SINDO1 Study of the Photochemical Synthesis of Cyclobutadiene from α-Pyrone

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The mechanism of the photochemical decomposition of α-pyrone to cyclobutadiene and carbon dioxide was investigated by the semiempirical MO method SINDO1. The relevant singlet and low-lying triplet potential energy hypersurfaces were studied, and intermediates and transition structures were optimized with limited configuration interaction (CI). The first step transforms α-pyrone into a bicyclic lactone via internal cyclization. Then a stepwise bond breaking mechanism yields cyclobutadiene and CO_2, whereas a simultaneous bond breaking mechanism is not important.

1. Introduction

In the 1950s Criegee and co-workers[1] used thermal reactions to synthesize cyclobutadiene. Due to its high reactivity cyclobutadiene was obtained as a dimer. During the following two decades the ground state of cyclobutadiene was intensively studied both experimentally and theoretically. It was important to synthesize monomer cyclobutadiene in order to answer the question of structure and stability of the ground state by recording ESR or IR spectra or obtaining crystallographic data, respectively. Transition metal complexes which contain cyclobutadiene were appropriate for crystallographic determination.[2,3] Oxidation of the cyclobutadiene–transition metal complex resulted in free cyclobutadiene which then could undergo further reactions, e.g., with alkenes. From the stereoselectivity it was possible to determine that cyclobutadiene has a singlet state.

It proved advantageous to generate cyclobutadiene photochemically in a matrix at temperatures of below 100 K because no decay or consecutive reaction was to be expected under these conditions. Chapman et al.[4] were able to measure an IR spectrum of photochemically generated cyclobutadiene in an argon matrix at 8 K for the first time. Other groups[5-9] had prepared cyclobutadiene in a matrix before, but were unable to take IR spectra. On the basis of the spectrum Chapman et al. concluded that the ground state should have a D_{4h} symmetry and would therefore be a triplet. The same result was found in an investigation of deuterated reactants.[10] Previously, in 1970 Maier et al.[11] had taken an ESR spectrum of substituted cyclobutadienes without indication of a triplet ground state. Subsequently, many attempts were made to clarify the nature of the ground state of cyclobutadiene. From these studies a singlet ground state of D_{2h} symmetry was confirmed by many experiments[12-15] and quantum chemical calculations.[16-19] Yet in 1977 Dewar and Kormonicki[20] postulated by their quantum chemical calculations a triplet ground state of D_{4h} structure. Finally, this was disproved through experiments by Masamune[21] and calculations by Kollmar and Staemmler.[22]

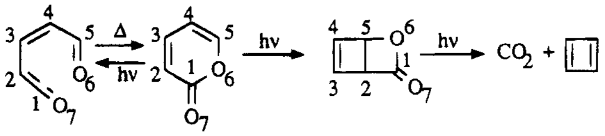

Figure 1. Experimental reaction scheme of α-pyrone.

Chapman et al. used α-pyrone as a reactant which is slowly quantitatively transformed into the bicyclic lactone bicyclo[2.2.0]-5-oxahex-2-en-6-one, the so-called Dewarpyrone (Figure 1)[23] after photochemical excitation at an energy of not more than 4.3 eV. During this reaction a ring opening to an ω-ketenal (Figure 1)[24,25] can occur which can react backwards thermally and reversibly to α-pyrone even at low temperatures in a matrix. If one irradiates Dewarpyrone with an energy larger than 4.3 eV, CO_2 is eliminated and cyclobutadiene is formed. Due to a cage effect of the matrix CO_2 remains close to cyclobutadiene, which was the reason for the misinterpretation of the IR spectrum by Chapman et al.[4] This

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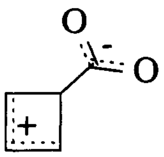

Figure 2. Cyclobutenecarboxyl zwitterion.

complexation has been described in the literature both by experimentalists[26-29] and quantum chemists.[30] We use a labeling for the molecules (Figure 1) different from the IUPAC notation in order to have a consistent labeling along a reaction pathway.

