

Theoretical Study of the Kolbe-Schmitt Reaction Mechanism

Zoran Marković, Johan P. Engelbrecht, and Svetlana Marković

Department of Chemistry and Physics, Technikon Pretoria,
P. O. Box 56208, Arcadia 0007, Republic of South Africa

Reprint requests to Dr. Z. M.; Faculty of Science, University of Kragujevac, 12 Radoja Domanovića
St., POB 60, 34000 Kragujevac, Yugoslavia; e-mail: mark@knez.uis.kg.ac.yu

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A theoretical study of the Kolbe-Schmitt reaction mechanism, performed using a DFT method, reveals that the reaction between sodium phenoxide and carbon dioxide proceeds with the formation of three transition states and three intermediates. In the first step of the reaction, a polarized O-Na bond of sodium phenoxide is attacked by the carbon dioxide molecule, and the intermediate NaPh-CO₂ complex is formed. In the next step of the reaction the electrophilic carbon atom attacks the ring primarily at the ortho position, thus forming two new intermediates. The final product, sodium salicylate, is formed by a 1,3-proton shift from C to O atom. The mechanism agrees with the experimental data related to the Kolbe-Schmitt reaction.

Key words: Sodium Phenoxide; Carbon Dioxide; Density Functional Calculations.

Introduction

In 1860 Kolbe prepared salicylic acid by heating a mixture of phenol and sodium in the presence of carbon dioxide at atmospheric pressure [1]. Kolbe found that by starting with sodium phenoxide, the yield of salicylic acid was increased to 50%. A modification of the Kolbe reaction, performed under enhanced pressure, was carried out in 1884 by Schmitt [2]. This modification significantly increased the yield of salicylic acid. The carboxylation reaction of alkali metal phenoxides with carbon dioxide to hydroxybenzoic acids is known as the Kolbe-Schmitt reaction. The main product of the reaction between sodium phenoxide and carbon dioxide is salicylic acid (94-97%), though p-hydroxybenzoic and 4-hydroxy-isophthalic acids are also identified in the reaction mixture, at low yields (2 - 4%) [3]. It is worth noting that if potassium phenoxide is used instead of sodium phenoxide, p-hydroxy benzoic acid is formed in excess, imposing that the distribution of products in the Kolbe-Schmitt reaction is highly dependent on the metal cation used. The Kolbe-Schmitt reaction has been used in industry since 1874 [4].

The reaction is not much affected by variation of the pressure between 80 and 130 atm [5]. The minimal pressure required for a quantitative carbonation probably corresponds to the dissociation pressure of the

intermediate complex, at the temperature employed. For the sodium phenoxide-carbon dioxide complex (NaOPh-CO₂), the dissociation pressure at temperatures above 140 °C lies between 3 and 4 atm [6].

Much effort has been devoted to the elucidation of the Kolbe-Schmitt reaction mechanism, and determination of the structure of the intermediate NaOPh-CO₂ complex [3]. Schmitt supposed that the reaction occurred with the formation of alkali metal phenyl carbonate (PhO-CO₂Na) as a plausible intermediate [2]. This idea was also supported by Hentschel [7]. The ideas of Johnson and Luttringhaus are also worth noting. They supposed that the Kolbe-Schmitt synthesis involved cyclic stages that led to an ortho substitution [8, 9]. Hales supposed a mechanism based on the preliminary association of sodium phenoxide with carbon dioxide to form a complex, involving an intramolecular reaction with displacement of the ortho-hydrogen by electrophilic attack [10]. The intramolecular mechanism is supported by the absence of disodium salicylate in the carboxylation products. A structure of an intermediate complex, where the π -electrons of sodium phenoxide are attracted by carbon dioxide, with the formation of a weak Na-O bond [4,10], has not been experimentally confirmed. More details on experimental aspects of the Kolbe-Schmitt reaction, as well as on its mechanism, can be found in the review [3].

