# IS A GAS-PHASE CANNIZZARO-TYPE REACTION PERSPECTIVE?

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*Dedicated to Dr Karel Mach on the occasion of his 60th birthday.*

Quantum chemical calculations for model processes $CH_2{=}O + CH_2{=}O^{\bullet-} \rightleftharpoons CH_3O^- + CH{=}O^{\bullet}$ and $C_6H_5CH{=}O + C_6H_5CH{=}O^{\bullet-} \rightleftharpoons C_6H_5CH_2O^- + C_6H_5C{=}O^{\bullet}$ indicate convincingly their endoergicity. Therefore, spontaneous gas-phase Cannizzaro-type reaction between formaldehyde and benzaldehyde and their radical anions is unlikely to occur. This suggests a significant difference between the gas phase reaction under investigation and the classical Cannizzaro reaction.

**Key words:** Cannizzaro reaction; MP2/6-311G**; Calculations; Formaldehyde; Formaldehyde anion radical; Benzaldehyde; Benzaldehyde anion radical.

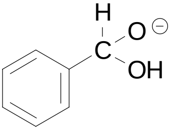
Our interest in gas-phase ion-molecule reactions has been mostly associated[1] with interactions between cations and molecules. Passing from cations to anions is tempting and is a real challenge to both experimental and computational chemists. The reason is that experiments with anions as well as reliable quantum chemical calculations are more demanding than dealing with cations. In the course of a few recent years, calculations connected with reactions between small hydrides and their radical anions, were carried out in our laboratory. Studies of reactions between LiH and LiH$^{\bullet-}$ (ref.[2]) and related processes with beryllium-[3] and boron-containing[1,4] systems were reported.

Because of practical reasons (including preparative aspects), we are now getting interested in reactions between more extended molecules and their radical ions, in particular anions. The purpose of this note is twofold. Firstly, we wish to know whether gas-phase Cannizzaro-type of process could take place between formaldehyde and benzaldehyde and their radical anions leading to methyl alcohol anion and the formyl radical with the former and benzyl alcohol anion and the benzoyl radical with the latter aldehyde. Secondly, the reaction under investigation may shed new light on the mechanism of the classical Cannizzaro reaction[5–9] even if the activated forms of the aldehyde are different.

In the Cannizzaro reaction an aldehyde oxidation state disproportionates into a product of oxidation, the carboxylate anion, and a product of reduction, the alcohol. The reaction requires strongly alkaline conditions and it is limited to those aldehydes which do not carry a hydrogen atom in α-position such as formaldehyde and benzaldehyde. Specifically, in case of the latter it refers to the following reaction.

$$2\ C_6H_5CHO\ +\ OH^- \rightarrow C_6H_5CH_2OH\ +\ C_6H_5COO^- \qquad (1)$$

In the currently accepted reaction mechanism of the Cannizzaro reaction[9], the activated form of the aldehyde is an anion **1** formed *via* addition of a hydroxide anion to the carbonyl double bond. The anion **1** is capable of hydride transfer to a carbonyl double bond of a second aldehyde molecule.



**1**

Experiments carried out with deuterium oxide as a solvent suggest strongly[7] a direct hydride transfer between **1** and an aldehyde molecule. Based on these facts, a mechanism alternative to the classical Cannizzaro reaction involving an aldehyde radical anion as an activated aldehyde form was theoretically studied.

## CALCULATIONS

These were frozen-core MP2/3-21G* and MP2/6-311G** calculations with geometry optimization. The model processes under investigation are depicted in Scheme 1.

## RESULTS AND DISCUSSION

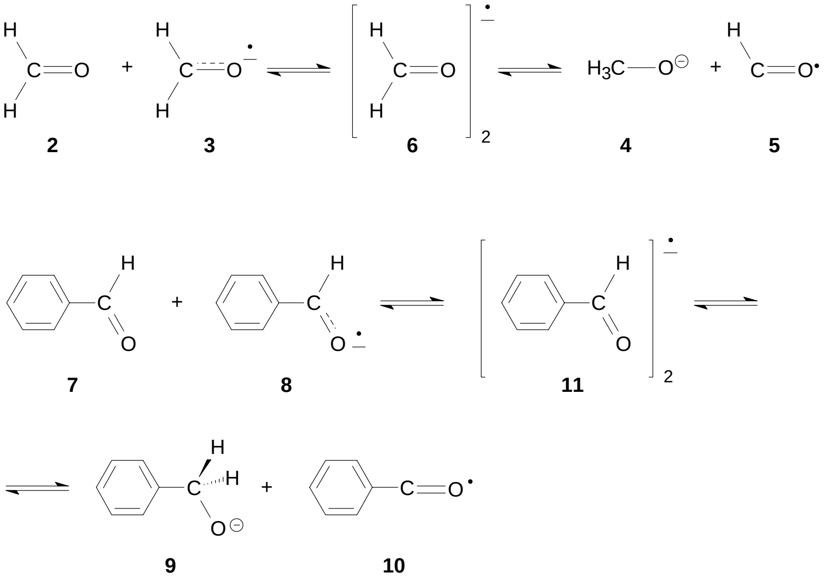
Energies of species **2** through **5** and **7** through **10** are given in Table I. In Figs 1 and 2 optimized geometries of the systems related to formaldehyde and benzaldehyde are given. We use these data first for the discussion of the energetics of the reactions (*2a*) and (*2b*).

