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Decarbonylation Path of 5-Phenyl-2,3-dihydrofuran-2,3-dione: *Ab Initio* Calculations

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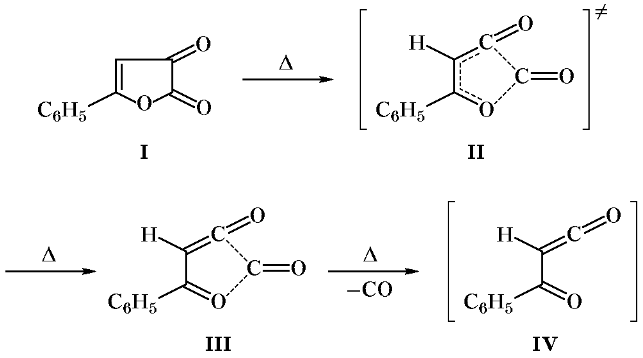
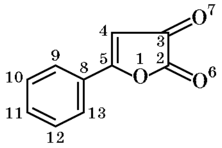
Abstract—The gradient path of decarbonylation of 5-phenyl-2,3-dihydrofuran-2,3-dione in the gas phase was calculated *ab initio* [RHF/6-31G(*d*)]. It includes formation of a planar transition state which is less polar than the initial compound.

Thermolysis of 5-aryl-2,3-dihydrofuran-2,3-diones is a convenient method for generation of aroylketenes [1, 2] which are key intermediates in the synthesis of various acyclic and heterocyclic compounds [3, 4]. Andreichikov *et al.* [5] previously studied the kinetics of decarbonylation of 5-aryl-2,3-dihydrofuran-2,3-diones by volumetry. In the present communication we report the results of a more detailed quantum-chemical study of the mechanism of this reaction. In particular, we calculated the reaction paths, analyzed the geometric parameters and electron density distribution in the initial molecule and transition state, and calculated energy parameters of the process. Nonempirical calculations were performed in terms of the restricted Hartree–Fock procedure (RHF) with the 6-31G(*d*) basis set [6] using GAUSSIAN 94W software [7].

According to the calculations, decarbonylation of 5-phenyl-2,3-dihydrofuran-2,3-dione involves formation of planar cyclic transition state **II**, weak molecular complex **III**, and benzoylketene (**IV**) as final product:



Structures **I**, **III**, and **IV** correspond to energy minima on the potential energy surface (PES), i.e., to the critical points where λ = 0 (λ is the number of negative Hessian eigenvalues [8]). The principal geometric parameters of the initial compound, 5-phenyl-2,3-dihydrofuran-2,3-dione (**I**), are given in Table 1. The dihydrofuran ring in molecule **I** is almost planar, as follows from the dihedral angles $C^4C^3C^2O^1$, $C^5O^1C^2C^3$, and $C^5C^4C^3C^2$, which are equal to 0 deg, and $C^4C^3C^2O^6$, $O^7S^3C^2O^1$, and $O^6C^2O^1C^5$, which are equal to 180 deg.



The benzene ring is located almost in the same plane as the heteroring: the dihedral angles $C^9C^8C^5C^4$, $C^9C^8C^5O^1$, and $C^{13}C^8C^5O^1$ are equal to 0, 180, and 0.3 deg, respectively. According to the PPP and MNDO calculations of molecule **I**, performed in [9, 10], the benzene ring and the heteroring form an angle of ~70 deg. The C^2-C^3 bond (1.542 Å) in the heterocyclic fragment is considerably longer than the standard bond between two *sp*^{2}-hybridized carbon atoms (1.47 Å), while the $C^2=O^6$ bond is slightly shorter than $C^3=O^7$. The bond lengths and bond angles in the benzene ring have their usual values, and no comment is required. For comparison, Table 1 also contains the calculated data for unsubstituted 2,3-dihydrofuran-2,3-dione (**Ia**). On the whole, the

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Table 1. Calculated principal geometric parameters of structures **I**, **Ia**, **II**, **IIa**, and **III** and X-ray diffraction data for 5-*p*-chlorophenyl-4-methoxycarbonyl-2,3-dihydrofuran-2,3-dione (**V**)

