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Study of the thermal decomposition of 3-cyclopentenone by using the AM1 semiempirical method

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Summary. RHF/AM1 and UHF/AM1 low-dimensionality surfaces were calculated by applying the reaction-coordinate technique to the thermal decomposition of 3-cyclopentenone. Several stationary points were accurately located within the entire coordinate space. Although the two formalisms used predicted asynchronous reaction pathways for the process, our results illustrate the limitations of single reference treatments of "two-bond" reactions while the nature of the reaction path remains uncertain.

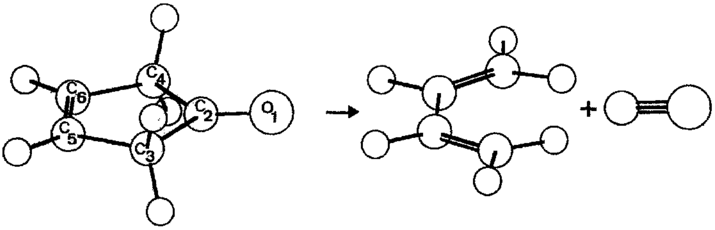
Key words: Thermal decomposition – 3-cyclopentenone – AM1 – Transition states

1 Introduction

Some aspects of two-bond pericyclic reactions such as the symmetry or asymmetry of the transition state, the concerted or nonconcerted nature of the process, the rationalization of the effects of substituents, etc., have aroused great interest among chemists. One such reaction, viz. the Diels–Alder (DA) prototype reaction, owing to its versatility in organic syntheses, has been the subject of much theoretical and experimental research.

Theoretical studies on the DA reaction [1] have aroused much discussion regarding the computational method to be used rather than the chemistry of the process. In this respect, the use of semi-empirical methods in theoretical studies of two-bond reactions, which was occasionally questioned in the past, has been revitalized by Choi et al. [1] as a consequence of the appearance of the AM1 method, whose predictions for the DA reaction coincide with those from ab initio calculations at the 3–21 G or a higher level (e.g. RHF/AM1 calculations are consistent with the CASSCF 4–31 G results of Bernardi et al. for a synchronous transition state in DA reactions [2, 3]). In the opinions of Choi et al., the AM1 method is an affordable choice for studying this type of reaction, particularly when large zones of the potential hypersurfaces involved are to be explored.

We therefore believed it of interest to use the AM1 method in a theoretical study of cheletropic reactions and, specifically, the elimination of carbon monoxide



from 3-cyclopentenone (Scheme 1), which had previously been investigated [4–6] by using the MINDO/3 and MNDO methods. Cheletropic reactions [7] are two-bond reactions where the two sigma bonds involved in the process, viz. C_2–C_3 and C_2–C_4, share one atom of one of the reactants (two in the DA reaction).

2 Computational method

Calculations were carried out by using the AM1 method [8] as implemented in the program MOPAC 6.0. Both the RHF and UHF formalism [9] were employed in the search for potential-energy surfaces (PES).

The approximate locations of stationary points on the PES were first determined by using the reaction-coordinate method, according to which the energy of the supermolecule can be expressed as a function of only the two geometric variables that should make the greatest contributions to the actual process coordinate. The variables selected for this purpose were the C_2–C_3 (R_1) and C_2–C_4 (R_2) interatomic distances. All other geometric parameters were optimized at each pair of (R_1, R_2) values in order to minimize the energy of the system.

RHF and UHF grid searches were carried out at R_1 and R_2 variations from 1.4 to 4.5 Å, using an increment of 0.1 Å or smaller in some regions of special interest.

The stationary points thus obtained were subsequently refined by minimizing the Euclidean norm of the gradient energy [10] down to below 0.1 kcal mol^{-1} Å^{-1}, and then characterized by calculating the associated force constants.

3 Results and discussion

3.1 *RHF/AM1*

Figure 1 shows the RHF/AM1 surface obtained for the thermolysis of 3-cyclopentenone and Table 1 lists the stationary points located after refining from the surface points.

As can be seen in Fig. 1, there is a broad valley from which the reactants can rise in order to be converted into products with the energy requirements for the synchronous and asynchronous modes being quite similar. The zone of the synchronous diagonal maximum ($R_1 = R_2$) was investigated in greater detail by calculating a denser point network (by increasing R_1 and R_2 by a 0.01 Å interval between 1.8 and 2.2 Å). The surface thus obtained showed a single maximum with a very small curvature in the direction of the asynchronous diagonal. No transition state (TS) of C_s symmetry such as that obtained by Choi et al. [1] using the same methodology for the DA reaction was found.

