

Effect of three alkaline impurities on the pressure of 1,2,4-triazole pyrolysis gas

Chenyang Pu^{1,2,b}, Bin Zhang^{1,a,*}

¹ International Center for Chemical Process Safety, Nanjing Tech University, Nanjing 211816, China

² Changzhou Feilian Technology Co., Ltd, Changzhou 213161, China

^a bzhang@njtech.edu.cn, ^b p1648748067@163.com

Abstract. 1,2,4-triazole is now widely used in the production of pesticides and medicine, and progress has been made in the application of materials. The structural characteristics of 1,2,4-triazole with high nitrogen content will cause it to the release of a large amount of gas when it occurs pyrolysis, which may have a certain impact on industrial production safety. In the industrial process, there will be some other impurities mixed into it, so the influence of these impurities on the 1,2,4-triazole pyrolysis gas is worth exploring. In this study, the adiabatic acceleration calorimeter was used to simulate the adiabatic conditions to study the pressure value of the gas generated by the pyrolysis of 1,2,4-triazole itself, and the influence of the addition of three basic impurities on the overall pyrolysis pressure value. Experiments show that these three impurities can affect the pressure value of pyrolysis gas in different degrees. The results can provide reference for the loss prevention and control of 1,2,4-triazole in industrial production.

Keywords: 1,2,4-Triazole; Impurities; Pyrolysis; ARC; Pressure.

1. Introduction

1,2,4-Triazole is a kind of nitrogenous organic matter, its character is colorless needle-like crystal, soluble in water and ethanol[1]. As an important intermediate in the production of medicine and pesticides, 1,2,4-triazole has an irreplaceable value, such as the production of triadimefon, paclobutrazol, uniconazole and diniconazole and other pesticides, and the production of fluconazole and other medicines[2]. 1,2,4-Triazole, as a member of the triazole organic compounds, also has a large heat release, so it has a relatively large potential thermal risk[3]. 1,2, 4-Triazole is used in so many production, then the safety of industrial production needs to be guaranteed, which is reflected in two aspects, one is the understanding of its own thermal risk, and the other is the thermal risk of the raw materials involved in the production process and the material mixed with 1,2, 4-triazole[4]. If it occurs pyrolysis, then whether the gas generated by this process will lead to the occurrence of accidents needs to be studied and discussed to avoid some incalculable consequences[5]. Related accidents have also occurred in recent years, which are summarized in the **Table 1**.

Table 1 Statistics of accidents caused by triazole

Year	Accidents
2005	An explosion occurred in a benzotriazole distillation column at a chemical plant in Rugao, Jiangsu Province, China.
2015	A chemical plant in Taizhou, Jiangsu Province, China, exploded due to the violent decomposition of benzotriazole under the influence of impurities in off-working conditions.
2019	On April 15, 2019, Qilu Tianhe Pharmaceutical Co., Ltd. in Jinan, Shandong Province, China, suffered a major fire and poisoning accident. The main reason is that the company in the process of reforming the basement pipeline, illegal fire operation ignited the refrigerant accelerator, which contains benzotriazole, the accident caused 10 deaths, 12 injuries, direct economic losses of 2.62 million dollar.

Some existing studies focus on its heat release. The pyrolysis of 1,2,4-triazole was studied by

using Differential Scanning Calorimeter (DSC), and its melting point and initial decomposition temperature were obtained. The pyrolysis of 1, 2, 4-triazole was studied by DSC. For 1, 2, 4-triazole, there is an endothermic peak in the range of 112-135 °C, corresponding to the melting of 1, 2, 4-triazole at 119 °C. The heat release region contains three stages, the small first stage is decomposed in the range of 300-342 °C, the large second stage occurs in the range of 320-430 °C, and the third stage appears in the range of 430-486 °C[6]. These data may be different when using different brands and types of test instruments. For example, when using DSC testing, the sensitivity of different materials to the heat release of substances is not the same, and there will be certain differences in the obtained thermal parameters[7]. Different from the use of instruments, some scholars use the simulation method to study the passage. The ground and transition states of 1,2,4-triazoles were investigated by using Sparatan '10 simulation software. After model optimization, the values of ΔE , ΔS and ΔG are the energy differences between the ground state (GS) and transition state (TS)[6]. The existing research on 1,2,4-triazole is currently limited to the pyrolysis representation analysis of 1,2,4-triazole itself and its derivatives[8]. However, in view of the structural characteristics of 1,2,4-triazole, no scholars have made relevant research on the pressure rise caused by its pyrolysis and release of gas. The pyrolysis of 1,2,4-triazole not only releases a lot of heat, but also produces a lot of gas. For the safety of industrial production, it is necessary to have a certain understanding of its gas generation process. At the same time, some other substances will inevitably be added in the production process, so what impact these substances have on the gas production of 1,2,4-triazole cannot be ignored[9]. However, the existing research is negligent in this respect, which leads to certain safety risks in related industrial production.

