# Effects of UV Irradiation fo r Thermal Stability of ADVN

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## ABSTRACT

2,2'-Azobis(2,4-dimethyl)valeronitrile (ADVN), an azo compound, is widely used as free initiator in the polymer industry due to its specific chemical structure, N-N bond, which can supply abundant free radicals and high energy to promote cross-linking and initial reaction. It is also applied for dope dyeing. However, ADVN is extremely photo sensitive. The thermal decomposition properties may be changed by UV irradiation, resulting in amounts of heat and toxic gas being released that can cause human injury or environmental disruption. To avoid the above thermal hazards for ADVN, we studied the thermal stability characteristics and decomposition products with different exposure time of UV irradiation by calorimetric and product analysis technology for ensuring the safe use, storage, transportation, and discard conditions. Kinetic parameters were also obtained by various kinetic models to predict the kinetic behaviors of ADVN. Historically, the concerns of environmental protection and sustainable energy are crucial topics for industrial process. In this study, a preventive mechanism was established for eliminating the hazards of highly energetic chemicals to reduce the occurrence of industrial accidents.

***Keywords:*** free initiator, calorimetric and product analysis technology, kinetic parameters, kinetic behaviors, environmental protection

## 1 INTRODUCTION

The evaluation of thermal characteristics for reactive chemicals has been a major concern of chemical industries. The main reason of many accidents is due to the lack of knowledge of reactants, intermediates, products, or various catalysts. In general, a small change of temperature or pressure may sporadically cause a serious runaway reaction for highly energetic chemicals. The most hazardous information could be obtained from the literature, but if this information is incomplete, the related safety parameters should be assessed by thermal analysis technology [1].

2,2'-Azobis(2,4-dimethyl)valeronitrile (ADVN), a common azo compound, is an excellent free radical supplier for a chemical process. When azo is involved in an exothermic reaction, it could abundantly provide free radical and energy for synthesis of organic compounds or polymer, such as styrene, methyl acrylate, epoxy resin, or propylene, as initiator, cross-linking, or curing agent. However, ADVN has thermal instability and sensitivity because of its N–N structure, which may incur violent thermal decomposition by external fire, other igniting sources, or irradiation. Thus, it is crucial that we understand the thermal hazard behaviors for azo which can be used efficiently and safely during operating, transportation, and storage [2].

In the past, most of the research of ADVN for runaway reaction has been the analysis of pure substances. However, the photo effect of ADVN has rarely been explored. Because ADVN has extreme photo sensitivity with UV, the decomposition mechanism may be changed with exposure time and mass. Often, UV irradiation exists ubiquitously, and even its intensity may be different from located latitudes. Simultaneously, if the optical isolation of UV for package or container is not complete, the photo effect may decrease the thermal stability of ADVN, resulting in the risk of thermal runaway reaction being increased [3].

We used calorimetric technology and kinetic models to obtain the thermal stability parameters, such as apparent onset temperature ($T_0$), peak temperature ($T_p$), final temperature ($T_f$), apparent activation energy ($E_a$), frequency factor ($\ln k_0$), and reaction order ($n$), to establish the hazard characteristics and to explore the decomposition products by employing differential scanning calorimetry (DSC) and thermogravimetry (TG) for determination of UV effects of ADVN [4].

## 2 EXPERIMENTAL AND METHOD

### 2.1 Sample

The sample chosen was ADVN 98 mass%, which was purchased from ACE Chemical Corp, Taoyuan, Taiwan. ADVN is light sensitive and thermally unstable, so it should be keep in a dark space and at low temperature of 4.0 $^{o}$C. The exposure time and intensity of UV irradiation is 6.0, 12.0, and 24.0 hr, and 100.0 W, respectively, for UV effect of ADVN.

