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PHOTOAMIDATION OF OLEFINS—I†
THE ELECTRONIC STRUCTURE AND PROPERTIES OF GROUND AND EXCITED STATES OF FORMAMIDE

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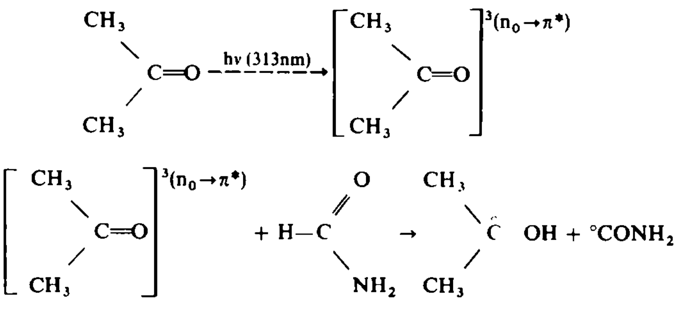
Abstract—The modified CNDO-CI method is applied for an analysis of electronic properties of formamide in its ground and excited states. Results obtained from the total wave function are in complete agreement with available data. The unobserved first triplet of formamide is predicted to be of $n_0 \rightarrow \pi^*$ type, located at 4·2 eV; this result indicates that in the photoamidation of olefins, the only role of excited acetone is the abstraction of the formyl hydrogen of ground formamide.

INTRODUCTION

IN THE COURSE of a detailed experimental study of the photoamidation of olefins in the presence of acetone, the setting up of a completely consistent kinetic model led us to reexamine, from a theoretical point of view, the problem of the role of acetone in this reaction.

Up to 1964, the first step of the reaction was given as an energy transfer from the excited $^3(n_0 \rightarrow \pi^*)$ triplet state of acetone to a triplet of formamide, a molecule for which no phosphorescence spectrum is known. In 1964, after an examination of the reaction products, Elad and Rokach[1] proposed another mechanism consisting in the abstraction of the hydrogen atom bonded to carbon in formamide by the excited triplet of acetone:



but they did not exclude the possibility of a simultaneous generation of carbamoyl radicals $^{\circ}CONH_2$ by an energy transfer from the photoactivated acetone molecule.[2,3]

More recently, by measurements of the EPR spectrum during the photolysis of acetone in the presence of formamide, Livingston and Zeldes[4] observed the formation of $(CH_3)_2\overset{\circ}{C}OH$ and $\overset{\circ}{C}ONH_2$ radicals.

In any case, it may be considered as interesting to obtain theoretical information

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about the nature. position and reactivity of the lowest triplet states of formamide and. with this end in view. semi-empirical SCF calculations have been performed. The results presented in this paper have been obtained using the classical CNDO method[5] as modified by Jaffe and Del Bene[6] for a more specific spectroscopic use; the parameters employed are the original ones. adapted by the authors in order to reproduce the O, O transition energies of benzene and related molecules.[6]

RESULTS

Molecular geometry

Because of the no small influence of adopted bond lengths and bond angles on the results of CNDO type calculations. particularly for low symmetry compounds. we have chosen for the present work the most recent geometry of formamide. as given by Costain and Dowling[7] from the microwave spectra of formamide and isotopic derivatives (Fig. 1). but. contrary to the experimental data. we have admitted the coplanarity of amide and carbonyl groups (which implies adopting pure sp^2 hybridization states for carbon and nitrogen atoms) and bond angles equal to 120° around nitrogen.

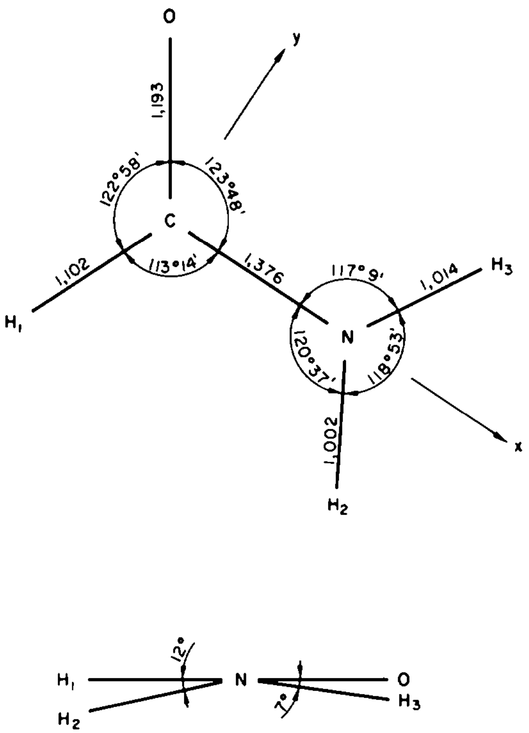

FIG. 1. Observed structure of formamide,[7] numbering of atoms and coordinate system