In this study, we selected three substances that are often mixed with 1,2,4-triazole in the industrial production of fluconazole and flutriafol. They are potassium carbonate, sodium bicarbonate and sodium hydride. In order to have a better study effect, the addition amount set in this study is 10% and 20% of the total mass, respectively. In this study, adiabatic acceleration calorimeter (ARC) was used to simulate the worst-case cooling failure and to collect the relationship between gas pressure and temperature with respect to time. This study revealed the change of gas pressure of 1,2,4-triazole pyrolysis, while adding other impurities to study their influence on the pressure of 1,2,4-triazole pyrolysis gas.

2. Experiments

2.1 Substances

All reagents used in this study are laboratory analytical grade and do not require further purification. The basic information of the substances is listed in the **Table 2**.

Table 2 Basic information about the substances used in this study

Substances	Manufacturer	Purity
1,2,4-triazole	Shanghai Aladdin	99%
Potassium carbonate	Shanghai Titan	99.5%
Sodium bicarbonate	Shanghai Titan	99.5%
Sodium hydride	Shanghai Titan	60%

2.2 Adiabatic experiments

The adiabatic acceleration calorimeter (ARC) produced by British Thermal Hazard Technology Limited (THT) was used in this study. The lowest detection sensitivity of ARC is 0.02°C/min, and the highest detection sensitivity is 200°C/min. In this study, a standard heat-wait-search (H-W-S) model was used to track the exothermic self-heating rate of samples[10]. The total mass of the

weighed sample is 0.6 g and the weighed sample is placed in a 10 mL Hastelloy ball. ARC set the heating step to 5 °C /min, wait for the search heat release time to 15 minutes, and the temperature range is 30 °C to 400 °C. Since ARC is measured under adiabatic conditions, it is possible to accurately simulate the thermal behavior of the sample during actual use. When the sample occurs thermal runaway, ARC can quickly detect the rapid change of heat, so as to timely abort the experiment and prevent the sample from burning or explosion and other dangerous situations, it has high precision, high sensitivity, wide temperature range and so on[11].

2.3 Modification of thermal inertia factor

The energy released by the substance in the ideal adiabatic state is only used as the temperature rise of the substance in the adiabatic system, but in the actual ARC experimental measurement, the heat released during the pyrolysis reaction of the sample to be measured not only increases its own temperature, but also heats the sample chamber of the instrument[12]. At this time, it is necessary to modify the adiabatic data obtained by the experiment, and the correction formula is shown in Eq.(1) [13]:

$$\varphi = 1 + \frac{(mC_p)_c}{(mC_p)_s} \quad (1)$$

In Eq.(1), φ is the thermal inert factor, m is the mass, C_p is the specific heat capacity of the substance, c represents the reactor, and s represents the reaction sample.

3. Results and discussion

3.1 1,2,4-triazole

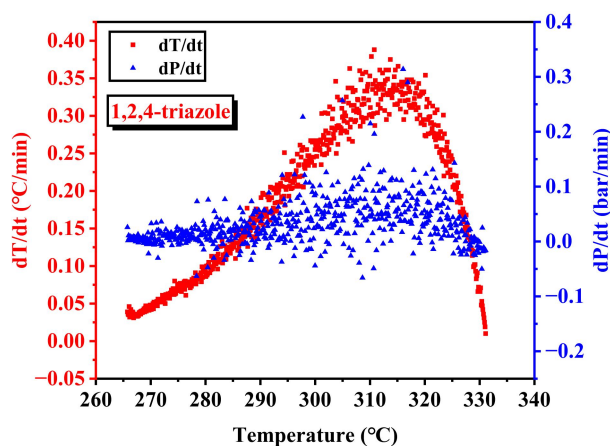


Fig 1 Temperature rise rate and pressure change rate of 1, 2, 4-triazole in adiabatic exothermic reaction versus temperature.