A subsequent analysis of the zone by using conjugate gradient methods revealed the presence of three saddle points. The first such point (S_1), where the

Table 1. Properties of stationary points on the RHF-AM1 potential-energy hypersurface of thermal decomposition of 3-cyclopentenone[a]

	S_1	S_2 (TS)	S_3 (TS)	S_4 (TS)
O_1–C_2	1.184	1.184	1.185	1.185
C_3–C_2	2.065	2.185	2.347	2.579
C_4–C_2	2.029	1.929	1.805	1.597
C_5–C_3	1.389	1.380	1.368	1.360
C_6–C_4	1.391	1.394	1.397	1.418
C_6–C_5	1.399	1.402	1.411	1.412
C_6–C_2	2.517	2.488	2.410	2.334
C_3–C_2–C_1	137.9	141.6	137.7	122.1
C_4–C_2–C_1	137.0	133.9	131.2	138.6
C_5–C_3–C_2	92.0	89.4	84.5	80.3
C_6–C_4–C_2	92.9	95.5	96.8	101.3
C_4–C_2–O_1–C_3			136.2	−114.1
C_5–C_3–C_2–O_1	135.1	134.8	100.0	49.8
C_6–C_4–C_2–O_1	135.1	−135.0	−104.2	
C_6–C_4–C_2–C_3				−49.66
ΔH_f^0(kcal mol^{-1})	51.442	51.432	50.822	50.270
GNORM(UA)	0.150	0.769	< 0.014	0.018
λ	2	1	1	1

[a] S = Saddle; TS = Transition State; M = Minimum.

two-dimensional surface would roughly occupy the maximum of the synchronous diagonal, was second-order ($\lambda = 2$), i.e. the force constant matrix at such a point contained two negative eigenvalues, so it lacked chemical significance. Points of similar features were located in both the MINDO/3 PES [6] and MNDO PES [4, 5], but in these cases with higher relative energies.

The well-known tendency of MINDO/3 and MNDO to overestimate repulsive interactions between atoms when the distance between them is 1.5–2 times the length of a corresponding covalent bond (the lengths of the forming/breaking C–C bonds in the S_1 point, and its MINDO/3 and MNDO equivalent points, lie in this region) is, in the opinion of Dewar et al. [11], the explanation that MINDO/3 and MNDO systematically disfavor symmetrical TS for two-bond reactions. The overestimation of interatomic repulsions has been corrected in AM1 [8].

As we can see not only in literature [1, 12] but in our results, AM1 give different predictions for different two-bond reactions. Therefore, we cannot say a priori that the AM1 method systematically predicts synchronous or asynchronous transition states for two-bond reactions.

TS_2 and TS_3 are two other saddle points in the energy hypersurface and, based on our results, correspond to two possible reaction pathways that differ in the relative orientation of the two reactants [viz. nearly normal (TS_3) or at an angle of ca. 60° (TS_2)], as well as in the asynchrony of the process, which is quite low at TS_2 and somewhat higher at TS_3.

Therefore, the AM1 level of theory provides a concerted asynchronous mechanism for the reaction studied in its forward and reverse directions. Dewar demonstrated an inverse relationship between the exothermicity of two-bond reactions and asynchrony [11]. The addition of CO to butadiene is of intermediate exothermicity relative to other two-bond processes studied by Dewar et al. [13]; our results, in good accordance with such a relationship, are indicative of moderately asynchronous transition states.