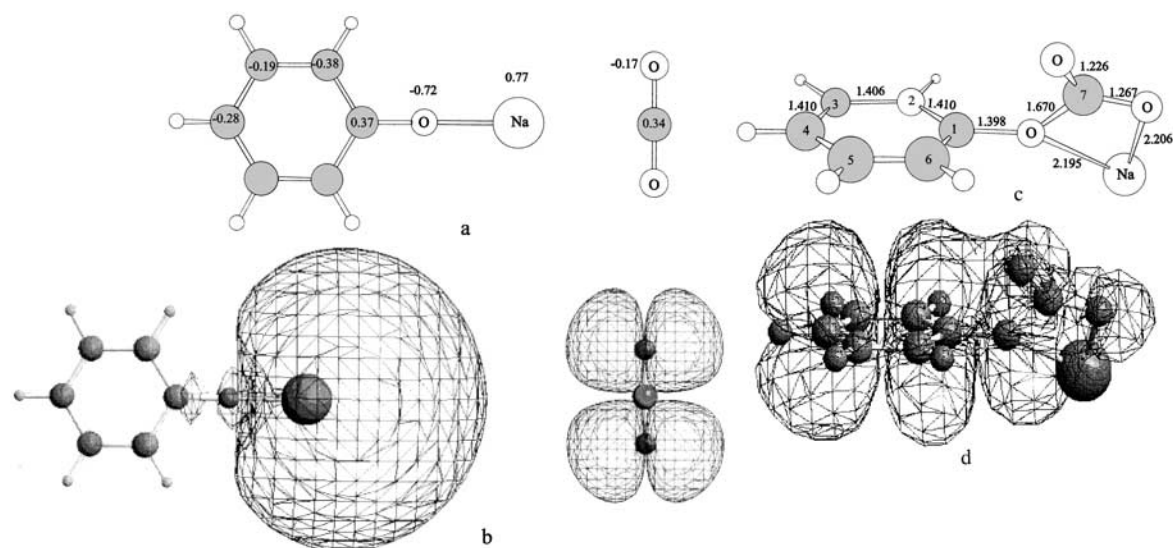


Fig. 1. (a) Distribution of Mulliken charges in the sodium phenoxide and carbon dioxide molecules. (b) HOMO-LUMO orbitals of sodium phenoxide and carbon dioxide. (c) The optimized geometry of the intermediate B (NaPh-CO₂ complex). (d) HOMO orbitals of the intermediate B. For better understanding, all C-atoms are represented by grey circles, and labelled by numbers. The same notation is used in Figs. 2 and 3.

The structure of solvent-free sodium phenoxide was recently determined [11]. It was found that solvent-free sodium phenoxide crystallised, forming polymeric chains, and the four-membered ring chain was separated by oxoligands [11]. This work also provides valuable information on the Kolbe-Schmitt reaction mechanism. It was shown, on the basis of the FT-IR study, that the NaOPh-CO₂ complex, when exposed to higher temperatures, underwent an irreversible phase transition. Namely, it was found that the asymmetric stretching vibration, $\nu(\text{CO}_2)_{\text{asym}} = 1685 \text{ cm}^{-1}$, was at higher temperatures divided into two bands at 1680 and 1651 cm^{-1} , thus indicating that a further intermediate of the Kolbe-Schmitt reaction was formed. This assumption was also confirmed by the DTA studies [11]. On the basis of these investigations, two intermediates can be expected in the Kolbe-Schmitt reaction.

Although the reaction is known since the middle of the XIX century, the elucidation of its mechanism has not been accomplished. Surprisingly, this reaction has not been considered by means of theoretical methods. In this paper we report the results of a theoretical examination of the reaction between carbon dioxide and sodium phenoxide. It is well-known that the Kolbe-Schmitt reaction occurs at high temperatures (note that the original Kolbe reaction was

performed at 220 - 250 °C, where the introduction of carbon dioxide caused a large amount of phenol to distil) [12]. In addition, the melting point of sodium phenoxide is 61 - 64 °C, imposing that the crystal structure of sodium phenoxide has to be destroyed under the conditions of the Kolbe-Schmitt reaction. For these reasons, we investigate the mechanism of this reaction in the gas phase and assume that this approximation is reasonable.