$$CH_2{=}O\ +\ CH_2{=}O^{\bullet -} \rightleftharpoons CH_3O^-\ +\ CH{=}O^{\bullet} \qquad (2a)$$

$$C_6H_5CH{=}O\ +\ C_6H_5CH{=}O^{\bullet -} \rightleftharpoons C_6H_5CH_2O^-\ +\ C_6H_5C{=}O^{\bullet} \qquad (2b)$$

TABLE I
Calculated energies of species **2–5** and **7–10** and energy changes (Δ*E* in kJ/mol) accompanying the process **2** + **3** → **4** + **5** and **7** + **8** → **9** + **10**

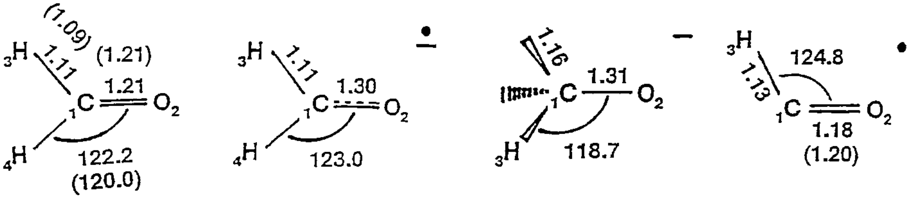
| System | *E*, a.u. | |
|---|---|---|
| | MP2/3-21G* | MP2/6-311G** |
| **2** | –113.43986 | –114.23517 |
| **3** | –113.33066 | –114.15951 |
| **4** | –113.93957 | –114.78749 |
| **5** | –112.80886 | –113.59370 |
| Δ*E* | 57.95 | 35.40 |
| **7** | –342.24132 | –344.65438 |
| **8** | –342.17088 | –344.61497 |
| **9** | –342.74497 | –345.22277 |
| **10** | –341.56351 | –343.95887 |
| Δ*E* | 271.96 | 230.12 |



SCHEME 1

Inspection of Table I makes it obvious that **3** (**8**) is not a strong enough hydride donor with respect to **2** (**7**) as a hydrid acceptor. The $\Delta E$ values suggest that the reactions **2** + **3** → **4** + **5** and **7** + **8** → **9** + **10** are endothermic and will not take place spontaneously. This is true regardless of whether the processes are materialized by the $H^-$ transfer from radical anions (**3**, **8**) to the aldehydes (**2**, **7**) or by H-atom abstraction from the aldehydes by the radical anions. On the contrary, it is quite a plausible assumption that the reverse of these reactions is a downhill process[1].

Geometry of formaldehyde and structures derived from it (**2**–**5**) are presented in Fig. 1 and the radical anion dimer **6** in Fig. 2. There is a fair agreement between the calculated and observed geometry characteristics[10,11] and the dipole moment[12]. Two possible structures of **6** which are energetically nearly equivalent are represented as a combination of **2** and **3** or **4** and **5**. Optimized structure of **6**, associated with the former possibility, is located on the potential energy surface of $(\mathrm{CH_2O})_2^{\overset{\bullet}{-}}$ 92.42 kJ/mol lower than the reactants (**2** + **3**) and 127.82 kJ/mol lower than the products (**4** + **5**). Finally, the



**2** **3** **4** **5**

FIG. 1
MP2/6-311G** optimized bond lengths (in $10^{-10}$ m) and bond angles (°) for species **2**–**5**. Experimental characteristics are given in parentheses

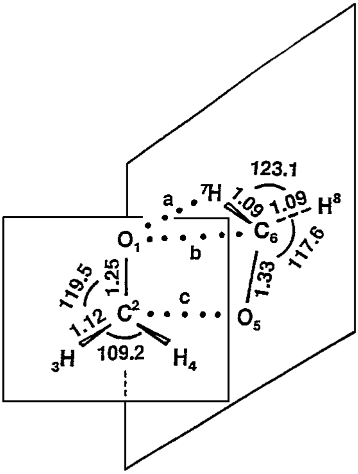
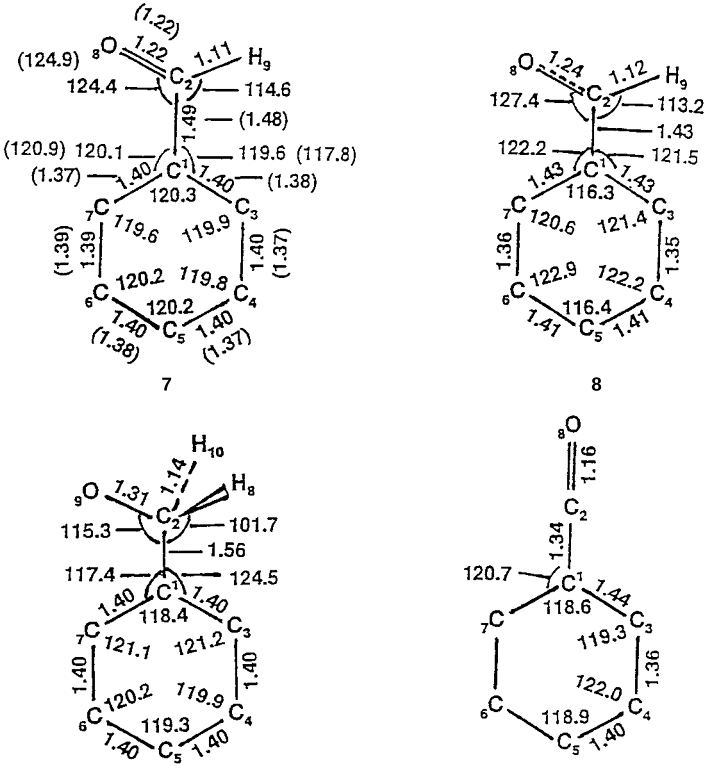


