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THE PHOTOREARRANGEMENT OF GASEOUS FURAN
A THEORETICAL APPROACH

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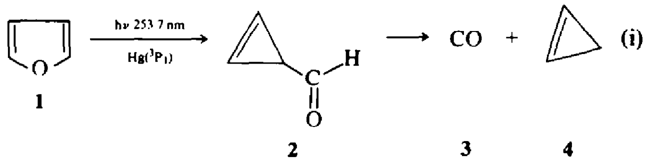
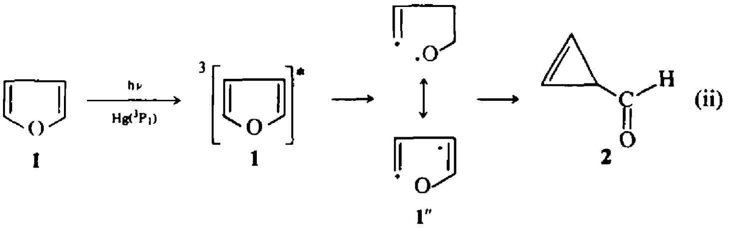
Abstract—The photorearrangement of gaseous furan when photolysed at 254 nm in the presence of mercury was studied using both an *ab initio* and a semiempirical treatment of excited states.

A reaction pathway towards the cyclization into cyclopropenylaldehyde is proposed. It is shown that the rearrangement of photosensitized furan involves a singlet or triplet excited state of the π, σ^* type.

INTRODUCTION

Valence isomerization is a common feature of the photochemical behavior of heterocycles. Isomerization mechanisms frequently involve a successive ring contraction—ring expansion process. In the case of 5-membered heterocycles, the primary photochemical reaction may produce a 3-membered ring. Furan and its substituted derivatives offer the prototype of such a contraction. At present, it is well-established[1-6] that the contraction of the furan ring to cyclopropenylaldehyde or to cyclopropenylketone accounts equally well for the photodecarbonylation of furan and for the photoisomerization of its substituted derivatives. Carbon monoxide and cyclopropene are the major products of the mercury-sensitized photolysis of gaseous furan.[1] The mechanisms proposed to account for the formation of the intermediate aldehyde 2 completely disregard the nature of the electronic state from which the cleavage of the ring proceeds, as well as the nature of the state which is a precursor of the formation of the 3-membered ring. At most, since the reaction is mercury-photosensitized, this state has been presumed to be a triplet state.





Scheme (ii) summarizes what is found in the literature about mechanisms. The fundamental contradiction discussed by Salem *et al.*[7] concerning this type of scheme for many photochemical reactions is once again encountered. Although the diradical 1″ proceeds from a triplet excited state of furan, it could just as well be produced by the thermal cleavage of furan in its ground state.

The present paper is an attempt, using the methods of theoretical chemistry, to find the reaction path from furan to the intermediary cyclopropenylaldehyde involved in the sensitized photolysis. For that purpose we had to choose a reaction path for the photolysis, in order to draw the energy diagram of the electronic states of furan during the nuclear configuration rearrangement. Then we had to situate the mercury-photosensitized electronic state of furan in its triplet manifold to get the starting point of the reaction pathway.

Model

Furan is planar; the intermediate cyclopropenylaldehyde 2 is not. The choice of the optimal geometric parameters to represent the reaction coordinates is therefore not evident. However, if one admits, like Hiraoka[2] for substituted derivatives of furan, that the first step of the photorearrangement is the cleavage of the bond between oxygen and one of the adjacent carbons, C_5 for example (Fig. 1), the choice becomes quite clear. It may be supposed that the decisive phenomena which bring about the subsequent molecular rearrangement occur as the ring opens, while the system is still planar. Consequently we retained a planar atomic configuration and simulated the progressive stretching of the O–C_5 bond by varying the $\widehat{C_3\text{–}C_4\text{–}C_5} = \alpha$ angle (Fig. 1) between 106° and 135°.