The cyclization of α-pyrone occurs directly via internal cyclization.[24] The fragmentation of Dewarpyrone should proceed in two steps. The experimentalists assumed that the $C^{(5)}-O^{(6)}$ bond is broken first and that a cyclobutenecarboxyl zwitterion (Figure 2) is formed. Pirkle and McKendry[31] have carried out their experiments in methanol solution and postulate a decay via a zwitterionic intermediate which is favored under these reaction conditions. Rosenblum and Gatsonis[32] have converted Dewarpyrone with iron tricarbonyl in ether. They suspect that the elimination of CO_2 can occur both in a concerted and stepwise fashion via an intermediate. In the case of stepwise elimination of CO_2 these authors also postulate a zwitterionic cyclobutenecarboxyliron tricarbonyl intermediate. Fitzpatrick et al.[33] could show that a positive charge in the C_4 ring can be stabilized by iron tricarbonyl, whereby a zwitterionic intermediate is preferred. In a matrix these stabilizing effects are missing.

In the present work we want to elucidate the mechanism and to determine the relevant intermediates of the reaction. Special attention is given to valencies which help to follow bond-breaking and bond-forming processes.

2. Method of Calculation

The calculations were performed with the semiempirical MO method SINDO1[34] which is also applicable for the treatment of second-row[35] and third-row elements.[36] The suitability of SINDO1 for photochemical reaction studies was demonstrated repeatedly.[37-42] In the following, we denote the ground state by R_0, the vertically excited singlet states by R_1, R_2, etc., and the triplet states by $^3R_1$, $^3R_2$, etc. Intermediates on the lowest singlet surface are denoted by I_1. Minima including intermediates are characterized by exclusively positive roots of the force constant matrix, whereas transition structures have one negative root. Ground and excited equilibrium structures were optimized by a Newton–Raphson procedure. Bond lengths were optimized within 1% and bond angles and dihedral angles within 1°. Excited state structures were optimized on their respective configuration interaction (CI) surfaces. Further details of the optimization procedure can be found in the furan treatment.[37] The size of configuration interaction was adjusted to guarantee an unambiguous qualitative explanation of the mechanism.

Table 1. Calculated Vertical Excitation Energies (eV) and Oscillator Strengths of α-Pyrone

transition	excitation energy	oscillator strength
$R_0 \rightarrow R_1$	4.38	3.0×10^{-6}
$R_0 \rightarrow R_2$	4.76	1.5×10^{-3}
$R_0 \rightarrow R_3$	4.77	3.0×10^{-3}
$R_0 \rightarrow R_4$	5.45	1.5×10^{-3}
$R_0 \rightarrow R_5$	5.67	1.8×10^{-3}

Table 2. Bond Lengths r (Å), Bond Angles α (deg), and Dihedral Angles ϕ (deg) of Reactant, Intermediate, and Product of the Cyclization of α-Pyrone

state	r_{12}	r_{16}	r_{17}	r_{23}	r_{34}	r_{45}	r_{25}	r_{56}
R_0, C_s	1.530	1.414	1.223	1.362	1.490	1.370	2.819	1.370
I_1	1.504	1.502	1.202	1.435	1.390	1.492	2.800	1.301
P_0	1.586	1.402	1.213	1.549	1.349	1.561	1.601	1.446

state	α_{123}	α_{234}	α_{345}	α_{456}	α_{561}	α_{217}
R_0, C_s	120.1	119.9	118.3	123.7	121.6	128.3
I_1	120.8	120.5	117.1	121.0	118.6	132.9
P_0	117.1	96.1	93.2	118.8	92.5	137.7

state	ϕ_{1234}	ϕ_{2345}	ϕ_{2156}	ϕ_{5617}
R_0, C_s	0.0	0.0	180.0	180.0
I_1	−2.0	2.5	*−148.8*	144.4
P_0	76.3	0.0	180.0	180.0