Computational Methods

A DFT method is used in this study. For the DFT calculations we use the hybrid gradient corrected exchange functional proposed by Becke [13, 14], combined with the gradient-corrected correlation functional of Lee, Yang, and Parr [14]. This functional, commonly known as B3LYP, turned out to be quite reliable for geometrical optimisations [15]. In this work, geometrical optimisations for all compounds are carried out using the LANL2DZ basis set. The first row atoms are described by the double zeta basis Dunning-Hay [16]. Quantum chemical calculations are performed by means of the Gaussian 98 program package [17].

The geometries for the stationary points are identified by the minimisation of the energy with respect to

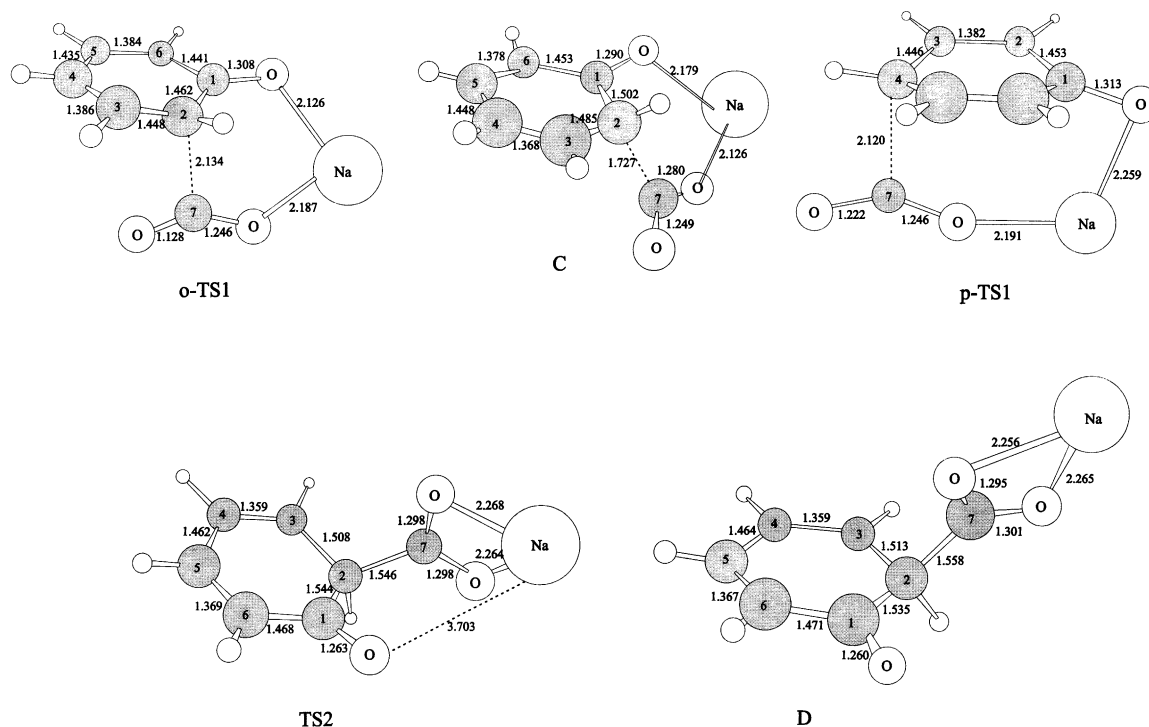


Fig. 2. The optimized geometries of the transition states o-TS1, p-TS1 and TS2; and the intermediates C and D.

all geometrical parameters. All vibrational frequencies are calculated at the B3LYP / LANL2DZ level of theory, in order to identify whether a certain structure is a ground state (zero imaginary frequencies) or a transition state (one imaginary frequency). The analysis of the vibrational frequencies is performed by means of the gOpenMol program, version 2.1 [18, 19].