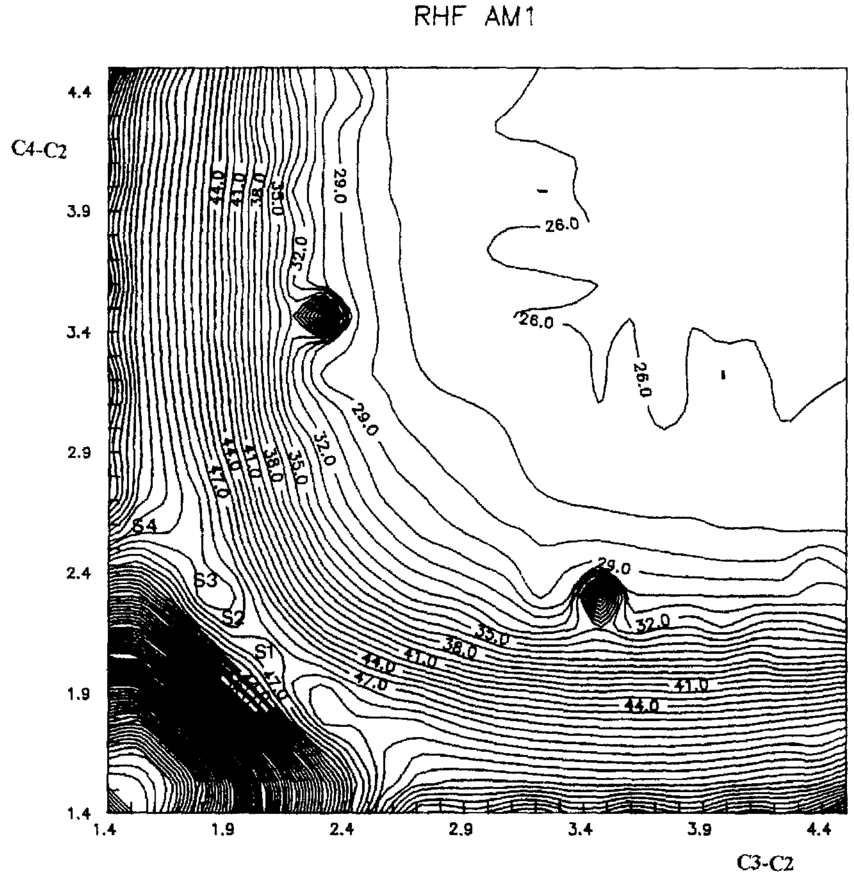


Fig. 1. RHF-AM1 potential-energy surface for the butadiene + CO reaction, in kcal mol^{-1}

The activation energy for the decomposition of 3-cyclopentenone calculated by using the minimum-energy pathway, $\Delta E^{\ddagger} = 73.1$ kcal mol^{-1}, is far larger than the experimental value (51.2 kcal mol^{-1}) [14, 15].

We also characterized a fourth saddle point, TS_4, corresponding to the transition state for the interconversion between the 1,4 adduct (the 3-cyclopentenone) and 1,2 adduct. The corresponding activation energy for direct reaction was 65 kcal mol^{-1}.

3.2 UHF/AM1

To neglect the coulombic electron correlation is the basis of the Hartree–Fock approximation, and so RHF procedures predict energies for open-shell systems (triplets, biradical or biradical-like species) that are too positive. To properly study nonsynchronous mechanisms for pericyclic reactions (DA, cheletropic, etc.) it is therefore necessary to use an appropriate open-shell treatment. The version of AM1 commonly used in this connections, that are available in the MOPAC program, are either those based on the UHF formalism [9] or the "half-electron" approximation [11]. Because both treatments (UHF and HE-3 × 3CI) lead in general to similar geometries, we have chosen the UHF-AM1 procedure in this study, which is the less cost-effective one.

A UHF treatment of a "normal" closed-shell molecule merely reproduces the restricted solution, the two sets of MOs (alfa and beta spin) being identical. However, for molecules with a significant biradical character the electrons tend to segregate themselves in different regions even though their spins are antiparallel. So the coulombic electron correlation is taken into account to some extent.

The UHF/AM1 potential-energy surface obtained is shown in Fig. 2. Notwithstanding their similarity with those reported by Choi et al. for the DA reaction, there are some substantial differences. Table 2 gives the geometric and miscellaneous characteristics of the stationary points located by gradient minimization throughout the entire coordinate space.

