_3-SO_2 is somewhat more strongly bound than its trimethylamine counterpart. Hence a value of 10.4 kcal/mole for the NH_3-SO_2 dissociation energy appears quite plausible. In the absence of a new geometry optimization, the addition of sulfur d functions reduces the double zeta binding energy to 9.3 kcal.

An especially interesting feature of donor-acceptor complexes is the dipole moment of the complex, and this property is also tabulated in Table I. These predictions are best understood in light of the theoretical dipole moments for the isolated molecules NH_3 and SO_2. Using the minimum basis we find $\mu(NH_3)$ = 1.79 debye (1.47 experimentally[32]) and $\mu(SO_2)$ = 1.72 debye (1.63 from experiment[30]). The double zeta basis, which generally exaggerates polarities, yields 2.34 and 2.78 debye, respectively. Finally, when sulfur d functions are added, the SO_2 dipole reduces to 2.53 debye. Thus a first observation is that the predicted complex binding energies correlate nicely with the isolated species dipole moments. In addition the NH_3-SO_2 dipole moments, 2.50 (minimum), 4.49 (double zeta), and 4.30 (sulfur d functions added) follow the same trend. If analogy with the NH_3 and SO_2 dipoles is valid, the minimum basis result of 2.50 debye should be the most reliable here. Extracting the part of the NH_3-SO_2 dipole moment due to the complex

itself is a little tricky, since both NH_3 and SO_2 have sizeable dipole
moments of their own. However, by performing a minimum basis computation
at R = 100 bohrs, α = 8.4°, and β = 86.8°, we obtain a "properly oriented
separated NH_3 + SO_2" dipole moment of 2.22 debye. The difference of 0.28
between that separated result and the 2.50 debye in Table I may in a
certain sense be attributed to the complex itself. The analogous treat-
ment of the double zeta results suggests a contribution of 0.95 debye from
the complex itself.

With our energetic results and dipole moments for NH_3-SO_2 in mind, the NH_3-O_3
results are readily understood. The smaller (0.53 debye[33] vs. 1.63 debye
for SO_2) experimental dipole moment of ozone explains why the NH_3-O_3
dissociation energy is only about half of that for NH_3-SO_2. The predicted
complex dipole moment of 1.89 is also somewhat less than that of NH_3-SO_2.
Note of course that the true binding energy of NH_3-O_3 should be about twice
the 2.24 kcal predicted with our minimum basis.

The same analysis is equally valid for the $N(CH_3)_3$-SO_2 complex. The
dipole moment of trimethylamine is known[34] to be 0.61 debye, substantially
less than the 1.47 debye observed[32] for ammonia. However, in our earlier
comparisons[13] between NH_3-F_2 and $N(CH_3)_3$-F_2 and between NH_3-Cl_2 and $N(CH_3)_3$-Cl_2,
we found the trimethylamine complexes to be $\sim$ 80% as strongly bound as the
analogous ammonia complexes. Thus it is clear that dipole moment ratios
must not be taken too literally. In any case, the same general trend is
seen here, as the $N(CH_3)_3$-SO_2 dissociation energy (4.06 kcal) is 82.2% of
the comparable quantity (4.94 kcal) for NH_3-SO_2. The complex dipole
momemts follow the same trend with the trimethylamine quantity being 80.2%
of that for NH_3-SO_2.

Concluding Remarks

Perhaps the most important qualitative result predicted in this theoretical study is that, consistent with the earlier amine-halogen work,[13] the gas phase charge transfer complexes of NH_3 are noticeably more strongly bound than those of $N(CH_3)_3$. This result is of course contrary to the chemical intuition that methyl is a better electron donating group than hydrogen. Gas phase experimental studies of the NH_3-SO_2 system would allow an immediate test of this theoretical prediction. The other major conclusion of this research is that the equilibrium geometries of complexes such as NH_3-SO_2 involve nearly perpendicular C_3 and C_2 axes, respectively.

Acknowledgments

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* Work performed under the auspices of the U.S. Energy Research and Development Administration.

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Table I. Summary of structural and energetic results for charge-transfer complexes.