Results

There are two positions in a sodium phenoxide molecule where carbon dioxide can attack (Fig. 1a): a benzene ring or a polarized O-Na bond. These two possible attacks of the carbon dioxide molecule are considered as the first step of the Kolbe-Schmitt reaction. Our calculations show that carbon dioxide can react only with the O-Na group, forming the intermediate NaPh-CO₂ complex (B), whose optimized geometry is presented in Figure 1c. The vibrational analysis of this complex shows a strong vibration of the CO₂ moiety at 1868 cm⁻¹.

In the next step of the reaction, the electrophilic carbon atom, which belongs to the CO₂ moiety, attacks the ring at the ortho, meta or para position. For con-

versions in the ortho and para positions, the activation energies of 5.44 and 10.37 kcal/mol, respectively, are found (Fig. 4). For the reaction in the meta position, a reaction path, as well as a transition state are not revealed. This agrees with the HOMO-LUMO analysis of the intermediate B (Fig. 1d), which clearly shows that the HOMO orbital is located on the ortho and para carbon atoms of the benzene ring. According to the Curtin-Hammond principle, the product distribution is determined by the difference of free energies of the two transition states. The 4.9 kcal/mol difference in free energy of the ortho and para products results in an about 3300:1 ratio of the products concentrations. On the basis of this, one should expect the para substituted product at a very low yield in the reaction mixture, which agrees well with the experimental data. For these reasons, the meta and para routes are excluded from the present investigation. The reaction in the ortho position proceeds via the transition states o-TS1 and TS2, with the formation of the intermediates C and D. In Fig. 2 the optimized geometries of o-TS1, p-TS1, TS2, C, and D are depicted. The vibrational analysis shows that D exhibits a strong vibration of the CO₂ moiety at 1730 cm⁻¹.

Table 1. The values of total energies in a.u. for all calculated structures.

	CO ₂	PhONa	B	o-TS1	— Structure — p-TS1	C	TS2	D	TS3	Salicylic acid
–E	188540119	307068880	495626395	495609856	495617712	495619661	495604534	495605580	495532804	495665666

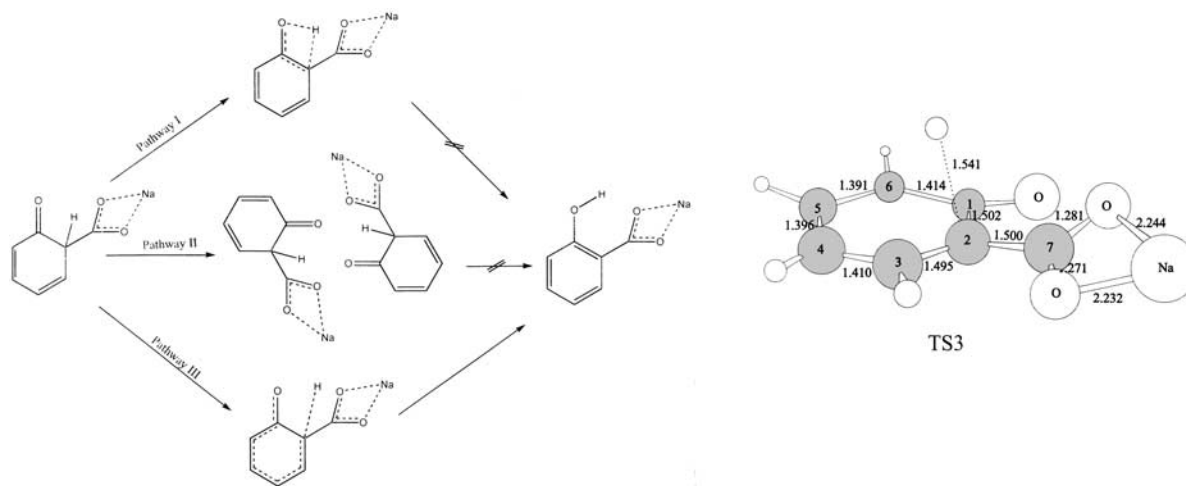


Fig. 3. Three reaction pathways for the last step of the Kolbe-Schmitt reaction and the optimized geometry of the transition state TS3.