Table 3. Bond Valencies of Reactant, Intermediate, and Product of the Cyclization of α-Pyrone

state	V_{12}	V_{16}	V_{17}	V_{23}	V_{34}	V_{45}	V_{52}	V_{56}
R_0, C_s	0.996	0.906	1.846	1.803	1.109	1.751	0.076	1.083
R_1, C_s	0.922	0.789	1.440	1.759	1.079	1.748	0.062	1.061
R_2, C_s	0.907	0.803	1.693	1.661	1.150	1.367	0.033	1.069
R_3, C_s	0.916	0.760	1.754	1.502	1.210	1.327	0.008	1.103
I_1	1.024	*0.555*	1.914	1.248	1.567	1.013	0.053	1.381
P_0	0.891	0.964	1.891	0.984	1.941	0.975	0.964	0.953

Energies and other properties of the optimized structures were calculated with a 225 × 225 CI which includes single excitations from the seven highest occupied MOs into all 14 unoccupied MOs. In addition double excitations of type HOMO/HOMO → LUMO/UMO were considered. UMO stands for all unoccupied MOs.

3. Results and Discussion

3.1. Cyclization of α-Pyrone. The photochemical cyclization of α-pyrone starts with an excitation to the S_2 or S_3 state. One can see this from the oscillator strengths which are contained in Table 1 together with the excitation energies. Subsequently, the molecule reaches the S_1 state by internal conversion (IC) and relaxes to I_1. In this process the molecule is distorted to a chair form as can be seen by the dihedral angle ϕ_{2156} in Table 2. In the intermediate I_1 the $C^{(1)}-O^{(6)}$ bond is substantially weakened as indicated by the related bond valence[43,44] V_{16} in Table 3. If this bond is broken,

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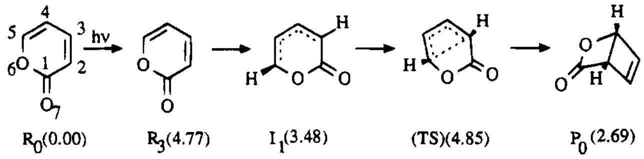

Figure 3. Reaction scheme of the cyclization of α-pyrone.

Table 4. Calculated Vertical Excitation Energies and Oscillator Strengths of Dewarpyrone

transition	excitation energy (eV)	oscillator strengths
$R_0 \rightarrow R_1$	4.49	3.0×10^{-6}
$R_0 \rightarrow R_2$	5.45	5.0×10^{-3}
$R_0 \rightarrow R_3$	5.69	2.9×10^{-2}
$R_0 \rightarrow R_4$	5.96	9.0×10^{-3}
$R_0 \rightarrow R_5$	6.12	3.3×10^{-2}

Table 5. Bond Valencies of Reactant, Intermediate, and Product of the Photofragmentation of Dewarpyrone

state	V_{12}	V_{23}	V_{34}	V_{45}	V_{25}	V_{56}	V_{16}	V_{17}
R_0	0.891	0.984	1.941	0.975	0.964	0.953	0.964	1.891
R_1	*0.777*	0.978	1.920	0.974	0.956	*0.953*	0.824	1.463
R_2	*0.603*	0.944	1.755	0.946	0.924	*0.903*	0.756	1.756
R_3	*0.810*	0.961	1.277	0.898	0.767	*0.941*	0.953	1.888
I_1	0.006	1.361	1.351	1.019	1.030	*0.384*	1.571	2.046
P_0		0.942	1.943	0.942	1.943		1.872	1.872

ω-ketenal is obtained which reacts opposite to α-pyrone (Figure 1) in a fast thermal reaction. The considerably slower and under experimental conditions irreversible reaction is the bicyclic ring closure to Dewarpyrone. Figure 3 shows the reaction scheme and Figure 4 the potential curves of the cyclization reaction of the S_1 surface. All optimized points in the following figures are marked by circles (○). The energies of all states are the result of the complete CI calculation at these optimized geometries. Other points between these optimized points are interpolated. Singlet states are marked by drawn lines (—), triplet states by dashed lines (– – –) and avoided crossings by fine dashed lines (- - -). R stands for reactant, P for product, and I for intermediates.