The Fig 1 shows the temperature rise rate and pressure change rate of 1, 2, 4-triazole in adiabatic exothermic reaction versus temperature. As a whole, the temperature rise rate increases first and then decreases with the increase of temperature. The pressure change rate is relatively stable at the initial stage of the reaction, and increases with the increase of temperature. From the point of view of temperature rise rate, the pyrolysis reaction process of 1,2,4-triazole is relatively slow, indicating that its instant release of heat is relatively small, so the thermal risk should be more focused on the overall heat release. From the point of view of the pressure rise rate, it can also be seen that the temperature of the most intense pyrolysis reaction is 314 °C, but the instantaneous pressure change is small, which also indicates that the possibility of explosion of 1,2,4-triazole during pyrolysis is relatively small, and more attention should be paid to the final gas production of 1,2,4-triazole pyrolysis.

3.2 Potassium carbonate

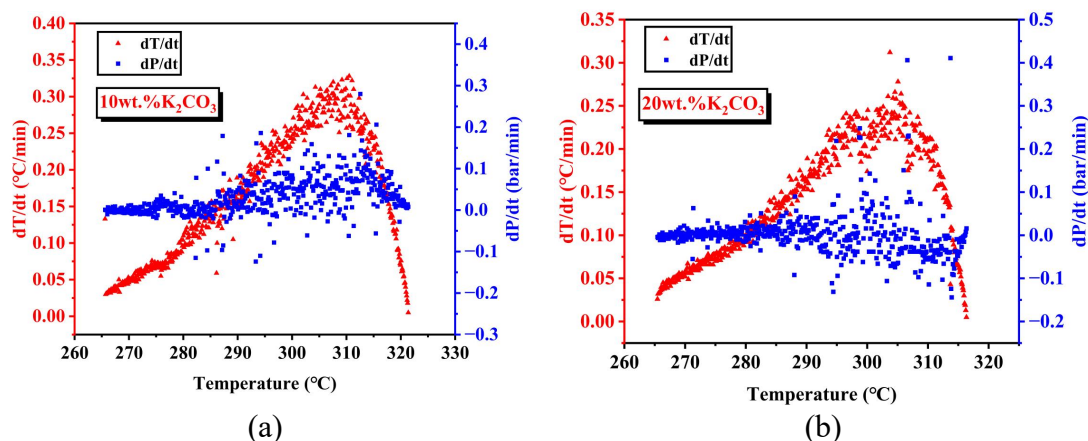


Fig 2 Temperature rise rate and pressure change rate of samples containing different proportions of potassium carbonate in adiabatic exothermic reaction versus temperature.

The Fig 2 shows the temperature rise rate and pressure change rate of samples containing different proportions of potassium carbonate in adiabatic exothermic reaction versus temperature. In both cases, the rate of temperature rise and the rate of pressure change with temperature did not change. However, the maximum temperature rise rate decreases and the maximum pressure rise rate increases, and the temperature corresponding to these two parameters also decreases. This trend indicates that the introduction of potassium carbonate will bring the pyrolysis reaction of 1,2,4-triazole to an early end, reduce the final temperature of the reaction, but increase the overall gas production, thus increasing the gas pressure. The introduction of potassium carbonate improves the thermal safety of 1,2,4-triazole to some extent.