As can be seen, the surface includes four distinct zones of minimum energy that correspond to the reactants (butadiene + CO) at an infinite distance (M_3 in Fig. 2 and Table 2), the 3-cyclopentenone as the reaction product (M_2), the 1,2 adduct (M_4, M_5 and M_6) and an open-chain intermediate (M_1) with two radical positions at C_2 and C_4 (or C_2 and C_3, depending on the particular zone in the two surface symmetric moieties). The four zones are connected to one another via several saddle points (TS_2, TS_3, TS_4 and TS_5). Two such zones, viz. those of the 1,2 adduct

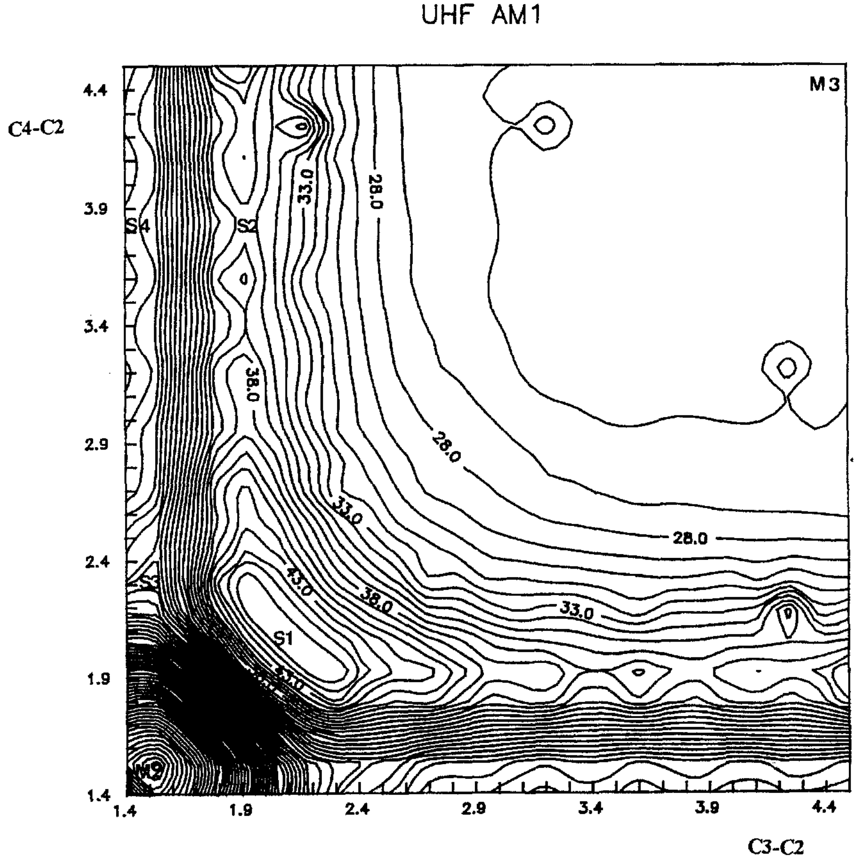


Fig. 2. UHF-AM1 potential-energy surface for the butadiene + CO reaction, in kcal mol^{-1}

Table 2. Properties of stationary points on the UHF-AM1 potential-energy hypersurface of thermal decomposition of 3-cyclopentenone[a]