### 2.2 Differential Scanning Calorimetry (DSC)

Temperature-controlled thermal curves of DSC experiments facilitate to understand the exothermic or endothermic reaction of a chemical, such as thermal decomposition reaction, curing reaction, crystallization, or phase change. Thus, it can be used as a safety assessment methodology to provide the thermal hazard information for ADVN. The type of DSC is selected in the Mettler DSC 821$^{e}$. To investigate thermal characteristics of ADVN with UV irradiation, we heated it from 30.0 to 300.0 $^{o}$C at different heating rates, here, 1.0, 2.0, 4.0, and 8.0 $^{o}$C min$^{-1}$, using the DSC test. The sample amount for each experiment was approximately 1.5–5.0 mg and the sample was sealed in a gold-plate crucible [5].

### 2.3 Thermogravimetry (TG)

Thermogravimetry, from PerkinElmer Clarus 680, was used to analyze the thermal decomposition products for ADVN and ADVN exposed by UV with different time 6.0, 12.0, and 24.0 hr. The TG experiments were performed from ambient temperature to 300.0 $^{o}$C with heating rates of 1.0, 5.0, 10.0, and 20.0 $^{o}$C min$^{-1}$ in nitrogen gas purged at a flow rate of 100.0 mL min$^{-1}$ [6].

### 2.4 Evaluation of integral procedural decomposition temperature (*IPDT*)

An evaluation parameter of thermal stability, *IPDT*, was used to consider the overall thermal stability during the decomposition process. Because thermal stability involves three important factors of chemicals including initial reaction, end reaction, and ratio for mass loss, *IPDT* was created based on different thermogravimetric regions of the TG experimental curve. The equations of *IPDT* are as follows [7]:

$$IPDT = A^{\circ} \times K^{\circ} \times \left(T_f - T_i\right) + T_i \quad (1)$$

$$A^{\circ} = \left(S1 + S2\right)/\left(S1 + S2 + S3\right) \quad (2)$$

$$K^{\circ} = \left(S1 + S2\right)/\left(S1\right) \quad (3)$$

where $A^{o}$ and $K^{o}$ is the ratio of mass loss from TG experimental curve for different partitioned regions. $T_i$ is mass loss onset temperature and $T_f$ is mass loss final temperature. S1, S2, and S3 are different partitioned regions from TG plots. S1 is thermogravimetric area under TG curve; S2 is thermogravimetric area of non-mass loss; S3 is thermogravimetric area above TG curve. The schematic diagram of *IPDT* is delineated in Fig. 1.

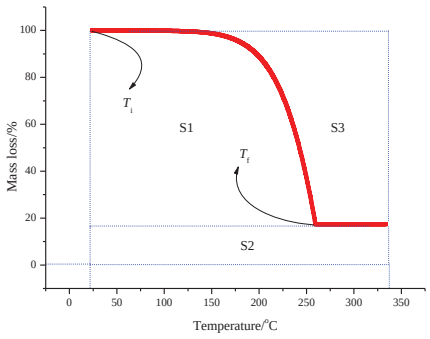


Figure 1: Schematic diagram for conception of *IPDT*.

### 2.5 Non-linear regression method to determine reaction kinetic of ADVN/UV irradiation

In general, typical fundamental reactions of azo are *n*th order and autocatalytic; they may be composed of either a one-stage or a multi-stage reaction. However, linear regression methods, such as Kissinger, Ozawa, or Friedman model, are unable to predict complex chemical reactions of azo. Therefore, the non-linear regression

method is usually used to directly fit the thermal curve of chemicals through kinetic models to appraise the chemical reaction stages and various kinetic parameters, such as $n$, $E_a$, $A$, and autocatalytic constant ($z$) for use in chemical engineering processes. The *n*th order and autocatalytic reaction models are presented in Eqs. (4) and (5), correspondingly [8, 9]:

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E_a}{RT}\right)(1-\alpha)^n \quad (4)$$

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E_a}{RT}\right)(1-\alpha)^{n_1}(\alpha^{n_2} + z) \quad (5)$$

where $n_1$ and $n_2$ are reaction orders for the two different reaction stages, $\alpha$ is degree of conversion, and $z$ is autocatalytic constant.