3.3 Sodium bicarbonate

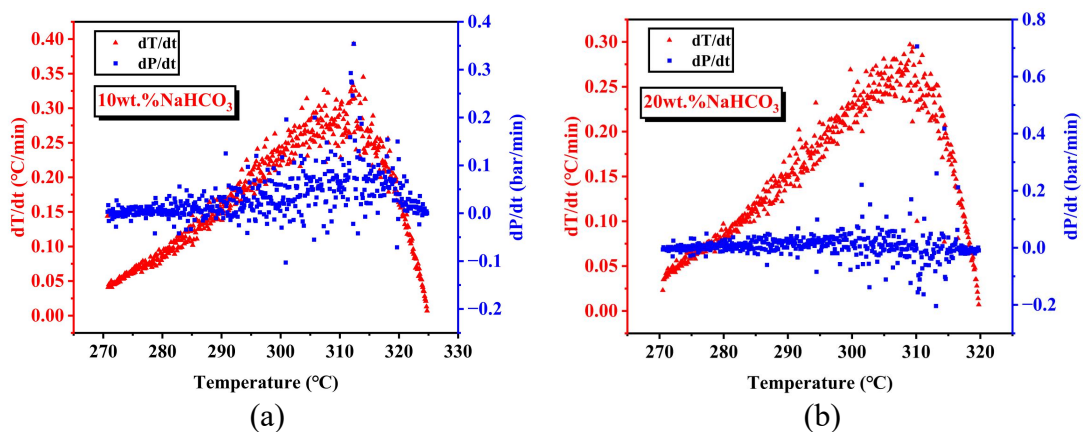


Fig 3 Temperature rise rate and pressure change rate of samples containing different proportions of sodium bicarbonate in adiabatic exothermic reaction versus temperature.

The Fig 3 shows the temperature rise rate and pressure change rate of samples containing different proportions of sodium bicarbonate in adiabatic exothermic reaction versus temperature. With the increase of sodium bicarbonate content, the release of gas becomes relatively flat in the whole process of pyrolysis, but the maximum pressure rise rate increases significantly. With the increase of sodium bicarbonate content, the final temperature of the overall pyrolysis reaction gradually decreases, while the overall gas production will increase substantially, resulting in a substantial increase in gas pressure. The introduction of sodium bicarbonate improves the thermal stability of 1,2,4-triazole to some extent.

3.4 Sodium hydride

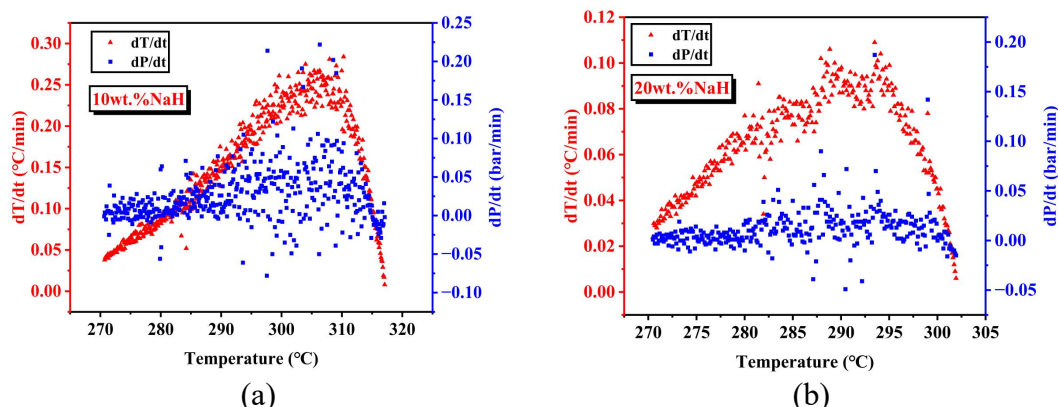


Fig 4 Temperature rise rate and pressure change rate of samples containing different proportions of sodium hydride in adiabatic exothermic reaction versus temperature.

The Fig 4 shows the temperature rise rate and pressure change rate of samples containing different proportions of sodium hydride in adiabatic exothermic reaction versus temperature. With the increase of sodium hydride content, the rise rate of gas pressure decreases significantly in the whole process of pyrolysis, and the maximum pressure rise rate decreases significantly compared with other conditions. With the increase of sodium hydride content, the final temperature of the whole pyrolysis reaction will decrease significantly, and the overall gas production will decrease significantly, so that the gas pressure will decrease significantly. The introduction of sodium hydride improves the thermal safety of 1,2,4-triazole to some extent.

4. Conclusion

In this paper, the temperature rise rate and pressure rise rate of the pyrolysis of pure 1,2,4-triazole were studied by ARC. The effect of adding potassium carbonate, sodium bicarbonate and sodium hydride on the pyrolysis of 1,2,4-triazole was also studied. In conclusion, this paper raises the following key points.