Then we built the energy diagram $E = f(\alpha)$ in order to infer a possible mechanism working on the assumption

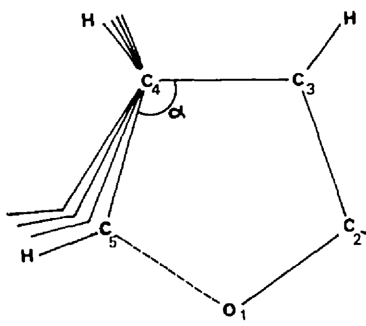


Fig. 1.

that angle α is the parameter of the reaction pathway and not simply one of the several reaction coordinates. Therefore, except for the angle $\widehat{C_3C_4C_5} = \alpha$ and the length $OC_5 = l$, the bond angles and bond lengths of furan have been kept constant in our calculations. We are aware of the very severe geometric constraints that such a hypothesis imposes on the molecular system and we know that the energies calculated and consequently those of the eventual crossing points are not the lowest possible. A better evaluation of the energies could have been obtained if we had allowed the system to relax in each of its electronic states, that is, if we had investigated the minimal energy for each value of α, with respect to all the other geometrical parameters and for each possible excited state. This would have implied very numerous and complex calculations, the usefulness of which is questionable, because this difficulty would have immediately arisen: the quasi-impossibility of finding any true crossing points on the energy diagram. In our work, on the contrary, if a crossing point occurs, it is a true crossing point since it corresponds to a unique nuclear configuration. In that case, even if the calculated energy of a crossing point is not the lowest, this point is necessarily situated on the line of crossing of two energy sheets and can thus indicate the ability of the system to pass from one energy sheet to another.

Methods

The energy data relative to ground and excited states result from a theoretical *ab initio* and semi-empirical treatment.

The *ab initio* calculations were performed with a version of the IBMOL program adapted to the study of the excited state. The gaussian type basis used for the heavy atoms was that of Roos and Siegbahn[8] contracted to 3s 1p, and for the hydrogens, that of Huzinaga.[9] The *ab initio* energy of the excited states was determined by the virtual orbital technique using the ground state wave function. A self-consistent treatment with Roothaan's formalism[10] was performed on the first excited π, π* and π, σ* triplet states for a single nuclear configuration corresponding to a rather large opening of the furan ring (α = 123°).

The semi-empirical calculations were carried out both by the CNDO/2 method with the original Pople formalism and by the CNDO/S CI method with the parametrization proposed by Jaffe for excited states. A UHF semi-empirical approach to the first triplet state representation was undertaken for four values of the ring opening, using the parameters initially proposed by Pople.

The bond lengths and bond angles adopted for furan in its ground state[11] were those used by Palmer and Gaskell[12] in a previous *ab initio* calculation.

RESULTS DISCUSSION

I. Ab initio *energy diagram as a function of the angle α*

Table 1 shows the evolution of the ordering of the occupied and virtual *ab initio* orbital levels as the ring opens.

The ground and excited triplet state *ab initio* potential energy curves are presented in Fig. 2. The potential energy of the A″ (σ, π*; π, σ*) singlet states evolves in the same way as that of the σ, π* and π, σ* triplets. To make Fig. 2 clearer, the corresponding curves, which are

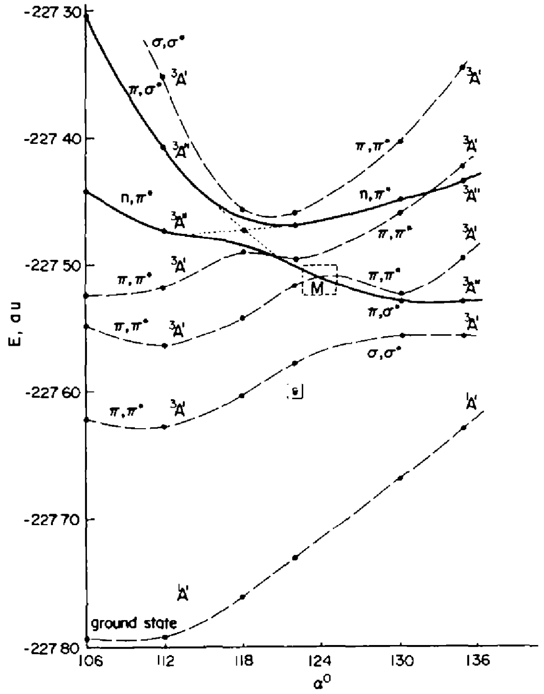


Fig. 2. *Ab initio* energy diagram for the cleavage of furan in its plane. ——, triplet states of A′ symmetry; ——, triplet states of A″ symmetry; ▲, self-consistent open shell *ab initio* energy of the lowest π, π* triplet state (α = 122°); □, self-consistent open shell *ab initio* energy of the lowest π, σ* triplet state (α = 122°).