In fact. these hypotheses have been justified by the non-empirical calculations published by Robb and Czismadia[8] in 1968 and much more recently by Christensen *et al.*[9]

Molecular orbitals and ground state properties

For the SCF ground state of the 18 valence electrons of formamide. the present calculation gives the molecular orbital energies reproduced in Table 1.

TABLE 1. SCF-MO ENERGIES OF FORMAMIDE (eV)

Occupied MO's			Virtual MO's		
No	Nature	Energy	No.	Nature	Energy
1	σ	-46.18	10	π^*	$+1.88$
2	σ	-37.99	11	σ^*	$+5.04$
3	σ	-25.49	12	σ^*	$+6.25$
4	σ	-22.21	13	σ^*	$+8.44$
5	σ	-19.20	14	σ^*	$+9.34$
6	σ	-16.59	15	σ^*	$+11.69$
7	π	-16.41			
8	π	-12.16			
9	n_O[a]	-11.61			

[a] Lone pair character on oxygen atom = 77%.

It is interesting to notice that contrary to non-empirical calculations[8, 10, 11] but in complete agreement with experiment,[12] the last occupied MO is found to be an oxygen lone pair.

The first ionization potential computed according to the empirical relation previously proposed by one of us[13]

$$IP^{corr.} = -\varepsilon_{N/2} - (0.9 \pm 0.2)\,eV$$

is then found equal to (10·7 ± 0·2) eV, which is in agreement with the experimental results[12, 14]

$$IP_{exp} = 10.2\,eV$$

More recently, a photoelectron spectrum of formamide has been reported in the literature[15] showing that the experimental energy difference between the two last occupied molecular orbitals $[\varepsilon(n_O) - \varepsilon(\pi)]$ equals 0·38 eV the theoretical difference we obtained is 0·55 eV.

In Table 2, the theoretical charge distributions, computed from the SCF eigen vectors, reveal net π charges [C: + 0·25; N: + 0·12; O: − 0·37], similar to those one could reach on the basis of pure calculations[16, 17] and total charges similar to those given by non-empirical methods[8, 9, 10, 18]

It must also be noted that for carbon and oxygen atoms, the total net charges are not very different from the pure π net charges, whilst for nitrogen, the situation is completely different $[\Delta P^{\pi}_N = +0.12;\ \Delta P_N = -0.27]$ and the high negative net charge on this atom agrees with the analysis of experimental data.[19, 20]

On other hand, in agreement with *ab initio* calculations,[8, 10] no charge transfer is predicted in the ground state of formamide between the amino and carbonyl groups

$$P(N) + P(H_2) + P(H_3) = 7.012$$
$$P(C) + P(O) \ + P(H_1) = 10.988$$

Table 2. Charge distributions in the ground state

Atomic Orbital \ Atom	H_1	H_2	H_3	C	N	O
1s	0·990	0·882	0·866	—	—	—
2s	—	—	—	0·986	1·197	1·677
$2p_x$	—	—	—	0·888	1·098	1·786
$2p_y$	—	—	—	0·968	1·089	1·574
$2p_z$	—	—	—	0·751	1·881	1·367
Total	0·990	0·882	0·866	3·593	5·265	6·404

For a molecule with such small symmetry. the calculation of the dipole moment gives a good criterion for the accuracy of the computed molecular wave function and for that of the adopted geometry since the orientation of dipole vector is not defined by symmetry. Based on the atomic densities given in Table 2 and including the contribution of atomic dipoles. this calculation gives:

$$\mu = 3{\cdot}88 \text{ Debyes}$$

$$\theta = (\vec{\mu}.\vec{CN}) = 46{\cdot}8^\circ \text{ (away from the oxygen atom)}$$

whilst. from Stark effect measurements on the microwave spectrum of formamide. Kurland and Wilson[19] obtained a value of (3·71 ± 0·06) Debyes with the dipole vector inclined at an angle of 39·6° from the CN bond directed away from the oxygen atom.