A 1,3-proton shift from the C to O atom in the intermediate D is considered as a plausible last step of the reaction. Three pathways are examined (Fig. 3): a shift from C to O via a cyclic transition state (pathway I), a reaction between two molecules of the intermediate D (pathway II) and a deprotonation from the C atom followed by the protonation of the O atom (pathway III). For the pathways I and II reaction paths are not revealed. The pathway III proceeds via the transition state TS3, whose optimized geometry is presented in Figure 3.

In Table 1 the values of the total energies in a.u. for all calculated structures are presented.

Discussion

On the basis of the results presented above, one can conclude that the Kolbe-Schmitt reaction proceeds via three transition states and three intermediates. A general outline of the mechanism, as well as the reaction profile, are presented in Figure 4. The reaction is apparently exothermic, what agrees with the experimental data [20].

Carbon dioxide is a weak electrophile, so that an attack at the benzene nucleus (in either ortho, or meta

or para position) does not reveal any possible reaction path. The reaction between CO₂ and polarized O-Na bond proceeds smoothly, with stabilization of the system (Fig. 4b) and formation of the intermediate B. This can be explained by the fact that the bonds O-Na in sodium phenoxide and C-O in carbon dioxide are particularly polar, as illustrated by the distribution of Mulliken charges for both molecules (Fig. 1a). In addition, the HOMO-LUMO analysis shows that the LUMO orbital of sodium phenoxide is located practically only on the sodium atom, whereas the HOMO orbital in carbon dioxide is located on the oxygen atoms (Fig. 1b). On the other hand, the HOMO orbital of sodium phenoxide is spread over both the benzene ring and oxygen atom, whereas the LUMO orbital of carbon dioxide is mainly located on the carbon atom. These facts confirm our prediction that the reactive site in the first step of the reaction is the O-Na bond. It is interesting that this step of the reaction proceeds without any activation barrier. It is well known that not all chemical reactions have transition states, especially in the gas phase. In fact, reactions without energy barriers are quite common [21].

The analysis of the geometry of the intermediate B (Fig. 1c) shows that the C7 atom is partially posi-

