Ab initio study of the Wolff rearrangement of C_6H_4O intermediate in the gas phase

Yu. A. Borisov,[a]* B. C. Garrett,[b] and D. Feller[b]

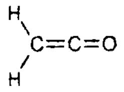
[a]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: yabor@ineos.ac.ru
[b]Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratories,*
906 Battelle Boulevard, Richland, Washington 99352, USA.
Fax: +1 (509) 375 6631. E-mail: bruce.garrett@pnl.gov; d3e102@emsl.pnl.gov

Ab initio calculations of the geometry and reactivity of 1,2-ketocarbene C_6H_4O as an intermediate in organic reactions were performed using the second-order Møller—Plesset (MP2) perturbation theory in the 6-311G* basis set. Only the singlet state of the intermediate was considered. An oxirene-like structure (**6**) with a six-membered ring and a ketene-like structure (**5**) with a five-membered ring were localized on the potential energy surface. Attempts to locate a quinone type structure characteristic of aliphatic ketocarbenes failed. The energy of structure **5** is ~70 kcal mol^{-1} lower than that of structure **6**. Harmonic frequencies and intensities of normal vibrations in the IR spectra of **6** and **5** were calculated. The activation energy of the Wolff rearrangement **6** → **5** was estimated at 12.5 kcal mol^{-1}. The geometry of the transition state of this reaction resembles the quinone-like structure.

Key words: *ab initio* quantum-chemical calculations, Møller-Plesset perturbation theory, 1,2-ketocarbene C_6H_4O, intermediates in organic reactions, oxirene-like structure, ketene-like structure, molecular and electronic structure, frequencies of normal vibrations, Wolff rearrangement, activation energy.

High-temperature production and conversion of polychlorophenol derivatives is the main source of environmental contamination by dioxin-related compounds. Studies of the thermolysis of sodium *ortho*-halophenoxides[1—3] suggest that chlorine derivatives of 1,2-ketocarbene, $C_6H_nO_{4-n}$, are highly reactive intermediates and serve as precursors of dioxin-related compounds. Previously,[4] the electronic structure and reactivity of $C_6H_nO_{4-n}$ compounds were studied by the AM1 semiempirical method and it was shown that dimerization of polychlorinated 1,2-ketocarbenes proceeds with a very low activation barrier to formation of polychlorinated dioxins.

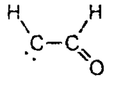
Intermediacy of ketocarbenes in organic reactions has been thoroughly studied by experimental and theoretical methods. The available experimental data include IR, UV, and matrix-isolated ESR spectra.[5] Ketocarbenes are of major interest as intermediates in the Wolff rearrangement.[6] Theoretical calculations[7—11] were performed only for the simplest alkylketocarbene, C_2H_2O, and gave the following basic structures of the intermediates: ketene (**1**), hydroxyacetylene (**2**), formylmethylene (**3**), and oxirene structure (**4**).



1

$H-C\equiv C-O-H$

2



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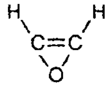

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The calculated relative stability of the structures is as follows: **1** > **2** > **3** > **4**. Selected areas of the potential energy surface (PES) for the C_2H_2O molecule, corresponding to oxirene, formylmethylene, and ketene structures, have been studied by *ab initio* methods.[12] The major conclusion drawn in this study is that the energy barrier between the formylmethylene and oxirene structures (**3** and **4**, respectively) is very low and the PES linking the minima corresponding to these two types of structures is extremely flat. At the same time, the barriers between the formylmethylene or oxirene structures and the ketene structure are much higher.

Although unsaturated 1,2-ketocarbenes of the $C_6H_nO_{4-n}$ type have been reported as intermediates of organic reactions (see Refs. 13 and 14), no information on the studies of their electronic structures and reactivities is available. The Wolff rearrangement in 6-diazo-2,4-cyclohexadienone irradiated by light with λ > 350 nm

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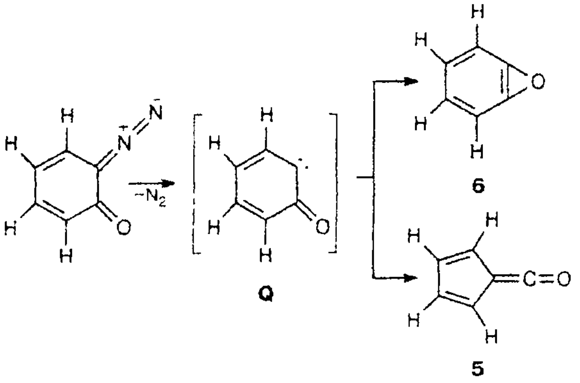
in an argon atmosphere at 15 K was reported.[13] The authors of this study suggested that 6-diazo-2,4-cyclohexadienone is decomposed under irradiation with the formation of the N_2 molecule (Scheme 1). The newly formed 6-oxo-2,4-cyclohexadienylidene (**Q**) undergoes the Wolff rearrangement to give the corresponding ketene.