Parameter	**I**	**Ia**	**V**	**II**	**IIa**	**III**
			Bond lengths *d*, Å			
O^1-C^2	1.361	1.362	1.395	2.019	2.012	3.223
O^1-C^5	1.368	1.360	1.398	1.235	1.229	1.204
C^2-C^3	1.542	1.546	1.524	1.812	1.784	3.773
C^3-C^4	1.452	1.463	1.460	1.366	1.372	1.326
C^4-C^5	1.339	1.326	1.368	1.426	1.411	1.467
C^2-O^6	1.168	1.168	1.182	1.114	1.114	1.114
C^3-O^7	1.185	1.182	1.215	1.168	1.168	1.132
			Bond angles ω, deg			
$O^1C^2C^3$	106.3	106.4	106.3	91.6	92.9	44.4
$C^2C^3C^4$	103.6	103.5	105.3	104.4	104.5	101.3
$C^3C^4C^5$	107.4	106.2	107.0	120.3	118.5	117.3
$C^4C^5O^1$	113.6	115.7	112.7	120.9	123.8	120.5
$O^6C^2O^1$	123.4	123.7	121.7	112.3	112.5	104.8
$C^5O^1C^2$	109.2	108.2	108.7	102.7	100.3	117.0
$O^7C^3C^2$	123.9	124.1	121.5	110.0	110.3	79.9

Table 2. Total charges (a.u.) on atoms in structures **I**, **Ia**, **II**, **IIa**, and **III**

Structure	O^1	C^2	C^3	C^4	C^5	O^6	O^7
I	–0.662	0.761	0.423	–0.347	0.455	–0.467	–0.505
Ia	–0.596	0.745	0.428	–0.342	0.188	–0.459	–0.481
II	–0.704	0.553	0.587	–0.480	0.609	–0.321	–0.521
IIa	–0.640	0.557	0.592	–0.489	0.364	–0.511	–0.311
III	–0.597	0.274	0.621	–0.506	0.598	–0.277	–0.388

calculated geometric parameters of molecules **I** and **Ia** are consistent with those found experimentally for 5-*p*-chlorophenyl-4-methoxycarbonyl-2,3-dihydrofuran-2,3-dione (**V**) by the X-ray diffraction method [11] (Table 1). According to the calculations, significant positive charges in both molecules are located on the C^2, C^3, and C^5 atoms of the dihydrofuran ring (Table 2). Among these, the most electron-deficient is C^2; therefore, nucleophilic attack by various reagents is directed mainly just at that carbon atom [12, 13]. Molecules **I** and **Ia** are located in the *xy* plane, and the *z* axis is orthogonal to it. The frontier molecular orbitals of **I** and **Ia** are contributed mainly by the carbon and oxygen p_z-orbitals. The total populations of the valence p_z-orbitals of C^4 in molecules **I** and **Ia** (Table 3) are considerably greater than those for C^5; presumably, this is the result of electrostatic effect of the oxygen atom O^1, which possesses a considerable negative charge.

Transition state **II** was localized using the Berni algorithm by a single negative Hessian eigenvalue ($\lambda = 1$). The geometric, electronic, and energy parameters of structure **II** are given in Tables 1–4. The heterocyclic fragment in transition state **II** remains planar, and the O^6 atom lies almost in the plane of the heteroring: the dihedral angles $C^4C^3C^2O^1$ and $C^5C^4C^3C^2$ are 0.9 and –0.3 deg, respectively. The phenyl group in position *5* is turned through an angle of ~15 deg with respect to the dihydrofuran ring plane. The C^4-C^5, O^1-C^2, and C^2-C^3 bonds in **II** are slightly longer than the corresponding bonds in

Table 3. Total populations of the valence p_z-orbitals of carbon and oxygen atoms in structures **I**, **Ia**, **II**, **IIa**, and **III**, calculated by the RHF/6-31G(d) method