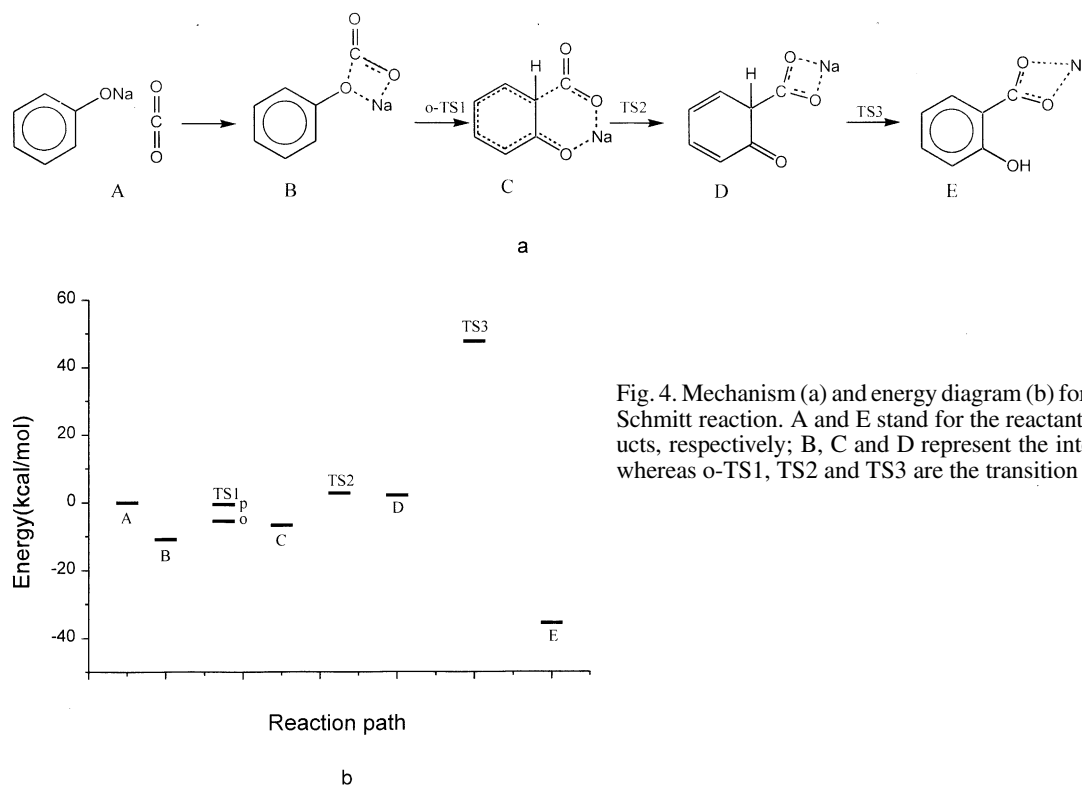


Fig. 4. Mechanism (a) and energy diagram (b) for the Kolbe-Schmitt reaction. A and E stand for the reactants and products, respectively; B, C and D represent the intermediates, whereas o-TS1, TS2 and TS3 are the transition states.

tively charged. The C7-O bonds are longer than those in the molecule of CO_2 . The bond $\text{O}-\text{C}_{\text{sp}^2}$ is also significantly elongated, as compared to the $\text{O}-\text{C}_{\text{sp}^2}$ bond in sodium phenoxide, whereas the aromatic structure of the benzene nucleus is completely maintained.

In the transition state o-TS1 (Fig. 2), a bond between the C2 and C7 atoms is partially formed. The consequence of the formation of this weak bond is that the geometry of the benzene ring is slightly deformed in the o-position. This carbon atom is out of plane by 10 degrees. The bond lengths in the benzene ring of o-TS1 are close to the values for aromatic bonds, but a partial bond alternation in the ring can be observed. It is well known that an alternating bond elongation and contraction in benzene rings can be induced [22, 23] by imposing enough strain on a six-membered ring (Mills-Nixon effect [24]). The geometry and energy of the intermediate C are very similar to those of o-TS1, probably due to the fact that o-TS1 is a late transition state. The bond between C2 and C7 in the intermediate C is shorter, and the bond between C1 and C2 is significantly longer. An interesting feature of o-TS1 and the C is that three C-atoms, two O-

atoms and an Na-atom form a six-membered ring, in which the Na atom is chelated by two oxygen atoms. It is well known that sodium phenoxide readily forms chelate compounds with oxygenated substances [10].

A remarkable feature of the geometry of p-TS1 (Fig. 2) is that both C1 and C4 atoms are out of plane by about 10 degrees, causing a significant deformation of the benzene ring. The bonds between the phenoxide oxygen and sodium, as well as between the sodium and oxygen atoms of the CO_2 moiety, are significantly longer than those in o-TS1. We assume that the pronounced deformation of the benzene ring in p-TS1 is an important reason for the distribution of the products in the reaction between carbon dioxide and sodium phenoxide.

In the transition state TS2 the bond between phenoxide oxygen and sodium is almost completely broken (Fig. 2). As compared to the intermediate C, the sodium atom in TS2 is bonded to both oxygen atoms of the CO_2 moiety. The conversion from the intermediate C to D causes the geometrical changes in the benzene ring, so that the C1-C2 bond of TS2 is significantly longer than the analogous bond in the in-

intermediate C. The C1-O bond is shorter, whereas the C1-C7 bond is almost completely formed. Similarly to the case of o-TS1, TS2 is a late transition state, implying that minor changes in the geometry and energy between TS2 and the intermediate D can be observed. The most important difference between these two geometries is that the bond between phenoxide oxygen and sodium is completely broken in D.