Scheme 1



To establish the energy difference between the oxirene-like (**6**) and ketene-like (**5**) forms of the intermediate and to find the transition states of the rearrangement of one form into another, in this paper we studied the molecular and electronic structure of the simplest unsaturated 1,2-ketocarbene, C_6H_4O, and its isomers in the singlet state by the MP2 method.

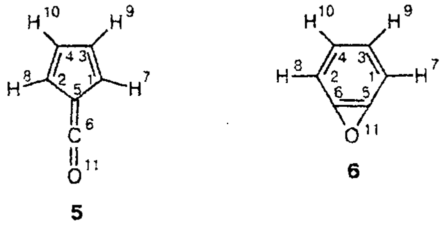
Calculation procedure

The geometries of all systems were optimized at the second-order Møller—Plesset (MP2) level of perturbation theory[15] using the 6-311G* basis set. No symmetry restrictions were imposed. We identified approximate transition states using the quasi-Newtonian linear synchronous transition (LST) and quadratic synchronous transition (QST3) methods.[16] Then the structures of the transition state were refined by the gradient method, the frequencies of vibrations at the saddle point of the PES were analyzed, and correlation between the results obtained and the reaction studied was proved by the intrinsic reaction coordinate (IRC) method. All calculations were performed using the GAUSSIAN-92,[17] GAUSSIAN-94,[18] and GAMESS[19] program packages on CRAY C-90 (National Energy Research Supercomputer Center, Livermore, USA), CRAY J-90 (National Energy Research Supercomputer Center, Berkeley, USA), HP-9000/735 (Pacific Northwest National Laboratories, Richland, USA), and DEC AXP 3000-400 workstations (Institute of Organoelement Compounds of the Russian Academy of Sciences, Moscow, Russian Federation).

Results and Discussion

To investigate the stability of the structures of the analogs of aliphatic ketocarbenes **1**, **2**, and **4**, we first calculated the unsaturated 1,2-ketocarbene C_6H_4O. According to calculations with full geometry optimization, there are only two types of stable structures (**5** and **6**, Scheme 2).

Scheme 2



No minimum corresponding to the quinone type (**Q**) structure of C_6H_4O was localized on the PES. The optimized geometric parameters, total energies, and dipole moments of structures **5** and **6** calculated by the MP2/6-311G* method are listed in Table 1 (the numbering of atoms is shown in Scheme 2).

The oxirene-like structure **6** of 1,2-ketocarbene was studied previously at the HF/TZ2P(f,d) level of theory[20] and it was shown that this intermediate has a planar structure. However, according to our MP2 calculations, the oxirene-like structure is nonplanar. The C(1)—C(5)—C(6)—C(11) dihedral angle differs by 5.1° from 180°. The six-membered ring, also nonplanar, is folded along the C(1)—C(2) bond. The C(6)—C(2)—C(4)—C(3) dihedral angle is equal to 2.7°. The ketene-like form of the intermediate has a planar structure.

No experimental data on the geometry of unsaturated 1,2-ketocarbene in the gas phase or in the condensed phase are available. Therefore, the results of our calculations for structure **5** can be compared only with

Table 1. Bond lengths, bond angles, total energies without and with zero-point energy corrections (E and $E + ZPE$, respectively), and dipole moments (μ) of intermediates **6** and **5** and the transition state (TS) of the Wolff rearrangement of C_6H_4O