## 3 RESULTS AND DISCUSSION

### 3.1 TG results

TG can be used to observe the relationship between temperature and mass loss for the decomposition or combustion reaction for chemicals. Therefore, the thermal stability of chemicals can be evaluated in a heating system.

Figure 2 shows mass loss versus temperature diagram from TG test for ADVN and ADVN with different exposure time 6.0, 12.0, and 24.0 hr of UV irradiation at heating rate 20.0 $^{o}$C min$^{-1}$. There are two decomposition stages for ADVN and ADVN exposed with UV, and the main decomposition stage is the second stage. We found that when ADVN exposed by 6.0 and 12.0 hr of UV, the profiles of TG curve are not obviously different between each other and for both $T_0$ is 78.0 $^{o}$C. However, although the $T_0$ of first stage of ADVN is close to ADVN exposed by 24 hr of UV, the $T_0$ of second decomposition stage is shortened from 132.0 to 127.0 $^{o}$C and the mass loss is increased from 80.0 to 70.0%. According to literature reports [10], $T_0$ and mass loss can be used to determine the thermal stability for chemicals. Therefore, if ADVN is exposed to UV for over 24.0 hr, the thermal decomposition behavior may be changed, causing abnormal aging or thermal runaway during storage, transportation, and use conditions.

Table 1**:** Thermal stability parameters by TG test for ADVN and ADVN exposed with 6.0, 12.0, and 24.0 hr of UV at heating rate 20.0 $^{o}$C.

| Sample | $T_{01}$ /$^{o}$C | $T_{02}$/ $^{o}$C | Mass loss (first stage)/% | Mass loss (second stage)/% | *IPDT* /$^{o}$C |
|---|---|---|---|---|---|
| ADVN/ No UV | 78.6 | 132.1 | 30.0 | 70.0 | 119.0 |
| ADVN/6 hr of UV | 78.7 | 133.2 | 30.0 | 70.0 | 125.0 |
| ADVN/12 hr of UV | 78.9 | 133.5 | 25.0 | 85.0 | 124.0 |
| ADVN/24 hr of UV | 77.9 | 127.3 | 20.0 | 80.0 | 112.0 |

In addition, we compared the *IPDT* for ADVN and ADVN with different exposure time 6.0, 12.0, and 24.0 hr of UV irradiation, corresponding to the value of 119.0, 125.0, 124.0, and 112.0, respectively. The results show that when the exposure time of UV is 6 and 12 hr, the *IPDT* could be increased, but *IPDT* of ADVN is decreased after exposing to 24.0 hr of UV. In general, 24.0 hr is usually considered as a standard emergent time or transportation for chemical industries, so that ADVN should avoid being contacted with UV irradiation under any conditions.

Based on above-mentioned results, the following experiments focused on the UV effect for ADVN with exposure time of 24.0 hr. ADVN exposed by UV of 24.0 hr was tested by TG at heating rate 1.0, 5.0, 15.0, and 20.0 °C, as shown in Fig. 3. We also compared the *IPDT* for the results of four heating rates and the value of *IPDT* was increased from 101.0 to 119.0 °C with increasing heating rate. Moreover, we plotted the *IPDT* versus heating rate curve that there was an extremely high $R^2$ value from linear regression. According to the results, the heating rate can determine the *IPDT* for decomposition reaction of ADVN exposed by UV of 24.0 hr. From the viewpoint of safety design, when the operating conditions of chemical process involving ADVN exposed by UV of 24.0 need low reaction temperature, a low heating rate should be proper. However, a high heating rate is better for high reaction temperature. *IPDT* will be used as basic and rudimentary and dependable thermal stability parameter for future study. The linear dependence of *IPDT* with different heating rates is depicted in Fig. 4.

