**Answers to the Reviewers by the Authors**

Reviewer 2 raised the following issue: *«In page 5, Line 29: “According to 7a” please include the name of the authors here»*.

Authors’ reply: We apologize for this inaccuracy. Unfortunately, the references have shifted during the automatic numbering. We made appropriate corrections in the revised manuscript.

Reviewer 3 raised the following issue: *«The authors perform DFT calculations of an isolated contact ion pair in vacuum. This means that strongly symmetrical* *electric field of crystal is simply neglected. As a result, electronic charge is not compensated from outer sides and edge effects take place. In other words, such ions bear some excess of energy, like surface ions in a crystal. How the authors account this physics in their calculations. Probably, the energies obtained are not strongly correct for thermodynamics. Some comments on this issue are important and must be included in the text»*

Authors’ reply: We share the reviewer's concern and are grateful for raising this important issue. To address this, we added the following passage to the Quantum chemical calculations section (highlighted in green within the manuscript):

«Importantly, the DFT calculations were carried out assuming reagents and products are isolated molecules, therefore, the electric field of crystal was neglected. However, the very fact that the predicted energies are in good agreement with the experimental values measured by flow calorimetry for the decomposition reactions of five diazonium salts with different counterions and ring substituents **1b-d**, **2** and **3** (Table 8) indicates that the major contribution to the reaction thermodynamics is made by the chemical transformations, whereas the effects of changing the crystal lattices are minor. Possibly, it is due to the fact that both reagents and products remain solid (except N2), thus, there is a compensation for the thermal effects of the transformation of the crystal lattices of the starting material and products. It is also important from an application prospective that the proposed quantum-chemical approach to assessing the thermodynamics of decomposition reactions of diazonium salts is relatively easy to implement. While calculations taking into account unknown transformations of crystal lattice are much more laborious, sophisticated and cannot yet be widely used to predict the thermal effects of chemical reactions, despite the known progress in calculating the crystalline state of benzenediazonium chloride and tetrafluoroborate. 2c,d»

Reviewer 3 raised the following issue: *It is known, that aryl cations have close lying singlet and triplet states. Moreover, the ground state not always singlet and depends on the ring substituent (J. Phys. Chem. A 2014, 118, 3201-3210). This also determines chemistry of the aryl cations. How the authors account the different spin states of the aryl cations (say, 4-MeOC6H4+)? The appropriate citation and comments in the text are required*

Authors’ reply: Since we calculated the reaction thermodynamics based on the initial and final states of the system, the ground state (singlet or triplet) of the intermediate aryl cations did not matter (Scheme 1). However, to explain the decomposition features of 2-nitrobenzene diazonium salt, we suggested the mechanism provided in the Supporting Information. In the revised manuscript we added the following refences (J. Phys. Chem. A 2014, 118, 3201-3210) and (Chemical Physics 389 (2011) 68-74) as [14 a,b].

Reviewer 3 raised the following issue: *The unusual chemistry of the 2-nitrophenyl cation was pointed out before (Chemical Physics 389 (2011) 68-74). The authors should provide some referencing and comments on this issue in the text.*

Authors’ reply: The reference was added to the revised manuscript (*vide supra*).

Reviewer 3 raised the following issue: *Literature numbering is damaged. Thus, it is not possible to assign reference numbers in the text with the same in the reference list»*.

Authors’ reply: We apologize for this inaccuracy. Unfortunately, the references have shifted during the automatic numbering. We made appropriate corrections in the revised manuscript.

Reviewer 3 raised the following issue: *BF3 cleavage. Probably, this must be BF3 detachment?*

Authors’ reply: We agree with the reviewer’s remark. The «*cleavage*» was replaced by «*detachment*» in the revised manuscript.

Reviewer 3 raised the following issue: *Supporting. Probably, this must be Supporting Information?*

Authors’ reply: We agree with the reviewer’s comments. The necessary adjustments were made in the revised manuscript.

Рецензент 4.

Reviewer 4 raised the following issue: *Page 6 line 10: any purity information of the tested samples, especially any moisture or solvent content? If a sample contains moisture or solvent, the data interpretation of TGA and open pan DSC is completely different since the small endothermic event can be caused by them, instead of melting. If data is not available, a drying procedure used by the authors is helpful if other researcher want to repeat this work*.

Authors’ reply: The purity degree of the diazonium salts tested is given in our previous papers referenced in the manuscript [Organic Lett. 2010, 10, 3961; Eur.J.Org.Chem. 2019, 2019]. In the revised manuscript we added the description of sample drying prior to the measurements: «All samples used in calorimetric studies were dried in vacuum for 48 h». This procedure is recommended in the study of the decomposition of arendiazonium chlorides [7a]. The observed endothermic effects are caused by melting as they match the experimentally found melting points. The latter we added to the Table 1 in the revised manuscript. (**А.А., не забыть это сделать!**)

Reviewer 4 raised the following issue: *Page 6 line 29: since the heat flux signal of TAM instrument is easy to be saturated, it is important for other researcher to know the typical sample size used in this study. Overloading such high energy materials may result in an uncontrolled reaction and make damage to the instrument*.