The main reaction coordinate is the distance r_{25} of the $C^{(2)}-C^{(5)}$ bond. If this bond length is successively shortened under complete optimization of all other coordinates at each step, an avoided crossing is found at $r_{25} = 2.1$ Å with a possibility for IC to the ground state. On the S_0 surface a reaction to either reactant or product is possible. The high barrier (Figure 3) furnishes an explanation for the long irradiation in the experiments, necessary to convert α-pyrone into Dewarpyrone photochemically quantitatively. From our own calculations we find that a cyclization via ω-ketenal is not possible because of a barrier of a few electron volts. This means good agreement with experiment.[24] A reaction in the T_1 state is less favorable because the triplet surface does not have a minimum close to the avoided crossing of the singlet state S_1 and S_0.

Table 6. Bond Lengths r (Å), Bond Angles α (deg), and Dihedral Angles ϕ (deg) of Reactant, Intermediate, and Product of the Photofragmentation of Dewarpyrone

state	r_{12}	r_{23}	r_{34}	r_{45}	r_{25}	r_{56}	r_{16}	r_{17}
R_0	1.586	1.549	1.349	1.561	1.601	1.446	1.402	1.213
I_1	3.385	1.411	1.398	1.524	1.482	1.614	1.243	1.176
I_2	1.614	1.495	1.376	1.537	1.643	1.416	1.397	1.218
P_0		1.578	1.339	1.578	1.339		1.190	1.190

state	α_{123}	α_{234}	α_{345}	α_{456}	α_{561}	α_{217}
R_0	117.1	96.1	93.2	118.8	92.5	137.7
I_1	110.7	94.4	88.9	113.3	144.4	120.5
I_2	119.5	92.8	97.1	121.1	90.7	129.4
P_0	90.0	90.0	90.0			

state	ϕ_{1234}	ϕ_{2345}	ϕ_{2156}	ϕ_{5617}
R_0	76.3	0.0	180.0	180.0
I_1	49.3	−1.0	170.2	−7.9
I_2	75.9	−3.6	175.1	−169.6
P_0		0.0		

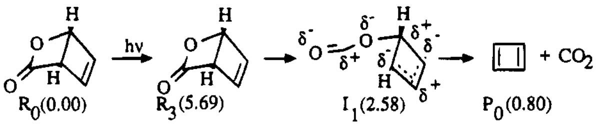

Figure 5. Reaction scheme of stepwise photofragmentation of Dewarpyrone.

3.2. Photofragmentation of Dewarpyrone. 3.2.1. Stepwise Bond Breaking. After 15 h of irradiation and quantitative conversion of α-pyrone into Dewarpyrone, the Pyrex filter[4] was removed so that new states above 4.3 eV could be reached. Table 4 contains the calculated excitation energies and oscillator strengths of Dewarpyrone. The excitation is here primarily into the S_3 state

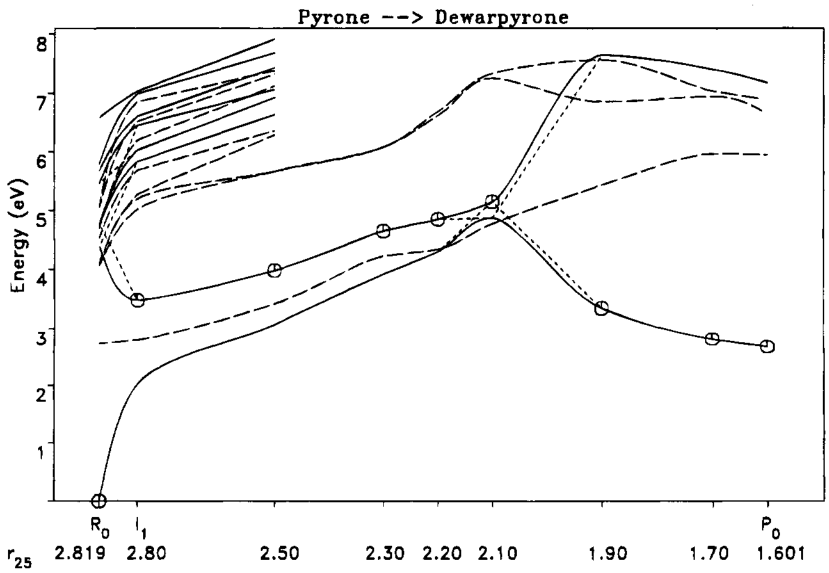

Figure 4. Potential curve for cyclization of α-pyrone to Dewarpyrone in the S_1 state; points of optimized geometry (○).

