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Charge-Transfer Complexes. NH_3–O_3, NH_3–SO_2, and $N(CH_3)_3$–SO_2[1]

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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_3O_3 and NH_3SO_2. Minimum basis sets were used for all three complexes, while for NH_3SO_2 two considerably larger sets (double ζ and double ζ 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/mol. Using the double ζ basis set the NH_3–SO_2 dissociation energy is increased to 10.40 kcal/mol. When a set of sulfur d functions is added to the latter set, the binding energy becomes 9.30 kcal/mol in the absence of geometry reoptimization.

Experimental[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[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 of 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 the internal energy changes of all steps in the thermodynamic cycle 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 (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.

$$\begin{tikzcd}
\mathrm{D(g)} \arrow[d, "\Delta E = -4.8\ \mathrm{kcal}"] & \mathrm{A(g)} \arrow[d, "\Delta E = -3.8\ \mathrm{kcal}"] \arrow[r, "\Delta E = -9.1 \pm 0.4\ \mathrm{kcal}"] & \mathrm{DA(g)} \arrow[d, "\Delta E = -10.5\ \mathrm{kcal}"] \\
\mathrm{D(soln)}\ + & \mathrm{A(soln)} \arrow[r, "\Delta E = -11.0 \pm 0.3\ \mathrm{kcal}"'] & \mathrm{DA(soln)}
\end{tikzcd}$$

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

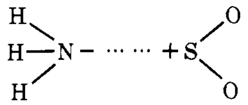
All the research reported here was carried out using single determinant self-consistent-field (SCF) theory and the programs GAUSSIAN 70[20] and POLYATOM.[21] Minimum basis sets were used for all systems studied, with each Slater function being expanded as a linear combination of three Gaussians, following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

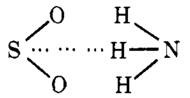
For the NH_3-SO_2 system, a much more thorough study of basis set dependence was completed. Following the minimum basis studies, a basis twice as large (double ζ) was adopted. We accepted Dunning's recommendations[24] in contracting Huzinaga's H(4s/2s), N(9s5p/4s2p), and O(9s5p/4s2p) primitive basis sets.[25] For the sulfur atom, Veillard's (12s9p) primitive set[26] was contracted to (7s5p) 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 ζ 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 $\theta_e = 119.5°$.

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 (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 ζ basis, yielding R_e = 3.60 Å and 3.36 kcal/mol. The opposite geometrical configuration (2) was also investigated, and, as expected classically, proved to be repulsive in nature. It should be noted that while 1 does allow the most favorable dipole-dipole interaction, there is another simple argument suggesting a repulsive interaction. Namely, if one accepts the idea that the lone pair of electrons of NH_3 lies along the C_3 axis and the lone pair of SO_2 lies along the C_2 axis, such a repulsion follows.


(1)


(2)

Further explorations of the NH_3SO_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 Figure 1. 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 ζ 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 (~7 kcal in the double ζ calculations) in the binding energy as β goes from 0 to ~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 D) dipole moment of SO_2. However, this geometry does allow a sizable 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 ($\alpha = 0°$, $\beta = 0°$) structure. In this sense the tilting of the SO_2 group to $\beta = 95.2°$ 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 ζ result. The angle α is nearly unchanged, differing by only 0.2° between the two cases. The N-S separation decreases y 0.16 Å in going from the minimum basis to the double ζ prediction, and the angle β increases by 8.4°. The latter change means that in the double ζ 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 ζ basis yields a much stronger binding energy than the minimum basis. However, for hydrogen bonds, the double ζ basis often yields dissociation energies significantly greater than experiment (e.g., for the water dimer the double ζ binding energy is ~8 kcal/mol,[31] while the experimental value is ~5 kcal/mol). On the contrary, for the NH_3-SO_2 complex our double ζ prediction appears to be quite reasonable. The word "appears" is present in the previous

Table I. Summary of Structural and Energetic Results for Charge-Transfer Complexes

Complex	Basis set	R, Å	α, deg	β, deg	Total energy, hartrees	Dissociation energy, kcal/mol	Dipole moment
NH_3-O_3	Minimum	2.88	0 (assumed)	86.9	−276.74713	2.24	1.89
NH_3-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 ζ	3.60	0 (assumed)	0 (assummed)	−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 ζ plus sulfur d functions	2.70 (assumed)	8.2 (assumed)	95.2 (assumed)	−603.35744	9.30	4.30
$N(CH_3)_3$-SO_2	Minimum	2.86	0 (assumed)	90 (assumed)	−711.79749	4.06	2.22