Table 1. Ordering of the *ab initio* orbital levels as a function of the angle α

α	106°	112°	118°	122°	130°	135°
Energy (a.u.)	− 227.795	− 227.793	− 227.76	− 227.731	− 227.688	− 227.629
Energy and Symmetry of the molecular orbitals (a.u.)	σ^* 0.367	σ^* 0.295	π^* 0.207	π^* 0.210	π^* 0.215	π^* 0.218
	π^* 0.198	π^* 0.202	σ^* 0.202	σ^* 0.149	π^* 0.074	π^* 0.072
	π^* 0.107	π^* 0.095	π^* 0.087	π^* 0.082	σ^* 0.068	σ^* 0.030
	π − 0.415	π − 0.412	π − 0.406	π − 0.401	π − 0.390	π − 0.382
	π − 0.473	π − 0.468	π − 0.469	π − 0.470	σ (n) − 0.468	σ (n) − 0.444
	σ (n) − 0.588	σ (n) − 0.567	σ (n) − 0.535	σ (n) − 0.512	π − 0.474	π − 0.473

very close to the A″ triplet ones, are not shown. However they will be discussed from a qualitative point of view in the next section.

The most noticeable points of these data are as follows:

The ordering of orbital levels is altered as α approaches 118°, a virtual σ^* level coming between the first two virtual π^* levels.

The first two π, π^* triplets, especially the second triplet, are stabilized by the relaxation of α, that is to say of the O_1–C_5 bond, to about 112°

At 123° an intersection occurs between the second π, π^* triplet and the first A″ (σ, π^*; π, σ^*) triplet curves. At the proximity of the intersection, the A″ state is of the π, σ^* type.

The n, π^* triplet state, although slightly stabilized by the relaxation of α, is the fifth highest excited state whatever the value of α.

For the limiting value $\alpha = 135°$, the ordering of what we may call the "diradical" states of A′ and A″ symmetry is, using Salem's notation, as follows: $^1D_{\sigma,\sigma}$, $^3D_{\sigma,\sigma}$, $^3D_{\pi,\sigma}$, $^1D_{\pi,\sigma}$.

The energy of the π, σ^* triplet state corresponding to $\alpha = 120°$ is considerably lowered by a self-consistent open-shell treatment. The energy of the first π, π^* triplet is however only slightly modified (Table 2). We can assume that this is also true for the second π, π^* triplet. We thus conclude that the intersection of the second π, π^* and first π, σ^* triplet curves, as well as that of the corresponding π, σ^* singlet, actually occurs much earlier than shown in Fig. 2.

Table 2. *Ab initio* calculations for $\alpha = 122°$

Method	Energy of the first triplet π, π^* state (a.u.)	Energy of the first triplet π, σ^* state (a.u.)
Virtual orbital technique	- 227.579	- 227.502
Self-consistent open-shell treatment	- 227.599	- 227.594
α = 122°		

II. *Electronic structure of the π, σ^* lowest triplet state*

The semi-empirical treatment of the model provides a more detailed picture of the electronic structure of the entities concerned in the photorearrangement. The CNDO/2 UHF method was applied to the lowest triplet state of furan for four values of α, 106°, 112°, 118°, 123°. The results show that, for $\alpha > 112°$, the lowest triplet state is an antisymmetric π, σ^* state (Fig. 3).† We report in Table 3 the CNDO/2 UHF charge and spin densities of the opened form ($\alpha = 123°$) in its triplet π, σ^* state. These values suggest the schematic drawing of the Fig. 4 and can be compared to the CNDO/2 CI charges of closed furan ($\alpha = 106°$). The diradical nature, π on the 5-membered chain, σ on carbon C_5, appears clearly from the spin densities mentioned in the last two columns of the same Table. For $\alpha = 123°$ the σ spin density on the C_5 atom is indeed relatively large and the π spin density on the C_3 atom is the highest in the carbon chain.

Table 3. CNDO/2 electronic and spin densities

	α = 106° Ground state CNDO/2 treatment			α = 123° π, σ^* lowest triplet state CNDO/2 UHF treatment				
	electronic charges			electronic charges			spin densities	
	Total	π	σ	Total	π	σ	π	σ
O_1	6,14	1,76	4,38	6,07	1,10	4,97	0,79	0,16
C_2	3,90	1,07	2,85	3,93	1,10	2,83	- 0,20	0,00
C_3	4,04	1,05	2,99	3,94	0,85	3,09	0,32	0,01
C_4	4,04	1,05	2,99	4,03	1,09	2,94	- 0,11	- 0,02
C_5	3,91	1,07	2,84	4,05	0,87	3,18	0,20	0,61

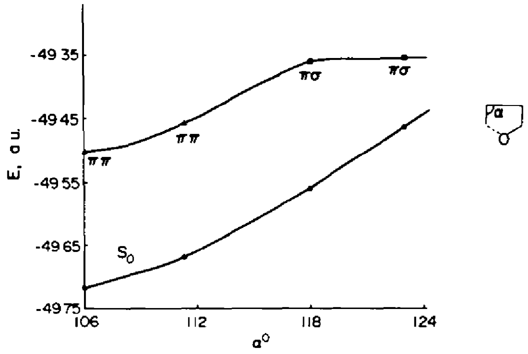


Fig. 3. Variation, as a function of α, of the energy of the lowest triplet state calculated with the CNDO/2 UHF method.