FIG. 2
MP2/6-311G** optimized bond lengths (in $10^{-10}$ m), bond angles and dihedral angles (°) for the radical anion dimer **6**. The orientation of the monomers is given by three parameters, $a = 2.27$, $b = 2.76$, $c = 1.73 \cdot 10^{-10}$ m and dihedral angles $D(3,2,1,7) = -D(4,2,1,7) = 110.55°$

calculated electron affinity of formaldehyde amounts to 1.98 eV; we have been unable to find an experimental value in literature.

Concerning the benzaldehyde system (Fig. 3), the exocyclic carbon and the oxygen in all four species (**7–10**) carry the lowest (0.38, 0.23, 0.33, 0.39) and highest (–0.41, –0.60, –0.79, –0.32) electron density (Mulliken population), respectively. On the basis of extensive general experience and with respect to the result on the formaldehyde radical anion dimer it is plausible to assume that the complexes formed by interaction between **7** and **8**, and **9** and **10** (Fig. 4a, 4b) will have significantly lower energy than the respective free components. These complexes are likely to form minima on the potential energy surface of the radical anion dimer, $C_{14}H_{12}O_2^{\bullet-}$. Computational investi-



**7** **8**

**9** **10**

FIG. 3

MP2/6-311G** optimized bond lengths (in $10^{-10}$ m) and bond angles (°) for species **7–10**. Experimental characteristics are given in parentheses. For the sake of simplicity, the calculated geometric features are presented only for the basic skeleton and the CHO group. The systems **7**, **8**, and **10** are planar, radical **10** possesses the $C_2$ symmetry axis. Positions of H-8, H-10, and O-9 in the anion **9** are given by angles *A*(8,2,9) = 116.9, *A*(1,2,10) = 101.8, *A*(8,2,10) = 101.7 and dihedral angles *D*(8,2,1,3) = 52.5 and *D*(10,2,1,3) = –52.4°

gation of the structure of the complexes presented in Fig. 4 were beyond capacity of our computational resources.

The reliability of our calculations is supported by the fair agreement between calculated and experimental structural data[14], dipole moment[12] (Table II), and electron affinity[13] (calculated 1.07, observed 0.42 eV).

In conclusion, the results of this work suggest that it would be expedient to investigate systematically prototypes of gas-phase analogues of ion-molecule reactions of classical organic chemistry. Combination of theoretical and experimental methods could elucidate new features of the mechanism of those processes.

TABLE II
Calculated and experimental dipole moments of species **2**, **5**, **7**, **10**

| System | μ, D | |
|---|---|---|
| | MP2/6-311G** | experimental |
| **2** | 2.81 | 2.34 |
| **5** | 2.18 | |
| **7** | 3.64 | 2.77 |
| **10** | 2.12 | |

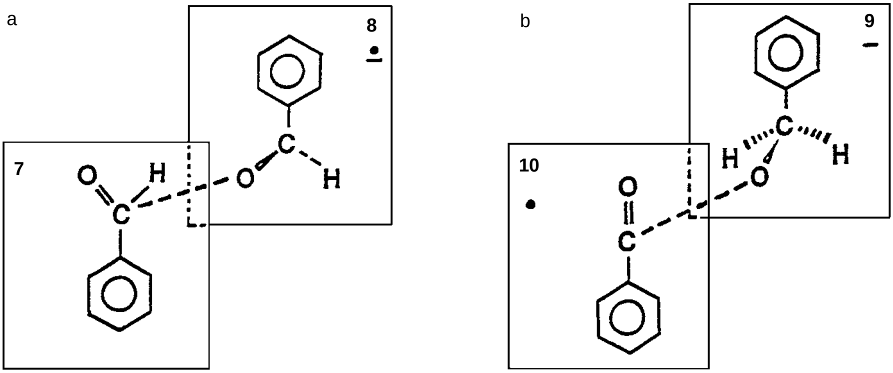


FIG. 4
Assumed structures of the benzaldehyde radical anion dimer, **11**. The two forms are indicated by a and b

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