Complex	Basis Set	R(Å)	α	β	Total Energy (hartrees)	Dissociation Energy (kcal/mole)	Dipole Moment
$NH_3\text{-}O_3$	Minimum	2.88	0° (assumed)	86.9°	-276.74713	2.24	1.89
$NH_3\text{-}SO_2$	Minimum	3.54	0° (assumed)	0° (assumed)	-596.05886	1.42	3.57
		2.86	0° (assumed)	90° (assumed)	-596.06444	4.94	2.76
		2.86	8.4°	86.8°	-596.06456	5.00	2.50
	Double Zeta	3.60	0° (assumed)	0° (assumed)	-603.14801	3.37	5.45
		2.73	0° (assumed)	90° (assumed)	-603.15842	9.90	4.39
		2.70	8.2°	95.2°	-603.15921	10.40	4.49
	Double Zeta plus Sulfur d functions	2.70 (assumed)	8.2° (assumed)	95.2° (assumed)	-603.35744	9.30	4.30
$N(CH_3)_3\text{-}SO_2$	Minimum	2.86	0° (assumed)	90° (assumed)	-711.79749	4.06	2.22

Figure Caption

The three most important degrees of freedom in determining the equilibrium geometry of NH_3-SO_2 and related molecules. R is the distance between the central atoms of the two molecules.
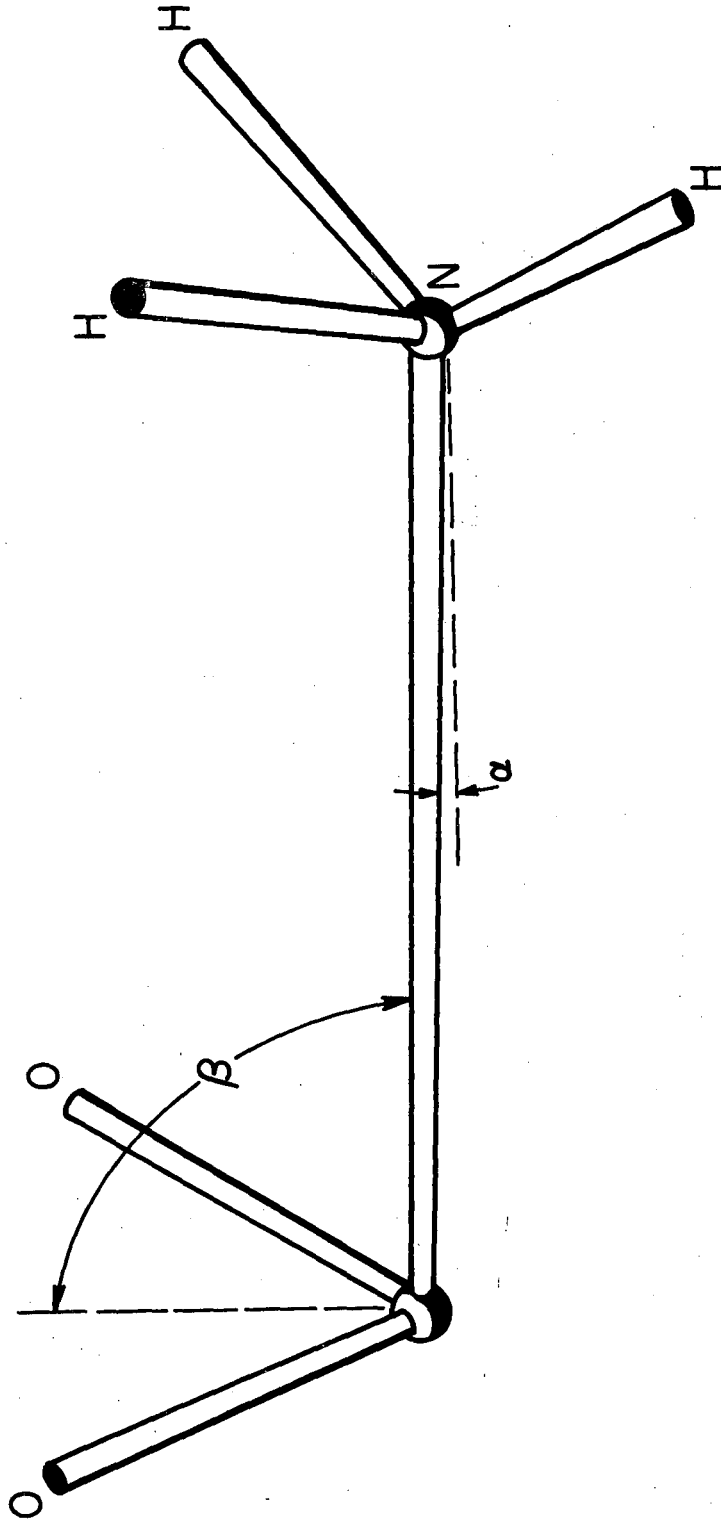
Figure 1

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