	S_1	S_2 (TS)	S_3 (TS)	S_4 (TS)	S_5 (TS)	
C_2–O_1	1.183	1.182	1.197	1.196	1.182	
C_3–C_2	2.045	1.882	1.473	1.441	1.881	
C_4–C_2	2.045	3.817	2.312	3.890	4.657	
C_5–C_3	1.403	1.401	1.483	1.501	1.402	
C_6–C_4	1.403	1.362	1.420	1.359	1.363	
C_6–C_5	1.394	1.416	1.366	1.418	1.416	
C_6–C_2	2.539	2.499	2.672	3.892	3.509	
C_3–C_2–O_1	137.2	124.3	140.8	156.2	123.33	
C_5–C_3–C_2	92.6	107.0	109.0	78.1	108.60	
C_4–C_4–C_2	92.6	66.2	88.1	29.6	27.76	
C_4–C_2–O_1–C_3						
C_5–C_3–C_2–O_1	136.2	124.6	154.1	−180.0	160.33	
C_6–C_4–C_2–O_1	−136.2	60.5	−152.5	−134.13	−132.31	
C_6–C_4–C_2–C_3	43.9	60.5	27.5	36.5		
ΔH_f^0(kcal mol^{-1})	50.65	38.84	25.45	41.69	38.35	
Gnorm(U.A.)	0.143	0.178	0.013	0.014		
λ	2	1	1	1	1	
$\langle S^2 \rangle$	0.398	0.815	0.991	0.824	0.844	
	M1	M2	M3	M4	M5	M6
C_2–O_1	1.194	1.228	1.171	1.209	1.209	1.209
C_3–C_2	1.460	1.520	∞	1.466	1.467	1.467
C_4–C_2	4.860	1.520	∞	3.672	3.743	3.491
C_5–C_3	1.476	1.500	1.335	1.533	1.532	1.529
C_6–C_4	1.378	1.500	1.335	1.332	1.332	1.331
C_6–C_5	1.392	1.346	1.450	1.464	1.446	1.464
C_6–C_2	3.724	2.380				
C_3–C_2–O_1	141.7	125.9		149.1	149.0	149.4
C_4–C_2–O_1	178.1	125.9				
C_5–C_3–C_2	112.5	104.0				
C_5–C_2–O_1				148.3	148.3	148.0
C_6–C_4–C_2	29.7	104.0				
C_6–C_5–C_2				120.3	120.8	121.1
C_4–C_6–C_5				123.4	123.5	124.8
C_4–C_6–C_5–C_3				−154.7	−180.1	−30.0
C_4–C_2–O_1–C_3		180.0				
C_5–C_3–C_2–O_1	172.5	180.0				
C_6–C_4–C_2–O_1		180.0				
ΔH_f^0(kcal mol^{-1})	18.03	−22.31	30.69	20.93	21.68	21.40
GNORM(U.A.)	0.178	0.083	0.009/0.012	0.515	0.860	0.840
$\langle S^2 \rangle$	1.187	0.000	0.0/0.0	0.000	0.000	0.000

[a] S = Saddle; TS = Transition State; M = Minimum.

and the biradical intermediate, exhibit the typical sequence of local minima lying parallel to one of the surface axes, which arise from rotation about some of the bonds at a fixed value of one of the variables (R_1 or R_2). Obviously, the UHF/AM1 surface for the DA reaction [1] does not include the minimum zone for the 1,2 adduct and only shows different rotamers of the biradical intermediate, analogous to M_1, with an $\langle s^2 \rangle$ value virtually identical with that obtained for M_1 in this study.

The presence of M_1 in the UHF surface and not in the RHF one is a result of the overstabilization introduced by UHF formalism in this type of structures. As a rule, the UHF treatment of biradical, triplets or biradical-like species in connection with semiempirical methods parameterized to reproduce experimental data

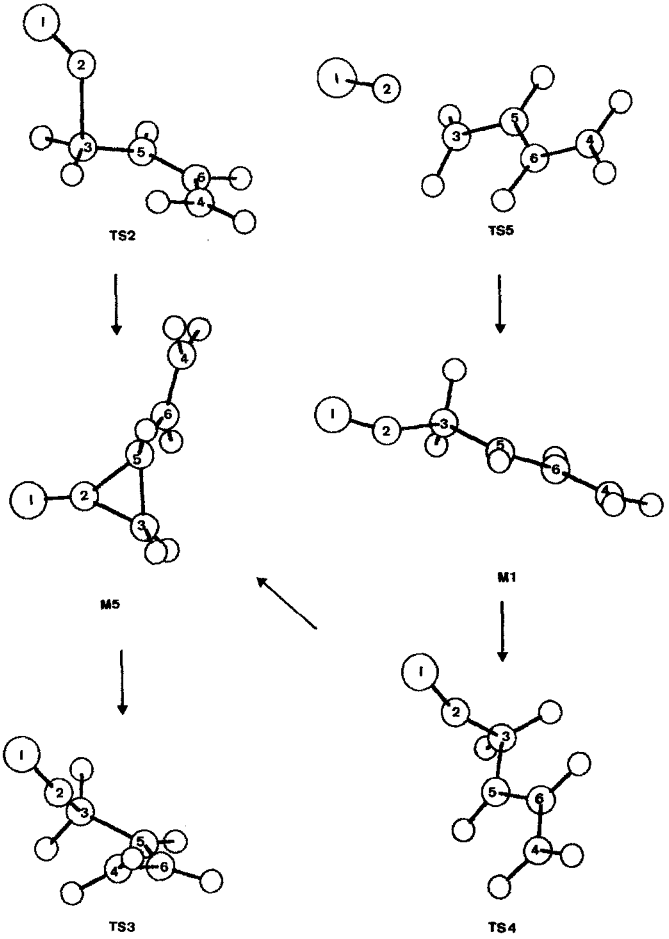


Fig. 3. Structures of the transition states and intermediates in the UHF-AM1 potenti
surface

