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ELECTRONIC STRUCTURE OF THE EXCIPLEX R_2CO-NR_3 AND ITS PHOTOCHEMICAL IMPLICATIONS

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Amines have been known to be effective in the quenching of fluorescence and phosphorescence of the carbonyl group. Aldehydes and ketones abstract photochemically an α-hydrogen from substituted amines[1]. Exciplexes have been proposed as a possible intermediate for both of these processes[1]. However, as yet there is no experimental data available concerning the geometries, stabilities (if any) and electronic structures of such exciplexes.

In this communication, we report, as determined by ab initio molecular orbital calculations, the preferred geometries and electronic structures of a complex between H_2CO and NH_3. In the complex we assumed that either the C or O of formaldehyde is in direct contact with the N of ammonia, simulating tertiary amines. In addition to the SCF ground state, we were able to calculate, with the aid of the electron-hole potential(EHP) method[2], four excited states. The lowest lying singlet and triplet exciplex states are found to be interpretable as complexes of n-π* excited states of H_2CO with the ground state NH_3. Higher in energy are found singlet and triplet states which are, in principle, $H_3N \rightarrow H_2CO$ charge transfer (CT) states. A partial geometry optimization was carried out with the standard STO-3G basis set[3] in the SCF and EHP approximations. Experimental geometries of the n-π* triplet excited state of H_2CO (bent)[4] and the ground state of NH_3 were used and assumed not to change upon complex formation. Same calculations with the ground state geometry of H_2CO did not alter the qualitative conclusions of this paper. The relative geometry between H_2CO and NH_3 was varied widely as is shown in Fig. 1. The findings can be summarized as follows.

A. The ground state complex is repulsive for all the approaches studied. The least repulsive approach for NH_3 is from above the oxygen atom, as is indicated by G in Fig. 1.

B. For either the lowest singlet or triplet exciplex state, the most favorable approach is in the xz plane with <CON~100°, as indicated by X in Fig. 1. At R~2.9 Å there are small minima of ΔE=-0.5 and -0.9 kcal/mol respectively for the singlet and triplet state. At the same geometry, the more flexible and reliable 4-31G basis set[3] gives 0.5 and -0.1 kcal/mol respectively within the EHP approximation and 0.4 kcal/mol for the triplet using the unrestricted Hartree-Fock (UHF) approximation. Though we cannot conclude whether or not the exciplexes are stable, it seems apparent that they have a very flat potential curve up to R~2.5 Å.[5]

C. The results of an energy decomposition analysis[6] and the amount of charge transfer ΔQ from NH_3 to H_2CO for the ground and UHF triplet state at this geometry (X, R=2.9 Å) are shown below.

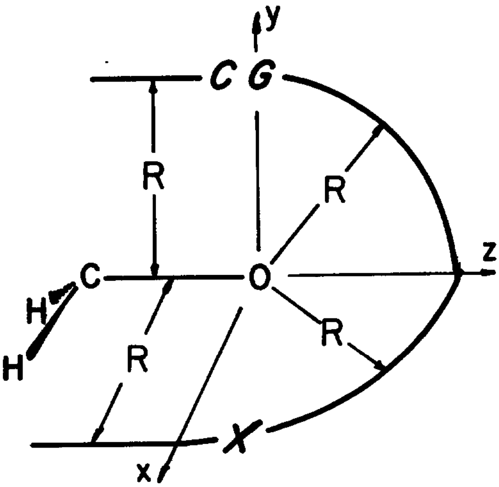

Fig. 1. H_2CO has its CO on the z axis and has a reflection plane yz. The nitrogen atom of amine was moved along the thick solid curve, keeping the hydrogen atoms away from H_2CO with the C_{3v} axis perpendicular to the solid curve. The distance R was changed from 3.1 Å to 1.8 Å.