Electronic spectrum

The electronic spectrum of formamide has been computed on the basis of a configuration interaction treatment between the 30 lowest mono-excited states given by the classical virtual orbital approximation. Table 3 summarizes the results of this calculation (transition energy from the ground state. oscillator strength and the one-electron transitions which contribute to each excited state).

Table 3. Singlet to singlet spectrum of formamide

$\Delta E_{(eV)}$	f	Nature	Main Configurations
4·17	0	$n_0 \to \pi^*$	0·99 (9 → 10)
7·47	0·14	$\pi \to \pi^*$	0·96 (8 → 10)
8·71	0	$\pi \to \sigma^*$	0·60 (8 → 11) + 0·34 (8 → 12)
9·17	0	$\sigma \to \pi^*$	0·96 (6 → 10)
9·56	0·06	$n_0 \to \sigma^*$	0·90 (9 → 11)
10·29	0	$\pi \to \sigma^*$	0·56 (8 → 12) + 0·36 (8 → 11)
11·20	0·08	$\pi \to \pi^*$	0·88 (7 → 10)
11·23	0	$\pi \to \sigma^*$	0·91 (8 → 13)

Experimentally[12, 21] the electronic spectrum of formamide exhibits

—a broad absorption band of weak intensity (f = 0·002) beginning around 4·3 eV with a maximum near 6 eV. experimentally assigned to a $n \rightarrow \pi^*$ excitation;

—a strong absorption (f = 0·24) at 7·19 eV identified as the first $\pi \rightarrow \pi^*$ transition;

—a moderately intense band (f = 0·06) at 9·19 eV which has been assigned to the second $\pi \rightarrow \pi^*$ excitation.

For the two lowest energy transitions. the agreement between the experimental data (energy. oscillator strength and assignment) and the results of the present calculation is very satisfying: but. for the next allowed absorption band. observed at 9·19 eV (f = 0·06). some discrepancy seems to appear. Our calculation predicts it to result from a $n_0 \rightarrow \sigma^*$ excitation (from the highest filled level to the first virtual σ^* molecular orbital which is antibonding with respect to the carbon-hydrogen and nitrogen-hydrogen interactions) while the second $\pi \rightarrow \pi^*$ transition is predicted some 2 eV higher. However. the exact nature of the 9·19 eV band must be viewed with some scepticism. since at this energy in the vacuum UV. Rydberg states are almost certainly present. Nevertheless. it is interesting to point out that Tinico *et al.*[22] proposed some years ago to reassign this band to an $n \rightarrow \sigma^*$ transition.

Concerning the absorption spectrum of formamide, the transition moment vector associated with the first allowed transition is predicted to be inclined away from the NO axis by 5·6°. whilst Peterson and Simpson.[23] measuring the orientation of this vector in the myristamide (1 – tetradecanamide) crystal. found. for the same angle. a value of 9·1°.

For the triplet states. similar calculations have been performed taking into account the interaction of the 30 lowest energy monoexcited triplets. In these conditions. the semi-empirical method adopted predicts

– a $n_0 \rightarrow \pi^*$ triplet at 4·17 eV
– a $\pi \rightarrow \pi^*$ triplet at 5·63 eV

As we said previously. no phosphorescence spectrum has been observed for this molecule.

Electronic structure of excited states

In Table 4. we have reported some of the results of our calculations for excited states (total charges. dipole moment and π bond orders) and in Table 5 the corresponding distributions of electronic densities for heavy atoms are given.

With respect to these charge densities. one can notice that the four reported excited states correspond to intramolecular charge transfer ones; in the $n \rightarrow \pi^*$ states. the electron transfer occurs essentially. as expected. from the oxygen lone pair to the carbon and oxygen π orbitals. whilst in the first $\pi \rightarrow \pi^*$ states. the transfer takes place essentially from the p_π (N) atomic orbital to the p_π (C) one. For these states. this result is in agreement with Nagakura's pure π analysis[21] of these charge transfer transitions in terms of an electron donating group (—NH_2) and an electron accepting group (—CHO) and the amount of electron transfer given by the present calculation (0·58 electrons) is almost identical with the value obtained by this author.