Authors’ reply: The typical sample size was 10 mg as indicated on page 6, line 22. The TAM instrument and Hastelloy ampoule are designed to study the properties of high-energy products. We calculated the amount of gaseous nitrogen (~ 0.7 mL) released during decomposition of the studied diazonium salts and found that this amount would not increase the pressure in the Hastelloy ampoule even up to 1.5-2 atm.

Reviewer 4 raised the following issue: *Page 6 line 33, were the samples purged with gases during the sample preparation and then sealed during the isothermal test? If this was the case, where did the decomposition product (assume N2 or BF3) go during the test? If they were purged for the whole time, please provide more information on purge gas flow rate, how to control it to ensure constant rate, and a reference cell with purging gas as well*

Authors’ reply: According to the reviewer’s comment, we clarified the experiment conditions as follows: «The ampoule was evacuated, then purged with nitrogen, argon or air depending on experimental conditions, and sealed».

Reviewer 4 raised the following issue: *Page 8 line 50: If the finding about BF3 generation around 33°C is true , this is a BIG safety hazard for storage and transportation of compound 3 since it will release BF3 gas around ambient temperature. A sealed package of compound 3 will be pressured at ambient temperature with BF3 which is an extremely toxic chemical (H330). But I didn’t see any available public information related to this. Please double check this conclusion, with other data/test (pressure rise test at ambient?). On the other hand, since the initial purity of 3 is unknown, the loss of mass on TGA can be caused by the removal of moisture or solvent. Therefore, this conclusion based on single supporting “evidence” can be wrong*.

Authors’ reply: We are grateful to the reviewer for paying attention to this issue. Indeed, the claim that BF3 is generated at 33 оС is clearly incorrect. In fact, the endothermic peak corresponding to the loss of BF3 is located at 58.7 оС and we made the corresponding corrections in Fig. 6 and in the text. The purity of the diazonium salt **3** is 98% (Aldrich). The reviewer's remarks stimulated us to analyze more carefully the literature on the thermal decomposition of tetrafluoroborates. The following paper Koval’chuk, E. P.; Reshetnyak, O. V.; Kozlovs’ka, Z. Ye.; Bła˙zejowski, J.; Gladyshevs’kyj, R. Ye.; Obushak, M.D. Mechanism of the benzenediazonium tetraﬂuoroborate thermolysis in the solid state. Thermochimica Acta, 2006, 444, 1-5 (referenced in the revised manuscript as [12]) made us to reconsider the conclusions regarding the nature of the endothermic peak at 58.7 оС. We modified the passage describing the decomposition of 4-nitrobenzene diazonium tetrafluoroborate **3** as follows:

«It might seem that the loss of BF3 at 58.7 ° C indicates that intermediate **3a** undergoes decomposition at 146.5 оС (equation 1). However, upon thermal decomposition of PhN2+BF4-, a small endothermic peak at 63 ° C was also observed on the DSC/TGA curves. The appearance of this peak was explained by the removal of water bound to DS via hydrogen bonds. 12 It cannot be applied to DS **3** thought, as the weight loss of DS 3 at 58.7 °C corresponds to 5.2 mol of water per 1 mol of DS **3**. Should it be such a large amount of water, DS **3** would have to be partially dissolved, but not crystalline. However, there are contradictions in explaining the cause of the endothermic peak appearance during the heating of DS **3** and PhN2+BF4-. Obviously, this issue requires further special studies. Therefore, at present, we can propose Equation 1 only as a hypothesis, partially consistent with the results of quantum-chemical modeling of DS decomposition reactions (*vide infra*). »

Reviewer 4 raised the following issue: *Page 8 line 33, and figure 5: the small exothermic around 69C can be caused by the baseline issue, or crystallization from amorphous phase. It may not be a decomposition. need to double check this conclusion*.

Authors’ reply: We did not interpret the exothermic peak around 69 °C in the manuscript. Due to the reviewer’s comment, we now better understand the possible reasons for the appearance of this peak. We added the explanation suggested by the reviewer (underlined) to the following passage: «The first one at 69.37 ° C is characterized by a small amount of heat released (24.47 J/g) and can be caused by the baseline issue, or crystallization from amorphous phase. While for the second one, located at 146.6 ° C, the heat release of 323.0 J/g is observed». In addition, the reviewer's comment prompted us to correct the sentence on page 8, line 40, as follows: «In the case of DSs **1a, 1b, 1d** the endothermic peaks are not accompanied by a weight loss and are probably associated with the rearrangement of the crystal lattice ». We also added the melting points of the diazonium salts tested to Table 1 for a better understanding of the discussed thermal effects.