Structure	O^1	C^2	C^3	C^4	C^5	O^6	O^7
I	1.815	0.680	0.723	1.169	0.826	1.364	1.346
Ia	1.808	0.684	0.72	1.127	0.843	1.356	1.325
II	1.606	0.558	0.774	1.370	0.627	1.424	1.550
IIa	1.588	0.562	0.768	1.372	0.624	1.415	1.527
III	1.437	0.523	0.756	1.359	0.678	1.494	1.635

Table 4. Total energies E_{tot} (kcal/mol), zero-point energies E_{ZPE} (kcal/mol), energies with correction for zero-point energy E (kcal/mol), dipole moments μ (D), entropies S_{tot} (cal mol^{-1} K^{-1}); Gibbs energies G (kcal/mol), and enthalpies H (kcal/mol, 80°C) of structures **I**, **Ia**, **II**, **IIa**, **III**, and **IV**

Structure	$-E_{tot}$	E_{ZPE}	$-E$	μ	S_{tot}	$-G$	$-H$
I	380746.874	82.693	380664.187	7.11	109.026	380693.391	380654.805
Ia	236694.111	34.086	236660.018	5.16	78.499	236682.546	236654.835
II	380712.222	79.907	380632.322	3.48	113.550	380662.405	380662.322
IIa	23660.822	31.156	236629.666	1.95	83.252	236653.204	236623.817
III	380745.186	78.621	380666.565	4.39	136.584	380702.942	380654.724
IV	309997.192	75.201	309924.790	2.49	103.861	309951.827	309916.274
CO	70744.091	3.112	70740.978	0.26	48.328	70755.580	70738.518

molecule **I** (Table 1). In going from structure **I** to **II** the $C^3C^2O^1$ bond angle considerably decreases, while the $C^3C^4C^5$ and $C^4C^5O^1$ angles increase. Transition state **IIa**, which was localized for unsubstituted 2,3-dihydrofuran-2,3-dione by analogy with **II** is also planar. The calculated dipole moments indicate that structures **II** and **IIa** are less polar than the initial molecules (Table 4); this is consistent with the conclusions drawn from analysis of the rate constants in polar and nonpolar solvents [5]. The formation of transition state **II** is accompanied by decrease of the populations of p_z-orbitals of O^1, C^2, and C^5 and increase of the populations of p_z-orbitals of C^4, O^6, and O^7. The same tendency is observed in going from **Ia** to **IIa** (Table 3).

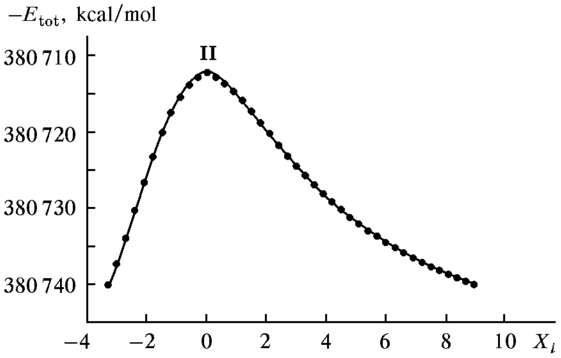


Fig. 1. Decarbonylation path of 5-phenyl-2,3-dihydrofuran-2,3-dione, according to the RHF/6-31G(*d*) calculations.

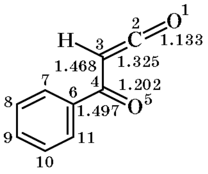
The gradient path of decarbonylation of compound **I** (Fig. 1) was determined by the fastest descend technique along both positive and negative directions of the normalized transition vector starting from the saddle point (**II**, $\lambda = 1$). The initial direction was set by a shift (3/10 of the transition vector) along the transition vector of the corresponding structure. The geometric parameters were optimized in each point in such a way that a segment of the reaction path between every pair of contiguous points was described by a circular arc and the gradient at the final point of the arc was a tangent to the reaction path.

Judging by the structure of transition state **II** (Table 1) and the calculated reaction path, concerted rupture of the $O-C^2$ and C^2-C^3 bonds occurs. In the initial part of the reaction path, prior to formation of transition state **II**, dissociation of the O^1-C^2 bond outpaces dissociation of the C^2-C^3 bond; but in the subsequent part, the latter process becomes faster.