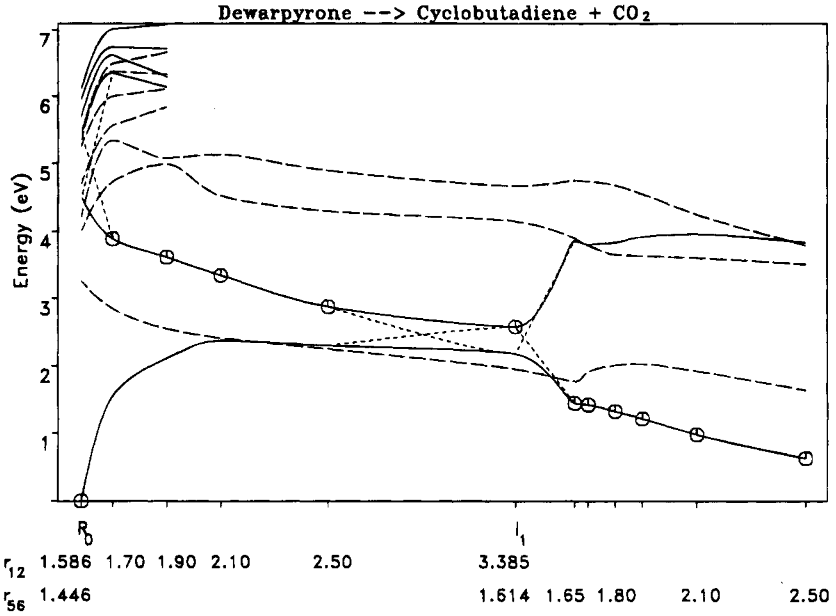

Figure 6. Potential curve for stepwise photofragmentation of Dewarpyrone; points of optimized geometry (O).

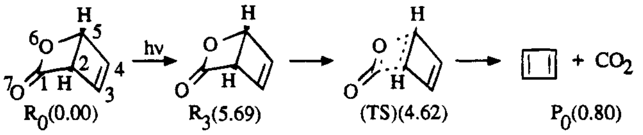

Figure 7. Reaction scheme of simultaneous photofragmentation of Dewarpyrone.

as can be seen from the oscillator strengths. From Table 5 it is apparent that the $C^{(1)}-C^{(2)}$ bond is substantially weakened in the first three excited singlet states. In particular, in the S_2 state which is mainly represented by a HOMO–LUMO excitation, there is a valence reduction of almost 0.3 compared to the ground state. An avoided crossing leads to the S_1 state via IC. Here the bond breaking of the $C^{(1)}-C^{(2)}$ bond and consequently relaxation to I_1 occurs. The reaction scheme is presented in Figure 5 and the reaction pathway in Figure 6. The reaction coordinate is r_{12} between R_0 and I_1 and r_{56} from I_1. The points are generated by complete optimization except for the reaction coordinate. I_1 is completely optimized. One can see that Dewarpyrone relaxes on the S_1 surface to I_1 without a barrier. Here IC to the ground state can occur, favored by an avoided crossing. In I_1 the $C^{(5)}-O^{(6)}$ bond is already very weak (Table 5). In the ground state it is now broken, and cyclobutadiene and CO_2 are formed. The geometries of all optimized structures are listed in Table 6. Since there is no minimum on the S_1 surface in the Franck–Condon zone, a transition to the T_1 state is unlikely. A reaction on the T_1 surface would lead to cyclobutadiene like on the S_1 surface. This is apparent from Figure 6, since the T_1 curve is parallel to the S_1 curve. Our calculations show that the zwitterionic intermediate (Figure 2) proposed by the experimentalists is not stable on the S_1 surface. The zwitterionic character is determined by our own method.[45]