Reviewer 4 raised the following issue: *Fig 1 to 6, make different line styles (such as dash vs. solid) and add legends for them. It is difficult to tell which one is which on the current graph*

Authors’ reply: Figures 1-6 have been changed according to the reviewer’s suggestion.

Reviewer 4 raised the following issue: *Table 2, 4 and 5: unit of k (g/mol/c). What is “c”. based on equation 2, the unit of k should be reciprocal of unit of A0 and divided by unit of time. I don’t see the unit of time anywhere in the right side of equation 2 with this k unit.*

Authors’ reply: Unfortunately, we made a typo translating the article.The reaction rate constants given in Tables 2, 4, and 5 are in g/mol/s units, where s stands for second. To clarify the issue, we expressed the kinetic equation (2) in terms of α conversion and the constant in *s-1* units. We made corresponding adjustments in the revised manuscript.

Reviewer 4 raised the following issue: *Table 2, 3 and 8: ΔH, In this study, the initial purity of the tested samples (reactants) is unknown, and also the conversion of the decomposition reaction is unknown. The measured heat release from the tests (J/g) can’t be converted into kJ/mol unless those information is well defined*.

Authors’ reply: The purity degree of the tested samples is given in our previous papers referenced in the manuscript [Organic Lett. 2010, 10, 3961; Eur.J.Org.Chem. 2019, 2019]. The value of ΔH is calculated by integrating a curve approximating the experimental heat flux according to equations (2) and (4), over the time interval (0, ∞).

Reviewer 4 raised the following issue: *Page 15 line 38: table 3, instead of table 1???*

Authors’ reply: We agree with the reviewer’s comments. The necessary adjustments were made in the revised manuscript.

Reviewer 4 raised the following issue: *Page 15 line 50 and table 3, for compound 1a and 1d, DSC results show the decomposition reaction happens after melting (liquid phase reaction). The temperatures for Isothermal tests are not high enough to melt the samples. this may explain the low Pmax in isothermal tests. However, I don’t know how the authors get the full integrated ΔH from the isothermal test since there is not much reactivity observed in days. how long time is these isothermal tests?*

Authors’ reply: We conducted all flow calorimetry experiments at temperatures significantly lower than the melting points. For a better understanding, we added the melting points to the Table 1 in the revised manuscript. The isothermal test was carried out until the heat flux decreased below 2 μW, which is less than 1% of the maximum heat flux and corresponds to the conversion degree α> 0.99. Time ranged from several hours to 50 days depending on temperature. We added the algorithm of the enthalpy calculation to the revised manuscript to the description of equations (2) and (4).

Reviewer 4 raised the following issue: *Page 16 line 39 and Page 17 line 3, the right side of equation 2 can be simplified to k\*[A]\*[C0]. To me, this is not autocatalytic equation since the rate is not dependent on [C]. Need more explanation or reference on this.*

Authors’ reply: We are grateful to the reviewer for raising this issue. We corrected the equation

(2) by changing С0 to C. To make it clear, we expressed the kinetic equation (2) in terms of α conversion and gave more detailed explanation with the reference to a paper on modeling the kinetics of solid-phase reactions [<https://doi.org/10.1021/ie8018615>].

Reviewer 4 raised the following issue: *Page 17 line 16, need better define the half-life. To me, the authors took the peak time as half-life. However, most of the times, peaks don’t follow symmetric shape*.

Authors’ reply: The half-life corresponds to the conversion degree of 0.5. We gave the corresponding definition in the description of the equations (2)-(4): « The half-life corresponds to the conversion degree of 0.5. Due to the symmetry of the approximating kinetic curve 4, the half-life coincides with the maximum heat flux (in the case of more complex kinetics, this rule is not fulfilled).»

Reviewer 4 raised the following issue: *Table 4, Pmax unit: mW/g?*

Authors’ reply: Table 4 showed the unnormalized values of the initial heat flux (P0) in μW. We reprocessed the data and presented the values in mW/g units as was suggested by the reviewer.

Reviewer 4 raised the following issue: *Figure 8, Pmax of 1c is around 120mW/g but Line 10 mentions 101.5 mW/g*

Authors’ reply: Indeed, the experimental Pmax value for diazonium salt **1с** is 119.5 mW/g. We corrected the misprint and carefully checked all the data in Tables 2, 3, 4, and 5.

Reviewer 4 raised the following issue: *Page 19 line53 5h vs. page 19 line5 4hr???*

Authors’ reply: The experimental value is 4 h. We corrected the misprint and carefully checked the text of the manuscript.

Reviewer 4 raised the following issue: *Page 20 line 43: define Arrhenius equation or add a reference for it*

Authors’ reply: We added the Arrhenius equation (5) to the revised manuscript and showed how it is related to the kinetic equation (2).

Reviewer 4 raised the following issue: Page 30 line 49: DFT result is more for gas phase reactions, while the measurement result is for solid phase. Any reference for such comparison used in this paper or address such difference?