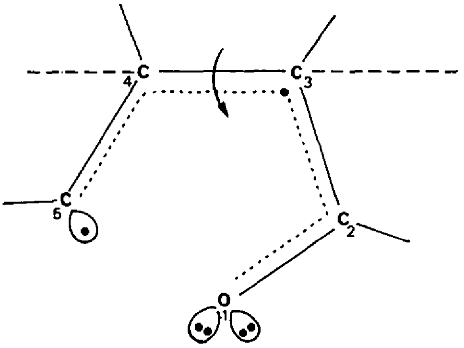


Fig. 4. Elelectronic structure of the $D_{\pi,\sigma}$ diradial.

III. *Nature of the mercury-sensitized triplet state of furan*

It is obvious that the *ab initio* transition energies are not directly comparable to the experimental data of electronic spectroscopy. This explains why, in addition to the *ab initio* study, the energies of a certain number of states were calculated using the CNDO/S method, essentially to determine the state populated by photosensitization. We note that, from a qualitative point of view, the semi-empirical CNDO/S results agree well with the *ab initio* data. This is particularly true with regard to the ordering of the orbital levels in relation to the angle α (Tables 1 and 4).

We have represented in Fig. 5, instead of the potential energy curves, since the CNDO/S is not adapted to the study of the ground state, the CNDO/S transition energies for the three first A′ states and the two first A″ states.

Table 4. Ordering of the CNDO/S orbital levels as a function of the angle α

α	106°	110°	118°	122°
Energy and Symmetry of the molecular orbitals (a.u.)	σ^* 0.185 π^* 0.078 π^* 0.038 π - 0.366 π - 0.427 σ - 0.506	σ^* 0.177 π^* 0.079 π^* 0.029 π - 0.365 π - 0.435 σ - 0.512	σ^* 0.100 π^* 0.080 π^* 0.018 π - 0.358 π - 0.452 σ - 0.493	π^* 0.081 σ^* 0.048 π^* 0.014 π - 0.355 π - 0.459 σ - 0.477

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†It is very likely that a systematic self-consistent *ab initio* treatment of the triplet energies would, past $\alpha = 122°$, invert the relative positions of the first A′ and A″ triplet curves in Fig. 2 and at 135°, that of the $^3D_{\sigma,\sigma}$ and $^3D_{\pi,\sigma}$ triplet diradicals.

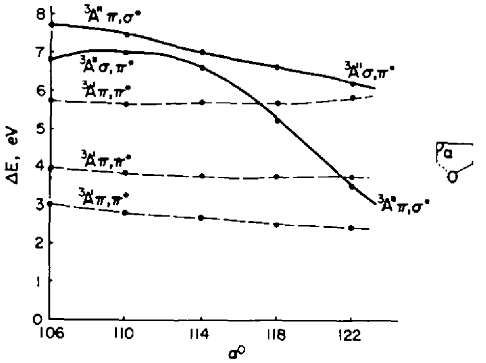

Fig. 5. CNDO/S CI So − T transition energies for the ring opening of furan.

Their evolution presents similar features to those observed in Fig. 2. As previously, in the region of 106° < α < 122°, the intersection of the curves of the second π, π^* triplet with that of the lowest π, σ^* triplet takes place at about α = 122°.

The energies calculated for the two first So–S electronic transitions are of the same order of magnitude than the energy corresponding to furan's first absorption band maximum: ΔE (exp) = 5.90 eV (our measurements in the vapour phase and Ref. 13); ΔE_1 (calc) = 5.11 eV; ΔE_2 (calc) = 5.75 eV. We assume that this is equally true for the So–T transitions. The energy of the mercury resonance line, $\Delta E = 4.89$ eV, being included between $\Delta E(So - T_2) = 3.88$ eV and $\Delta E(So - T_3) = 5.60$ eV, we state that the second triplet of furan is likely to be populated by mercury photosensitization. We recall that, since photolysis occurs in the gaseous state, an upper triplet is not excluded as starting excited state in the rearrangement.

We indicate in Fig. 6 the relative order of the ground levels of furan and cyclopropenylaldehyde, as well as of the $^3P_1$ triplet level of mercury. The first two energies come from a CNDO/2 calculation.