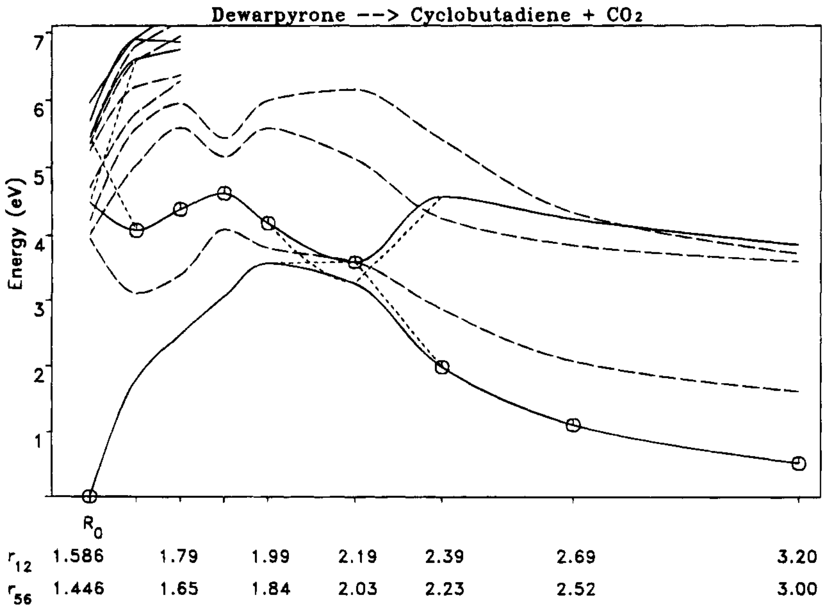

Figure 8. Potential curve for simultaneous photofragmentation of Dewarpyrone; points of optimized geometry (O).

3.2.2. Simultaneous Bond Breaking. Since the intermediate I_1 which occurs during a stepwise bond breaking process shows an extremely weak $C^{(5)}-O^{(6)}$ bond, we asked the question whether a simultaneous bond breaking as discussed by experimentalists[32] is possible. Figure 7 shows the reaction scheme and Figure 8 the related energy profile. The reaction coordinates are bond lengths r_{12} and r_{56}. We used a linear interpolation to generate starting geometries between the reactant and the two isolated fragments cyclobutadiene and CO_2. The fragments were placed apart at a distance $r_{12} = 3.2$ Å and $r_{56} = 3.0$ Å which is sufficient for negligible interaction. For each step of the interpolation procedure we kept r_{12} and r_{56} fixed and optimized all other coordinates. This means the pathway is not synchronous. In the subsequent interpolation all coordinates except r_{12} and r_{56} were optimized. At $r_{12} = 2.19$ Å and $r_{56} = 2.03$ Å IC to the ground state can occur because of avoided crossing. The barrier for simultaneous fragmentation is on the S_1 state. Since the reactions take place in experiment in an argon matrix at 8 K, vibrational relaxation can occur very fast. Since the stepwise elimination shows no barrier in contrast to the simultaneous elimination, the fast vibrational relaxation favors the former pathway.

4. Conclusion

The calculated SINDO1 results are partly at variance with the conclusions from experiments. The cyclization of α-pyrone is found to be direct, in agreement with experiment.[4] The formation of cyclobutadiene occurs via a stepwise mechanism. Here the $C^{(1)}-C^{(2)}$ bond, not the $C^{(5)}-O^{(6)}$ bond as assumed by experimentalists,[31,32] is broken in the first step. We did not find the ionic structures (Figure 2) postulated by the experimentalists to be stable. Furthermore, not one of the vertically excited states R_1, R_2, R_3 of Dewarpyrone shows a significant valence reduction for the $C^{(5)}-O^{(6)}$ bond which would be indicative for a bond breaking process. Therefore we conclude that the photoframentation of Dewarpyrone to cyclobutadiene and CO_2 is stepwise and that the $C^{(1)}-C^{(2)}$ bond is broken before the $C^{(5)}-O^{(6)}$ bond. The first step occurs in the first excited singlet state, since there is no barrier with respect to $C^{(1)}-C^{(2)}$ bond breaking. A simultaneous fragmentation has a barrier of 0.55 eV and therefore can play only a minor role.

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