Table 2**:** Thermal stability parameters by TG test for ADVN exposed with 24.0 hr of UV at heating rates of 1.0, 5.0, 10.0, and 20.0 °C $min^{-1}$.

| Sample | $T_{01}$/°C | $T_f$/°C | *IPDT*/°C |
|---|---|---|---|
| ADVN/No UV | 55.0 | 148.0 | 119.0 |
| ADVN/6.0 hr of UV | 72.0 | 158.0 | 125.0 |
| ADVN/12.0 hr of UV | 77.0 | 162.0 | 124.0 |
| ADVN/24.0 hr of UV | 77.0 | 175.0 | 112.0 |

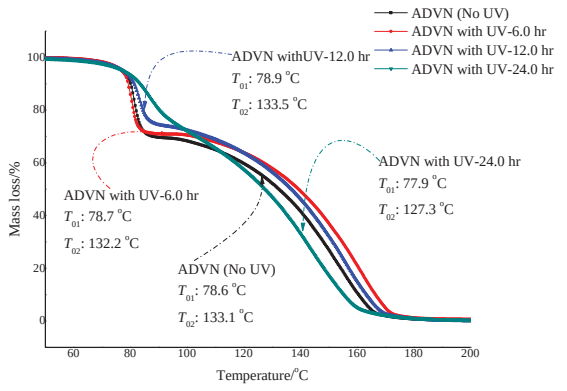


Figure 2: TG thermal curve of ADVN and ADVN with different exposure time of UV/6.0, 12.0, and 24.0 hr.

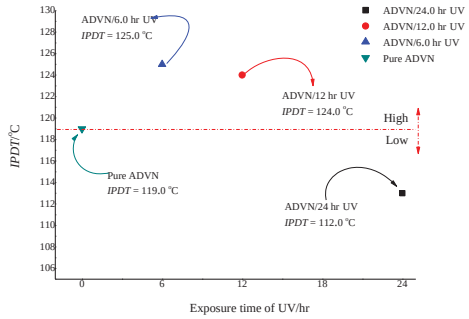


Figure 3: Calculation of IPDT for ADVN with different exposure time of UV/6.0, 12.0, and 24.0 hr by TG test.

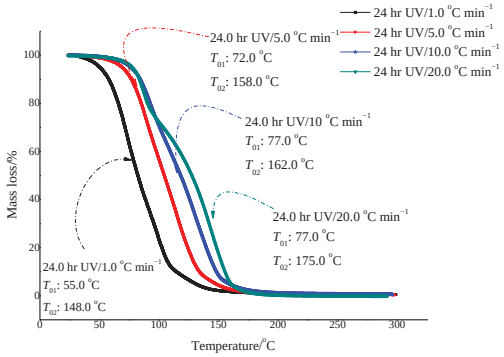


Figure 3: TG thermal curve of ADVN with UV/24 hr at heating rate 1.0, 5.0, 10.0, and 20.0 °C $min^{-1}$.

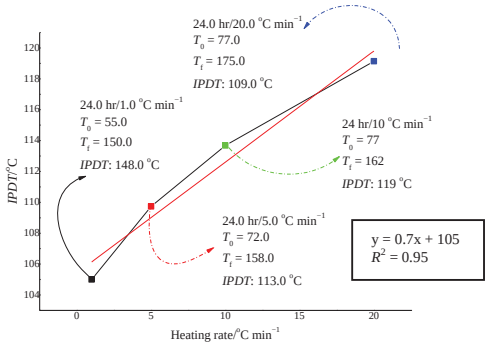


Figure 4: Linear dependence of *IPDT* for ADVN with 24.0 hr UV at heating rate 1.0, 5.0, 10.0, and 20.0 °C $min^{-1}$.

### 3.2 Determination of kinetic models for ADVN with UV irradiation

To investigate the reaction mechanism and predict the kinetic behaviors for ADVN exposed with 24.0 hr of UV, non-isothermal kinetic analysis was conducted based on DSC data, which is illustrated in Fig. 5. Figures 6 and 7 display heat production and heat production rate versus time, respectively, by experiments and simulations. From simulation results, we observed that there was great curve fitting and almost the same kinetic parameters, including $n$, $E_a$, $A$, and $\Delta H_d$, for both plots of heat production and heat production rate versus time of ADVN exposed with 24.0 hr of UV at heating rates of 1.0, 2.0, 4.0, and 8.0 °C $min^{-1}$ by

simple *n*th order kinetic models. Therefore, ADVN exposed with 24.0 hr of UV is determined as an *n*th order reaction, not autocatalysis, and the obtained kinetic parameters can be used to predict other heating rare or reaction temperature for reliable information in the future study. The related kinetic parameters are demonstrated in Table 1.