Parameter	6	5	TS
Bond length/Å			
C(1)—C(3)	1.440	1.378	1.431
C(1)—C(5)	1.363	1.452	1.361
C(2)—C(4)	1.441	1.378	1.397
C(2)—C(5)	2.413	1.453	2.406
C(2)—C(6)	1.363	2.485	1.416
C(3)—C(4)	1.398	1.444	1.418
C(5)—C(6)	1.323	1.340	1.359
C(5)—C(11)	1.473	2.500	2.009
C(6)—C(11)	1.473	1.160	1.303
Bond angle/deg			
C(1)—C(5)—C(6)	127.74	125.64	127.58
C(5)—C(6)—C(2)	127.83	28.40	120.23
C(5)—C(6)—C(11)	63.29	180.00	97.96
C(6)—C(2)—C(4)	108.50	132.12	112.08
C(2)—C(4)—C(3)	123.62	109.48	122.32
C(4)—C(3)—C(1)	123.63	109.44	123.35
C(3)—C(1)—C(5)	108.56	106.20	105.25
E/au	−305.2736	−305.3844	−305.2536
$E + ZPE$/au	−305.1956	−305.3056	−305.1760
μ/D	2.497	0.317	5.262

the experimental data for the simplest ketene $H_2C=C=O$.[21,22] The experimental C=O bond length (1.16 Å) is in good agreement with the calculated value for the ketene-like structure **5**. The experimental C=C bond length (1.314 Å) for $H_2C=C=O$ is comparable with the value of 1.339 Å obtained in our calculations. The energy difference between isomers **6** and **5** is equal to 69.5 kcal mol^{-1} (69.0 kcal mol^{-1} with inclusion of zero-point vibrational energy correction). Structure **5** is more stable than structure **6**.

The calculated Mulliken effective atomic charges for structures **5** and **6** of the unsaturated 1,2-ketocarbene are listed in Table 2, from which it follows that the electron density distribution in these structures is strongly different. The oxirene-like structure **6** is characterized by the rather large negative charge on the O atom and, correspondingly, by the large positive total charge on the six-membered ring (+0.45 e). The effective charge on the O atom in the ketene-like structure **5** is appreciably smaller and the five-membered ring has a negative charge (−0.21 e). As follows from our calculations, the oxirene-like structure **6** has a larger dipole moment than the ketene-like structure. Therefore, intermediate **6** is expected to have a higher solvation energy in the polar solvent, thus decreasing the energy difference between isomers **5** and **6**. We also calculated the frequencies of normal vibrations and intensities of transitions in the IR spectra of **5** and **6** (Table 3). The complete set of calculated data is of considerable interest for interpreting experimental spectra of different intermediates. We will dwell here only on several most characteristic absorption bands. For the oxirene-like structure **6**, the absorption band at 1140 cm^{-1} corresponds to the C—O vibration, while the band at 1906 cm^{-1} corresponds to the C=C vibration in the C=C—O triad. The calculated frequencies are close to the oxirene (C_2H_2O) frequencies obtained from *ab initio* calculations (1134 and 1866 cm^{-1}, respectively).[11] Characteristic of the ketene-like structure **5** are the frequencies of 2224 and 1491 cm^{-1}, which can be compared with the experimental values of 2150 cm^{-1} and 1120 cm^{-1} found for ketenes (see, *e.g.*, Ref. 23).

Table 2. Charges (q/e) on the atoms in intermediates **6** and **5** and TS of the Wolff rearrangement of C_6H_4O

Atom	6	5	TS
C(1)	−0.216	−0.257	−0.313
C(2)	−0.216	−0.257	−0.184
C(3)	−0.226	−0.221	−0.145
C(4)	−0.226	−0.221	−0.287
C(5)	0.197	−0.146	0.067
C(6)	0.197	0.499	0.378
H(7)	0.243	0.227	0.250
H(8)	0.243	0.227	0.263
H(9)	0.227	0.218	0.245
H(10)	0.227	0.218	0.243
O(11)	−0.450	−0.288	−0.516

Since the **6** → **5** transition is the Wolff rearrangement, we considered its energetics in more detail and calculated the structure of the transition state of the rearrangement. Since this rearrangement occurs as a cooperative motion of a large number of atoms, it is difficult to distinguish the main reaction coordinates in intermediates **6** and **5**. For this reason, we used the quasi-Newtonian linear synchronous transition method,[16] which appeared to be very efficient for determining the transition state of this reaction. The zeroth- and first-order approximations to the structure of the transition state were obtained by the linear and quadratic synchronous transition (LST [17] and QST3,[18] respectively) methods. Then, the structure of the transition state of the **6** → **5** rearrangement was refined by the gradient method with checking of the frequencies of normal vibrations at the saddle point. It was shown that only one imaginary eigenvalue of the Hess matrix corresponds to the calculated transition state (see Table 3).