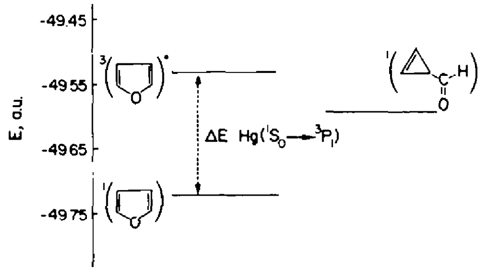

Fig. 6. Ground state energies of furan and cyclopropenylaldehyde calculated with the CNDO/2 method. Comparison with the energy of the mercury resonance line.

The aldehyde's geometry is deduced from a nuclear configuration optimization calculation. We see that the final state constituted by the aldehyde may be reached from the photosensitized triplet state of furan. We are now able to elucidate a part of the path to the final state.

MECHANISM—CONCLUSION

By imposing the cleavage of the O_1–C_5 bond, we chose a diradical pathway for the reaction. The ordering of the possible diradicals being now determined, the kind of diradical which is most likely to intervene can be found.

Every antisymmetric A″ state, n, π^* or π, σ^* state, since it may produce a diradical of the $\pi\sigma$ type, is of interest. A diradical possessing a σ radical center at the end of the carbon chain and a π radical center on the carbon chain, can give a ring contraction by partial rotation of the carbon chain. The n lone-pair orbital of the O atom lying too low in energy to be excited under the conditions of the photolysis, the n, π^* state is excluded as the starting state. Our energy diagrams (Figs. 2 and 5) show that it remains excluded when the ring opens. The same diagrams show, on the contrary, the possible role of a π, σ^* state in the transformation, which was by no means evident *a priori*, and they provide the details of the reaction as we will now set forth. We remember first that the reaction under study is mercury-photosensitized and the starting excited state a triplet state; thus an intersystem crossing must occur during the course of the cyclization. It is unlikely that furan can immediately reach a π, σ^* triplet state by photosensitization, the energy level of this state being far too high when the molecule is in its equilibrium nuclear configuration. But photosensitization may bring furan to one of the vibrationally excited levels of the second π, π^*A' triplet. An antisymmetric vibration of the furan ring in its plane may stretch one of the O–C bonds, O–C_5 for example. Two paths are then possible, either by an internal conversion with the system going onto the energy sheet of the A″ triplet, or by an intersystem crossing onto the sheet of the A″ singlet, very close to the sheet of the triplet. In view of the favorable $A' \rightarrow A''$ spatial symmetry change, this last crossing seems the more probable.

It appears, from these considerations, that in the mercury-sensitized photolysis of furan, in spite of initiation in a π, π^* triplet Franck–Condon state, the relaxation of one of the O–C bonds of furan can induce, by crossing onto a π, σ^* energy sheet, the formation of a π, σ diradical which is a likely precursor of the cyclopropenylaldehyde. Such a mechanism is easily included in the general scheme proposed by Salem[15] for the primary processes of some photochemical reactions chosen among the most exemplary.

Our fundamental purpose, to draw a diagram showing the evolution of the energies of the ground and excited states during the transformation of furan into cyclopropenylaldehyde, has been reached within the framework of a planar model. Such a model is evidently not the only one which can be imagined to account for the ring cleavage. A rotation of the $C_3C_2O_1$ part of the molecule around the C_3C_4 bond is for instance a possible mechanism and we cannot state for certain that it is not a better approach to the true behaviour of furan than ours. We may however indicate that in the first stage of our study, we rotated the C_4C_5 part of furan around the C_3C_4 bond in order to simulate the breaking of the OC_5 bond. This first attempt was unsuccessful, because we found triplet energies of the deformed molecule invariably higher than the triplet energies of the starting molecule; concluding that it was not the right way of tackling the problem, we tried a planar motion with the success shown above.

At the beginning of the transformation, the motion of the ring, however complex it is, can always be resolved into an in-plane and an out-of-plane stretching of the OC_5 bond. It seems, from our diagrams, that the first contribution to the motion can play an important part in the rearrangement. So, we shall consider the results presented as a rough and approximate picture showing the major features of what may occur during the actual motion of the furan ring under photocleavage.

As a conclusion, a rather simple way of exploring a part of the potential energy sheets of a molecular system has been able to reveal features with reasonably fit to the experimental data given by photochemists. Larger investigations using this kind of model could perhaps contribute to a better understanding of the phenomena which induce photochemical valence isomerisation in heterocycles.

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