(MINDO/3, MNDO, AM1, etc.) lead to an artificial overestima
stability. This is because the correlation energy of the unpaired electro
for twice over in UHF versions, one by the UHF procedure and one
the parameterization. Dewar estimates that this error amounts to
electron pair correlation energy, i.e. 20–25 kcal mol^{-1} [11]. Therefor
between calculated UHF-AM1 activation barriers and the correspo
mental ones must be made with caution. Moreover, the failing of AM
predict the heat of formation of CO (is ca. 20 kcal mol^{-1} more posi
experimental value) should tend to raise the energies of TS in reaction le

As Fig. 2 shows, the synchronous pathway is clearly not the min
pathway for the direct formation of the 1,4 adduct. Our results for the
pathway coincide with those reported by Choi et al. for the DA rea
quently, the conversion of reactants into products can proceed via
reaction pathways: from a situation with the reagents at an infinite di
Fig. 3), the system can evolve to the 1,4 adduct (bottom of Fig. 3) via

M_3-TS_2-1,2 adduct-TS_3-M_2, with the first step as the rate determinant step (r.d.s.), or, alternatively, via M_3-TS_5-M_1-TS_4-1,2 adduct-TS_3-M_2, with the second step as the r.d.s. The former choice is the more energetically favorable one. The two-dimensional surface $E(R_1, R_2)$ shows a saddle point in the vicinity of point (1.9, 2.3) that might correspond to the transition state for an asynchronous concerted pathway analogous to that predicted by the RHF/AM1 results. However, no stationary point could be located in that zone of the energy hypersurface by using any of the methods available as options in MOPAC (viz. NLLSQ, EF, SADDLE, SIGMA). In any case, this potential reaction pathway would have an activation energy ca. 10 kcal mol^{-1} higher than that of the minimum-energy pathway.

The activation energies obtained for the conversion of 3-cyclopentenone into the 1,2 adduct and the overall elimination reaction were 47.8 and 61.2 kcal mol^{-1}, respectively.

4 Conclusions

On the assumption of the asynchronous concerted pathway via point (1.9, 2.3), which was not rigorously optimized as a valid pathway, the RHF/AM1 and UHF/AM1 methods provide a similar description for the thermal decomposition of 3-cyclopentenone in regard to the reaction pathway type. However, the two formalisms predict a different minimum-energy pathway. Thus, the UHF treatment tends to stabilize structures containing lone electrons as biradical intermediates and, to a lesser extent, the transition states involved in bond formation or cleavage, so the reaction pathways via the 1,2 adduct and/or intermediate M_1 are more favorable in the UHF/AM1 model.

It should be noted that the AM1 method provides a description qualitatively different from those of other semi-empirical methods such as MINDO/3 and MNDO. In fact, UHF/MINDO/3 and UHF/MNDO calculations performed by Dewar et al. [4, 5] for the reaction studied here predicted a two-step mechanism via an intermediate of a high biradical character other than the 1,2 adduct, with two transition states corresponding to the cleavage of one sigma bond each. RHF/MINDO/3 [6] also support this conclusion.

The results provided by both treatments (RHF/AM1 and UHF/AM1) coincide in regard to the absence of a synchronous reaction pathway. This contradicts the predictions of our more recent ab initio calculations [16], made with basis sets from the STO-3G to the 6–31G*, and including the correlation energy at the MP2 level in 6–31G* calculations, even in full optimizations of minima and saddle points; all of them led to the characterization of a transition state of C_s symmetry corresponding to the synchronous-disrotatory reaction pathway. All this suggests that, as with the DA reaction, finding a conclusive answer to the questions addressed in relation to the mechanism of these reactions calls for more sophisticated calculations (e.g. MCSCF) in order to obtain a balanced description of every stationary point in the potential hypersurface for the reaction including those involving fully paired electrons (reactants, products, the 1,2 adduct) or species of a greater or lesser biradical character. The MCSCF-CASSCF calculations carried our by Bernardi et al. [2, 3] on the DA reaction allowed them to characterize the different possible synchronous and asynchronous reaction pathways.

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