The geometric parameters, total energy without and with inclusion of a zero-point vibrational energy correction, and dipole moment of the transition state of the gas-phase isomerization reaction **6** → **5** are listed in Table 1. It should be noted that the transition state of the Wolff rearrangement **6** → **5** has a nonplanar structure which resembles the quinone structure, which is characterized as a stable intermediate in the case of aliphatic ketocarbenes (**1**—**4**). From the data in Table 1 it also follows that the activation energy of isomerization calculated without and with inclusion of a zero-point vibrational energy correction is 12.5 and 12.3 kcal mol^{-1}, respectively. The Mulliken effective atomic charges calculated for the transition state (see Table 2) show that it is much more polarized as compared to the oxirene-like structure **6** of the intermediate.

Correspondence between the results obtained and the transition state of the **6** → **5** isomerization reaction studied was proved by additional calculations by the IRC method in the framework of the MP2/6-311G* approach. The dependence of the total energy on the reaction coordinate (R_c) in the vicinity of the point $R_c = 0$ calculated by the IRC method is shown in Fig. 1 ($R_c = 0$ corresponds to the saddle point on the PES, $R_c < 0$ corresponds to the initial state **6**, and $R_c > 0$ corresponds to the final state **5**). The analysis of structural changes along the reaction coordinate shows that the assignment of the transition state to the reaction in question is correct. In fact, a smooth conversion of structure **6** into structure **5** occurs on going from negative to positive R_c values. Structure **6**, the transition state, and intermediate forms are nonplanar. The intermediate becomes planar near the minimum on the PES corresponding to the ketene-like structure **5**.

Our calculations have shown that, in contrast to aliphatic ketocarbenes, the unsaturated 1,2-ketocarbene C_6H_4O has only two stable structures, namely, the oxirene-like (**6**) and ketene-like (**5**) structures. The energy difference between isomers **6** and **5** is 69.5 kcal mol^{-1} (69.0 kcal mol^{-1} with inclusion of zero-

Table 3. Calculated frequencies of normal vibrations (ν_i), intensities of transitions in IR spectra (I_i), and types of vibrations*

6			**5**			**TS**	
ν_i/cm^{-1}	I_i/km mol^{-1}	Vibration type	ν_i/cm^{-1}	I_i/km mol^{-1}	Vibration type	ν_i/cm^{-1}	I_i/km mol^{-1}
3255	0.44	CH$'$ (s), CH$''$ (s)	3272	4.97	CH$'$ (s), CH$''$ (s)	3243	4.62
3254	9.10	CH$'$ (as), CH$''$ (as)	3268	6.37	CH$'$ (as), CH$''$ (as)	3230	5.29
3225	9.99	CH$'$ (s), CH$''$ (s)	3250	2.97	HCC$'_i$ (s), HCC$''_i$ (as)	3210	6.16
3209	0.86	CH$'$ (as), CH$''$ (as)	3238	3.18	HCC$'_i$ (s), HCC$''_i$ (as)	3187	3.50
1906	0.13	CC$'$ (s)	2224	1047.10	CO	1720	32.30
1530	0.66	CC$'$ (as)	1547	0.04	CC$'''$ (as), HCC$'_i$ (as), HCC$''_i$ (as)	1523	24.49
1504	5.96	CC$''$	1491	81.37	C=C, C=O, HCC$'_i$ (s), HCC$''_i$ (s)	1470	3.33
1451	4.68	CC$'''$	1435	45.64	CC$'''$ (s), HCC$'_i$ (s), HCC$'_i$ (s)	1425	0.91
1391	35.11	CC$''$	1353	18.10	HCC$'_i$ (s), HCC$''_i$ (s)	1390	16.74
1273	0.70	HCC$'_i$ (as), HCC$''_i$ (as)	1334	3.49	HCC$'_i$ (as), HCC$''_i$ (as)	1316	2.44
1191	2.65	HCC$'_i$ (s), HCC$''_i$ (s)	1241	0.06	HCC$'_i$ (s), HCC$''_i$ (s)	1218	3.21
1140	18.56	O—(C—C), HCC$'_i$ (s)	1102	10.92	HCC$'_i$ (as), HCC$''_i$ (as)	1176	4.85
1087	3.08	HCC$'_i$ (as), HCC$''_i$ (as)	1101	21.29	HCC$'_i$ (s), HCC$''_i$ (s)	1117	3.13
968	6.41	HCC$'_i$ (s), HCC$''_i$ (s)	1059	0.62	CC$''$, HCC$'_i$ (s), HCC$''_i$ (s)	999	1.32
937	17.88	id	921	27.45	HCC$'_i$ (s), HCC$''_i$ (s)	955	18.66
838	0.06	HCC$'_o$ (as), HCC$''_o$ (as)	844	0.55	CC$'''$ (as)	916	14.32
835	82.34	id	806	1.76	HCC$'_o$ (s), HCC$''_o$ (s)	888	12.65
831	0.02	HCC$'_o$ (as), HCC$''_o$ (as)	797	0	HCC$'_o$ (s), HCC$''_o$ (s)	871	13.01
814	8.01	HCC$'_o$ (s), HCC$''_o$ (s)	687	139.97	HCC$'_o$ (s), HCC$''_o$ (s)	791	58.33
707	101.27	HCC$'_o$ (s), HCC$''_o$ (s)	651	5.87	id (as)	751	57.15
615	1.28	id (as)	624	0	HCC$'_o$ (as), HCC$''_o$ (as)	636	10.96
539	10.07	id (s)	556	0.08	id (s), HCC$'_o$ (s), HCC$''_o$ (s)	541	6.65
490	0.00	od (as)	536	0	od (as)	472	6.46
475	0.04	od (as), HCC$''_o$ (as)	536	0.01	od (s)	436	19.73
337	0.04	id (as)	508	3.68	od (s)	359	2.51