As mentioned above, the vibrational analysis reveals that both intermediates B and D show one strong vibration of the CO₂ moiety. Bearing in mind the results of the FT-IR study on the thermal behaviour of the NaPh-CO₂ complex [11], one can conclude that the splitting of the vibration $\nu(\text{CO}_2)_{\text{asym}}$ is caused by a transformation from B to D.

As indicated above, three pathways are considered for further transformation from D to the final product. Reaction paths for the pathways I and II (Fig. 3) are not revealed. In the pathway III (Fig. 3) the separation of the hydrogen atom requires an activation energy of 45.67 kcal/mol, and then, the formation of the O-H bond of sodium salicylate occurs smoothly. A relatively high energy barrier in the pathway III is supported by the fact that the reaction mixture has to be heated for 1 hour at 150 - 160 °C under enhanced pressure in order to form sodium salicylate [10]. In addition, it is well known that a similar 1,3-shift of a hydrogen atom in the conversion process for vinylacetaldehyde tautomerization requires an activation energy of 56.4 kcal/mol in the gas phase [25].

The optimized geometry of TS3 (Fig. 3) shows that all C-C bonds in the benzene ring have the expected bond lengths (about 1.4 Å), except the C1-C2 and C2-C3 bonds. They are shorter than the analogous bonds in the intermediate D, but they are still longer than ordinary aromatic bonds. The bonds in the CO₂ moiety, as well as the C2-C7 bond are almost completely formed, whereas the C2-H bond is almost completely broken.

The intermediate D can undergo a reverse reaction, forming the intermediate C. The energy barrier for the back reaction is very low, only 0.66 kcal/mol. The intermediate C can also undergo a reverse reaction yielding B, with an energy barrier of 1.22 kcal/mol. These low values of the energies of activation for the back reactions can explain the fact that Kolbe has never exceeded the yield of 50%. Schmitt significantly improved the yield by performing the reaction under higher pressure (i.e. by shifting the equilibrium to the right side of the reaction).

Concluding Remarks

This is the first theoretical study of the Kolbe-Schmitt reaction mechanism. Our calculations reveal that this reaction is an exothermic process, which proceeds via three transition states and three intermediates. The main product of the reaction is salicylic acid, whereas the para product can be expected at a very low yield.

The first step of the reaction is an attack of the carbon dioxide molecule on the polarized O-Na bond of sodium phenoxide (Fig. 1a), where the intermediate NaPh-CO₂ complex (B in Fig. 1c and Fig. 4) is formed. In the next step of the reaction, the electrophilic carbon atom attacks the ring primarily at the ortho position. The reaction proceeds via the transition states o-TS1 and TS2 (Fig. 2), with the formation of the intermediates C and D (Fig. 2 and Fig. 4). In the last step of the reaction, the intermediate D is converted into the final product, sodium salicylate, by a 1,3-proton shift from C to O atom (Fig. 3). This reaction path involves the deprotonation from the C atom followed by the protonation of the O atom via the transition state TS3 (Fig. 3), and, as expected, requires a high energy of activation. The intermediates C and D can easily undergo a reverse reaction (due to low activation energies), thus indicating that by performing the reaction under enhanced pressure of carbon dioxide, the equilibrium is shifted to the final products of the reaction.

Our work suggests that the Kolbe-Schmitt reaction occurs via three intermediates, whereas the FT-IR study on the thermal behaviour of the NaOPh-CO₂ complex indicates that two intermediates can be expected in the reaction. The absence of one vibration in the FT-IR spectrum can be attributed to relatively low activation energies for the conversion from B to D, and to the possibility for the reverse reaction from D to B.

As mentioned above, the distribution of the products in the Kolbe-Schmitt reaction is highly dependent on the metal cation, indicating that metal plays a significant role in the mechanism of the reaction. The investigations of the reactions of carbon dioxide with lithium phenoxide and potassium phenoxide are under intense scrutiny.

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