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/mol. 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/mol 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 ζ 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 $\mu(NH_3) = 1.79$ D (1.47 experimentally[32]) and $\mu(SO_2) = 1.72$ D (1.63 from experiment[30]). The double ζ basis, which generally exaggerates polarities, yields 2.34 and 2.78 D, respectively. Finally, when sulfur d functions are added, the SO_2 dipole reduces to 2.53 D. 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 ζ), 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 D 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 sizable dipole moments of their own. However, by performing a minimum basis computation at $R = 100$ bohrs, $\alpha = 8.4°$, and $\beta = 86.8°$, we obtain a "properly oriented separated NH_3 + SO_2" dipole moment of 2.22 D. The difference of 0.28 between that separated result and the 2.50 D in Table I may in a certain sense be attributed to the complex itself. The analogous treatment of the double ζ results suggests a contribution of 0.95 D 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 D[33] vs. 1.63 D 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 D, substantially less than the 1.47 D 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 ~80% as strongly bound as the analogous ammonia complexes.

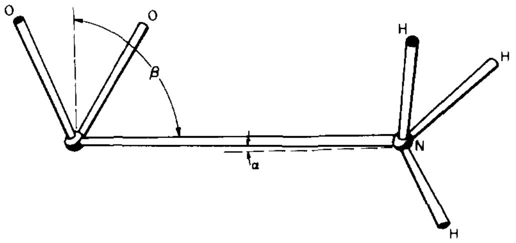


Figure 1. The three most important degrees of freedom in determining the equilibrium geometry of NH_3-SO_2 and related molecules. R is the distance between the central atoms of the two molecules.

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 moments 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. After this manuscript was completed, we learned of an unpublished crystallographic study[35] of the $N(CH_3)_3$-SO_2 complex. The geometry determined is rather similar to that predicted here.

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Calorimetric Titration Study of the Interaction of Several Uni- and Bivalent Cations with 15-Crown-5, 18-Crown-6, and Two Isomers of Dicyclohexo-18-crown-6 in Aqueous Solution at 25 °C and $\mu = 0.1$[1]

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Abstract: Log K, ΔH, and ΔS values for the 1:1 reactions at 25 °C in aqueous solution of several uni- and bivalent cations with 15-crown-5, 18-crown-6, and the cis-syn-cis and cis-anti-cis isomers of dicyclohexo-18-crown-6 have been determined by a calorimetric titration procedure. The marked selectivity toward uni- and bivalent cations shown by 18-crown-6 is not found with 15-crown-5. Tl^+ forms more stable complexes than Rb^+ (same crystal radius) with all three 18-crown-6 ligands. Favorable enthalpy and entropy changes contribute to this result. Ag^+ forms more stable complexes than K^+ (approximately same crystal radius) with only the cis-syn-cis isomer. Unfavorable ΔH and favorable ΔS values characterize formation of this complex. Only NH_4^+, of the cations studied, forms a more stable complex with 15-crown-5 than with the 18-crown-6 ligands. For the 18-crown-6 set of ligands, cation selectivity, particularly for bivalent metal ions, is enhanced when dicyclohexo groups are present in the cis-syn-cis conformation, but is diminished when these groups are present in the cis-anti-cis conformation.

The selectivity shown by certain cyclic polyethers toward cations is well documented[2-4] and constitutes one of the interesting features which distinguish them from most noncyclic ligands. The demonstration of cation selectivity by these compounds has resulted in much interest in them for possible use in many areas where this property is important,[2-4] e.g., sensing elements in cation selective electrodes, study of biological transport mechanisms, solubilization of salts in solvents of low polarity making possible new organic reactions with increased yields, and development of carrier-membrane systems. The synthesis of macrocyclic compounds for these or other applications requires a knowledge of the effect on cation selectivity of various ligand and cation parameters.[2-7] The present study is one of several designed to examine the effect of these parameters on cation selectivity as measured by the thermodynamic quantities, log K, ΔH, and ΔS, for complex formation. The compounds included in the present study are I, II, IIIa, and IIIb, and the parameters considered are: (1) ligand ring substitution and cavity size; (2) cation size, charge, and electronic configuration.

A plot[2,8] of log K for the reaction of dicyclohexo-18-crown-6[9] (IIIa or IIIb) with uni- and bivalent cations vs. cation radius results in regions of maximum stability for both cation types. Since the thermodynamic quantities for the reaction of these isomers with a given cation usually differ considerably, it is of interest to compare results for them with those for II to learn the effect on complex stability of ligand substitution and isomer conformation. The latter property has been determined for crystalline IIIa and IIIb by x-ray crystallography, their isomers having the cis-syn-cis[10] and cis-anti-cis[11] conforma-