State	4-31G Interaction Energy (kcal/mol)					ΔQ
	Total	Electrostatic	Exchange	Polarization	Charge Transfer	
Ground State	6.1	4.5	2.6	-0.4	-0.6	0.004
Triplet Exciplex	0.4	-0.3	1.9	-0.4	-0.9	0.009

In the exciplex as well as in the ground state only a small transfer of charge takes place. Essentially the exciplex is a complex between H_2CO^* and NH_3. This conclusion is consistent with the experimental observation that the queching has little solvent effect[1]. The energy components show that the exciplex state is more attractive (less repulsive) than the ground state principally due to a favored electrostatic interaction, though supplemented by a smaller exchange repulsion and a slightly larger charge transfer stabilization. These components are consistent with the qualitative picture that the exciplex lost a lone pair electron of O to the π* orbital of CO.

D. The CT states prefer an approach of N from above the oxygen atom, as is shown by C in Fig. 1, with the minima at around R=1.9 Å. More than 90% of an electron is transferred to form a $H_2CO^- - NH_3^+$ complex.

E. Fig. 2 shows the STO-3G potential energy curves (relative to H_2CO and NH_3) for the complexes as functions of R in the preferred exciplex approach X. The calculated curves are shifted to match experimental energies of H_2CO excited states (72 and 81 kcal/mol for the triplet and singlet, respectively). The triplet and singlet exciplex states seem to intersect the ground state curve at R~1.8-1.9 Å at energies about 24 and 28 kcal/mol, respectively, above the energy of the corresponding H_2CO excited state. The charge transfer state at R=1.9 Å for this approach is estimated to be about 140 kcal/mol (230 (ionization potential of NH_3) - 40 (electron affinity of R_2CO) - 50 (stabilization energy)), substantially above the exciplex states.

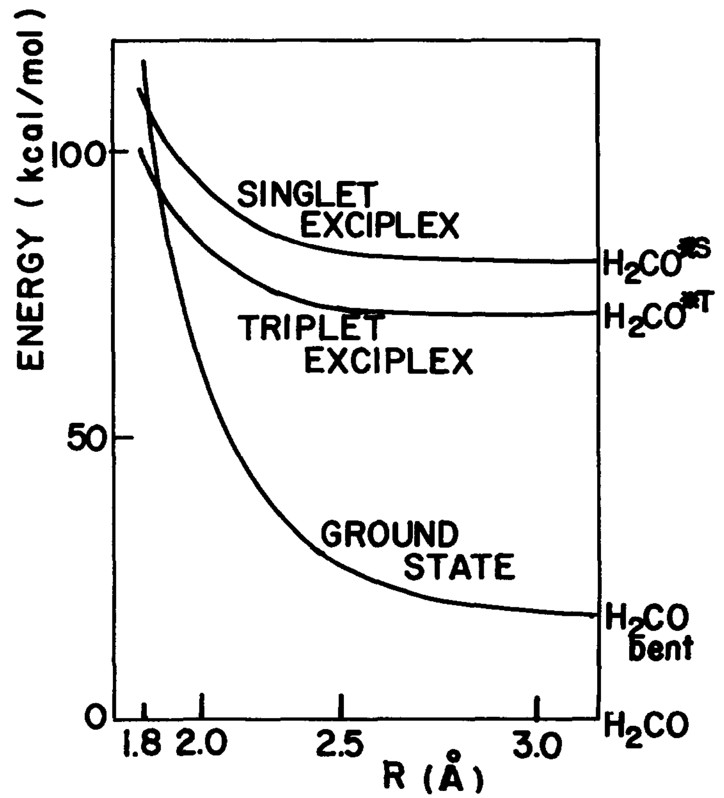

Fig. 2. The potential energy curves for the approach X.

If the crossover from the exciplex potential surface to the ground state surface is the critical step for quenching, any lowering of the intersection point would increase the efficiency. A lowering should be accomplished by (1) making the ground state repulsion steeper, (2) lowering the energy of the excited states of R_2CO, or (3) making the interaction in the exciplex state more attractive. An alkyl substitution on amine will lower the energy of the intersection by the mechanisms 1 and 3. Work is in progress on the alkyl substituent effect for this complex.

The role of the charge transfer state in quenching and photoreduction of aldehydes and ketones is not clear. In the case of quenching aromatic hydrocarbons, on the other hand, π-π type complexes will be preferred both in the exciplex and charge transfer states, and the interplay between the two kinds of states may be more important[7].

While this work was being completed, it was learned that Maharaj, Csizmadia and Winnik had carried out similar studies for the same complex[8]. Their findings are consistent with those reported here.

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