(to be continued)

Table 3 (*continued*)

6			5			TS	
ν_i/cm^{-1}	I_i/km mol^{-1}	Vibration type	ν_i/cm^{-1}	I_i/km mol^{-1}	Vibration type	ν_i/cm^{-1}	I_i/km mol^{-1}
329	0.14	od (s), HCC$'_o$ (s), HCC$''_o$ (s)	149	0.85	id (as)	225	4.87
101	1.56	od (s), HCC$'_o$ (s)	60	0.52	od (s)	656 i	201.88

* Notations of vibrations: CH$'$, stretching of the C(1)—H(7) and C(2)—H(8) bonds; CH$''$, stretching of the C(3)—H(9) and C(4)—H(10) bonds; CC$'$, stretching of the C(1)—C(5) and C(2)—C(6) bonds; CC$''$, stretching of the C(3)—C(4) bond; CC$'''$, stretching of the C(1)—C(3) and C(2)—C(4) bonds; HCC$'$, in-plane (indexed by "i") and out-of-plane (indexed by "o") bending of the H(7)—C(1)—C(5) and H(8)—C(2)—C(6) angles; HCC$''$, in-plane (indexed by "i") and out-of-plane (indexed by "o") bending of H(9)—C(3)—C(1) and H(10)—C(4)—C(2) angles; id, in-plane ring distortion; od, out-of-plane ring distortion; s, symmetric, and as, antisymmetric vibrations.

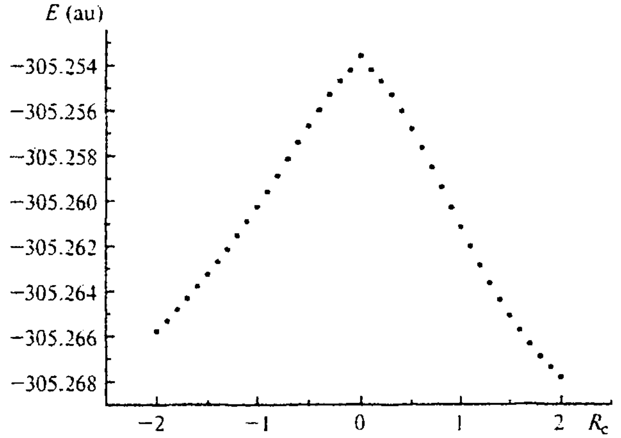


Fig. 1. Dependence of the total energy (E) on the reaction coordinate (R_c) of the Wolff rearrangement, calculated by the intrinsic reaction coordinate (IRC) method.

point vibrational energy correction), the latter being more stable. For the simplest aliphatic ketocarbene C_2H_2O, the ketene-like structure is more stable than the oxirene-like one. In this case, the energy difference is 78.0 kcal mol^{-1}. The "quinone-like" structure of aliphatic ketocarbene C_2H_2O (**3**) has a lower total energy than the oxirene-like structure (**2**). No quinone-like structure was found for the unsaturated 1,2-ketocarbene. The calculated activation energy of the **6** → **5** Wolff rearrangement of 1,2-ketocarbene in the gas phase is 12.5 kcal mol^{-1}. For the simplest aliphatic ketocarbene, C_2H_2O, the activation energy of the Wolff rearrangement (transition from structure **4** to structure **1**, see Fig. 1) is equal to 5 kcal mol^{-1}.

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