With respect to the π bond orders given in Table 4. the present results reveal:

—in the ground state. an important conjugation over the three π centers with a pronounced antibonding character between N and O atoms;

TABLE 4. ELECTRONIC STRUCTURE OF EXCITED STATES

Electronic State / Quantity	$1.3_{(n\rightarrow\pi^*)}$	$1_{(\pi\rightarrow\pi^*)}$	$3_{(\pi\rightarrow\pi^*)}$	Ground State
P (H_1)	0·892	0·993	1·001	0·990
P (H_2)	0·878	0·887	0·897	0·882
P (H_3)	0·859	0·872	0·878	0·866
P (C)	4·171	4·180	4·167	3·593
P (N)	5·251	4·663	4·660	5·265
P (O)	5·949	6·404	6·397	6·404
μ (Debyes)	1·56	7·11	6·95	3·88
P^{π} (CN)	0·192	0·309	0·319	0·385
P^{π} (CO)	0·445	0·388	0·404	0·889
P^{π} (NO)	−0·137	0·302	0·305	−0·274

TABLE 5. ATOMIC DENSITIES IN EXCITED STATES

Atomic Orbital	$1.3_{(n\rightarrow\pi^*)}$			$1_{(\pi\rightarrow\pi^*)}$			$3_{(\pi\rightarrow\pi^*)}$		
	N	C	O	N	C	O	N	C	O
2s	1·179	0·986	1·677	1·199	0·990	1·676	1·215	0·989	1·677
$2p_x$	1·044	0·864	1·270	1·099	0·889	1·782	1·102	0·895	1·787
$2p_y$	1·088	0·945	1·319	1·096	0·967	1·570	1·089	0·973	1·574
$2p_z$	1·941	1·376	1·684	1·269	1·334	1·377	1·255	1·310	1·359

—in the $n \rightarrow \pi^*$ states, a reduction by half of the ground state bond orders, indicating particularly the biradical structure of the carbonyl group;

—in the $\pi \rightarrow \pi^*$ states, the P_π (CO) and P_π (NO) are modified in such a way that the conjugation is quite uniform and circular over the three π centers.

With respect to the hydrogen atoms, it is to be noted that only the H_1 atom bonded to carbon exhibits a significant variation of its charge density when going from the ground state to the first ($n \rightarrow \pi^*$) singlet or triplet. The increase of "acidity" of this atom is also reflected in the change of bond populations calculated according to Wiberg (Table 6).[24]

TABLE 6. WIBERG BOND POPULATIONS IN FORMAMIDE

Bond	Ground State	$1.3_{(n\rightarrow\pi^*)}$ States
$C—H_1$	0·970	0·863
$N—H_2$	0·978	0·976
$N—H_3$	0·972	0·967
C—N	1·119	0·952
C—O	1·826	1·343

From their definition, these bond populations, closely related to the bond character, correspond to the number of covalent bonds formed by two atoms, corrected by the ionic character in each bond.

Besides the expected biradical structure of the carbonyl group in the $n \rightarrow \pi^*$ states, the values reported in Table 6 show a considerable decrease of C—H bond strength when going from the ground state to the first excited states of formamide; this conclusion agrees with the experimental fact that direct photolysis of formamide produces H° and $^\circ CONH_2$ radicals.[25]

DISCUSSIONS AND CONCLUSIONS

The semi-empirical wave function which has been computed for the eighteen valence electron system of formamide allowed a very satisfying interpretation of the electronic properties of this compound in its ground state, as well as in its excited states, and these encouraging comparisons between theoretical results and experimental data may be considered as giving some plausibility to the first triplet position.

So, if we return now to our initial problem of the role of acetone in the photoamidation of olefins, it becomes evident that a photosensitization of formamide (triplet energy = 4·2 eV) by excited acetone triplet [triplet energy = 3·5 eV[26]] is impossible, and, as a natural consequence, the only possible mechanism consists in the abstraction of the formyl hydrogen of ground formamide by the excited $n \rightarrow \pi^*$ triplet of acetone.

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