- The pyrolysis of 1,2,4-triazole is a relatively slow process, and the temperature rise rate and pressure rise rate are relatively small. Therefore, more attention should be paid to the final state of pyrolysis of 1,2,4-triazole.
- All the impurities selected in this study can improve the thermal safety of 1,2,4-triazole to varying degrees, and the introduction of sodium hydride can reduce the release of pyrolysis gas, thereby reducing pressure.

Acknowledgments

The authors are grateful for the support given by the Science and Technology Program of Changzhou City (CJ20230019).

Reference

- [1] A.A. Abbas, K.M. Dawood. Chapter Four - Recent developments in the chemistry of 1H- and 4H-1,2,4-triazoles, in: E.F.V. Scriven, C.A. Ramsden (Eds.) *Advances in Heterocyclic Chemistry*. Academic Press, 2023, pp: 209-273.
- [2] S.M. Hashemi, H. Badali, H. Irannejad, M. Shokrzadeh, S. Emami. Synthesis and biological evaluation of fluconazole analogs with triazole-modified scaffold as potent antifungal agents. *Bioorganic & Medicinal Chemistry*, 2015, 23: 1481-1491.

- [3] J. Zhang, L. Chen, L. Zhao, G. Jin, W. He. Experimental insight into interaction mechanism of 1H-tetrazole and nitrocellulose by kinetics methods and TG-DSC-FTIR analysis. *Journal of Analytical and Applied Pyrolysis*, 2023, 169: 105853.
- [4] A. Yu, N. Zhou, X. Liang, M. Hua, X. Pan, Y. Jiang, J. Jiang. Process hazard and decomposition mechanism of benzoyl peroxide in the presence of incompatible substances. *Journal of Molecular Liquids*, 2023, 372: 121146.
- [5] T. Opsomer, W. Dehaen. 5.02 - 1,2,4-Triazoles, in: D.S. Black, J. Cossy, C.V. Stevens (Eds.) *Comprehensive Heterocyclic Chemistry IV*. Elsevier, Oxford, 2022, pp: 78-121.
- [6] W. Kowhakul, D. Inoue, Y. Nakagawa, H. Masamoto, M. Shigematsu. Thermal decomposition mechanisms of 1H-1,2,4-triazole derivatives: A theoretical study. *Journal of Loss Prevention in the Process Industries*, 2017, 50: 37-54.
- [7] S. Vyazovkin, K. Chrissafis, M.L. Di Lorenzo, N. Koga, M. Pijolat, B. Roudit, N. Sbirrazzuoli, J.J. Suñol. ICTAC Kinetics Committee recommendations for collecting experimental thermal analysis data for kinetic computations. *Thermochimica Acta*, 2014, 590: 1-23.
- [8] M. Sikorska-Iwan, B. Modzelewska-Banachiewicz. Thermal behaviour of 1,2,4-triazole and 1,2,4-triazine derivatives. *Journal of Thermal Analysis and Calorimetry*, 2005,81 : 119-123.
- [9] X. Cui, X. Gui, J. Hu, Z. Gong, R. Zhou, D. He, S. Lin, Y. Dong, Y. Tu. Probe into effect of the initiator on the thermal runaway hazards of methyl methacrylate bulk polymerization. *Journal of Loss Prevention in the Process Industries*, 2023, 83: 105074.
- [10] Z.-C. Guo, L.-P. Chen, W.-H. Chen. Estimation of kinetic parameters from adiabatic calorimetric data by a hybrid Particle Swarm Optimization method. *Chemical Engineering Research and Design*, 2017, 122: 273-279.
- [11] M. Fujita, Y.-i. Izato, Y. Iizuka, A. Miyake. Thermal hazard evaluation of runaway polymerization of acrylic acid. *Process Safety and Environmental Protection*, 2019, 129: 339-347.
- [12] A.A. Kossoy, J. Singh, E.Y. Koludarova. Mathematical methods for application of experimental adiabatic data – An update and extension, *Journal of Loss Prevention in the Process Industries*. 2015,33: 88-100.
- [13] D.I. Townsend, J.C. Tou. Thermal hazard evaluation by an accelerating rate calorimeter. *Thermochimica Acta*,1980, 37: 1-30.