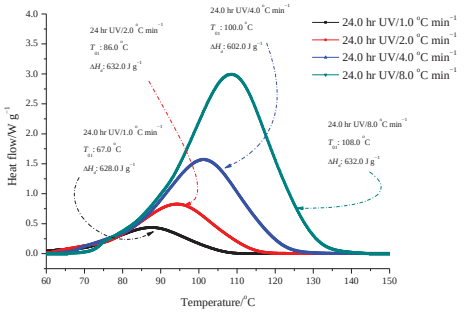


Figure 5: DSC thermal curves of ADVN with 24.0 hr UV at heating rates of 1.0, 2.0, 4.0, and 8.0 °C min$^{-1}$.

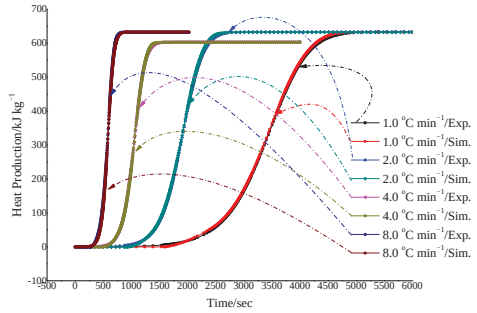


Figure 6: Heat production versus time of model fitting with non-isothermal DSC at heating rate of 1.0, 2.0, 4.0, and 8.0 °C min$^{-1}$ via experiment and simulations.

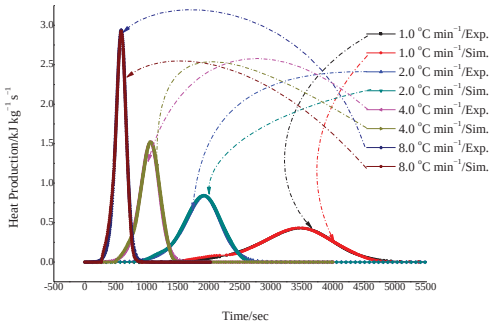


Figure 7: Heat production rate versus time of model fitting with non-isothermal DSC at heating rate of 1.0, 2.0, 4.0, and 8.0 °C min$^{-1}$ via experiment and simulations.

Table 3: Reaction kinetic simulation for ADVN with UV/24.0 hr using non-linear regression method at heating rates of 1.0, 2.0, 4.0, and 8.0 °C min$^{-1}$.

| $\beta$/°C min$^{-1}$ | $E_a$/kJ mol$^{-1}$ | ln ($A$)/s$^{-1}$ | Reaction order/$n$ | $\Delta H_d$ /kJ kg$^{-1}$ |
|---|---|---|---|---|
| 1.0 | 137.0 | 39.0 | 1.4 | 632.0 |
| 2.0 | 144.0 | 42.0 | 1.5 | 632.0 |
| 4.0 | 140.0 | 40.0 | 1.4 | 603.0 |
| 8.0 | 138.0 | 39.0 | 1.5 | 633.0 |

## 4 CONCLUSIONS

Based on the experimental results, when ADVN is exposed to 24.0 hr of UV, $T_0$ is not only shortened, but also the mass loss can be increased at the main decomposition stage. By no means, should we isolate UV contacting ADVN under any situations, avoiding ADVN being ageing or thermal runaway. In addition, *IPDT* and non-isothermal kinetic models are carried out to evaluate thermal stability, reaction mechanism, and related kinetic parameters of ADVN exposed with UV irradiation. This study provides significant information on a safer process under changing exposure time of UV for ADVN. Furthermore, the research method may serve as an important benchmark for handling potentially hazardous chemicals, here azo compounds.

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