Thermodynamic analysis of stationary points on the PES for the reaction under study at 80°C showed (Table 4) that the energy barrier (with correction for zero-point energy) is ~31.8 kcal/mol. The enthalpy of activation $\Delta H^{\neq}$ is ~32.5 kcal/mol. The entropy of activation $\Delta S^{\neq}$, including the contributions of specific degrees of freedom of translational, rotational, and vibrational motions, is ~4.5 cal mol^{-1} K^{-1}. The Gibbs energy of activation $\Delta G^{\neq}$ is ~30.9 kcal/mol; this value somewhat exceeds those found experimentally from kinetic data [5]. The experimental entropy of activation has a small negative value which suggests a concerted mechanism of decomposition; the calculated value is also small but positive. On the whole, the calculated parameters approach the experimental values for decarbonylation of 5-aryl-4-halo-2,3-dihydrofuran-2,3-diones [14]. The calculated activation parameters of thermal decarbonylation of 2,3-dihydrofuran-2,3-dione having no substituent in position *5* (Table 4) are similar to those found for 5-phenyl-2,3-dihydrofuran-2,3-dione: energy barrier ~31.0 kcal/mol, $\Delta H^{\neq}$ ~30.4 kcal/mol, $\Delta S^{\neq}$ ~4.7 cal mol^{-1} K^{-1}, and $\Delta G^{\neq}$ ~29.3 kcal/mol. Hence the 5-phenyl substituent insignificantly affects the transition state structure and the reaction path.

While searching for local minimum **III**, the final point of the reaction path was used to initialize the geometric parameters. The calculation showed that structure **III** has almost completed benzoylketene moiety. The $O^1C^5C^4C^3$ fragment is virtually planar (the $O^1C^5C^4C^3$ angle is –2.9 deg), and the departing carbonyl group $C^2{=}O^6$ deviates from the plane of the heteroring: $\angle O^6C^2O^1C^5$ –203.4, $\angle C^4C^3C^2O^1$ 42.0, $\angle C^2O^1C^5C^4$ 60.4 deg. The 5-phenyl group is turned through an angle of ~15 deg relative to the heteroring plane. The bond angle $O^7C^3C^4$ is 178.6 deg; i.e., it is close to the CCO angle in benzoylketene (181.9 deg). As follows from the calculation data (Table 3), the p_z-orbital population of O^1 in complex **III** is lower than in initial molecule **I** and transition complex **II**, and the p_z-orbital populations of C^3 and C^4 in **III** are slightly lower than in **II**. In keeping with the calculated dipole moments, structure **III** is more polar than **II** (Table 4).

The O^1, C^2, C^3, and C^4 atoms in the molecule of benzoylketene (**IV**) (Fig. 2) lie almost in one plane. The bond angles in the acylketene moiety are as follows: $C^2C^3C^4$ 117.1, $C^3C^4O^5$ 120.4, and $C^3C^4C^6$ 118.6 deg. The benzene ring plane and the $O^1C^2C^3C^4$ fragment form an angle of ~15 deg (the dihedral angles $C^7C^6C^4C^3$ and $C^{11}C^6C^4C^3$ are 15.6 and –165.3 deg, respectively. The calculations show the possibility for rotation of the ketene moiety (C=C=O) about the C^3-C^4 bond. Isomeric structures with *trans* and *cis* arrangement of the benzene ring and the $C^3{=}C^2{=}O^1$ group have similar energies: –309999.984 and –309997.160 kcal/mol (ΔE = 2.79 kcal/mol).



IV

Fig. 2. Principal bond lengths (Å) in the molecule of benzoylketene (**IV**), calculated by the RHF/6-31G(*d*) method. Charges on atoms, a.u.: O^1 –0.386, C^2 0.615, C^3 –0.506, C^4 0.595, O^5 –0.589.

Thus, according to quantum-chemical calculations, thermal decarbonylation of 5-phenyl-2,3-dihydrofuran-2,3-dione involves planar cyclic transition state which is less polar than the initial compound. The calculations predict concerted mechanism of bond dissociation in the course of elimination of carbon(II) oxide molecule.

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