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Study on thermal degradation and kinetic characteristics of insulating materials used in high voltage switchgear

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Abstract. This study adopts the FT-IR, DSC, TG and other methods, studied the commonly used in high-voltage switchgear XLPE, EP and organic silicone materials in the same heating rate under thermal degradation properties of three kinds of insulating materials by calculation under different temperature of pyrolysis reaction apparent activation energy E and refers to the former factor to determine its dynamic characteristics. The results showed that the activation energies of epoxy resin, crosslinked polyethylene and silicone rubber were 63.53 kJ • mol-1, 99.66 kJ • mol-1, 62.59 kJ • mol-1, respectively. The pre-exponential factors were 3.2 × 105 • s-1, 4.3 × 107 • s-1 and 1386.9 • s-1, respectively.

Keywords: High voltage switchgear; Crosslinked polyethylene; Hermal ageing; Thermal decomposition characteristics; Thermal decomposition gas

1. Introduction

Insulation components such as contact boxes, insulators, and wall bushings inside the high-voltage switchgear are often overheated and decomposed due to excessive load current and poor contact, which seriously affects the safe operation of the power grid [1]. Cross-linked polyethylene, epoxy resin, and silicone rubber, as the main insulating materials for high-voltage switchgear, have different advantages and disadvantages. Cross-linked polyethylene insulation materials have been widely used and developed in power transmission projects due to their light weight, high operating temperature, excellent electrical properties, large transmission capacity, and lightweight structure [2]. However, during long-term operation, the cross-linked polyethylene insulating material will be aged by various stresses such as electricity, heat, and machinery, resulting in irreversible defects or structural damage, resulting in crystallinity and melting temperature, dielectric properties, mechanical properties, and mechanical properties. Performance and insulation performance decline [3-5], resulting in power failure and shortened service life. Epoxy resin has the advantages of excellent adhesion, chemical stability, mechanical properties, dimensional stability, insulation, low shrinkage, easy processing and low cost; however, the cured epoxy resin has large internal stress and poor toughness. And the glass transition temperature (Tg) and thermal decomposition temperature are low, and it is easy to lose mechanical strength or even decompose at high temperature [6]. Silicone rubber material has the advantages of good high and low temperature resistance, ozone resistance, ultraviolet light resistance and weathering resistance [7], and is often used in the insulating parts of high-voltage switchgear, but its solvent resistance

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and oil resistance are relatively poor, which limits the its wider use [8]. This study is based on three commonly used XLPE, EP and silicone rubber materials for high-voltage switchgear from the perspective of thermodynamics and kinetics. Using FITR, DSC, TG and other methods, the thermal degradation and kinetic properties of three polymer materials at the same heating rate were studied, and the effect of temperature on the pyrolysis of polymer materials for high-voltage switchgear was investigated.

2. Materials and methods

The experimental materials are cross-linked polyethylene insulating sleeve, epoxy resin insulating board, and silicone rubber insulating sleeve. DHG-9053A Electric Heating Constant Temperature Drying Oven, Shanghai Jinghong Experimental Equipment Co., Ltd.; PTYE5120 Electronic Analytical Balance, Fuzhou Huazhi Scientific Instrument Co., Ltd.; Nicolet iS5 Fourier Transform Infrared Spectrometer, Thermo Fisher Scientific, USA; STA409PC /PG type comprehensive thermal analyzer, Germany NETZSCH Instrument Manufacturing Co., Ltd., nitrogen atmosphere, nitrogen flow rate 20mL/min, sample mass 2mg～4mg, heating rate 10℃/min, temperature range 60 ～ 600 ℃ ; A801S type contact angle test Instrument, Shanghai Solon Information Technology Co., Ltd.; DSC 204 Differential Scanning Calorimeter (DSC), NETZSCH, Germany, nitrogen atmosphere, heating rate 10 °C/min, temperature range 60 °C-350 °C.

3. Results and Discussion

3.1 Sample infrared spectrum analysis

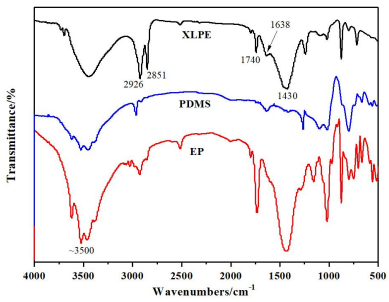

Figure 1. FT-IR infrared spectra of three materials

In the infrared spectrum of the cross-linked polyethylene material in Fig. 1, 2750cm-1-3000cm-1 is the absorption band of saturated carbon-hydrogen bond-CH, methylene-CH2, methyl-CH3, and the wave number is 720 cm-1. In-plane rocking vibrations corresponding to the long-chain methylene-CH2 in the amorphous region. The wavenumber of 1468 cm-1 corresponds to the antisymmetric bending vibration of methyl-CH3 and the scissor bending vibration of -CH2, and the vibration frequencies of the two coincide. 1638 cm-1 corresponds to the stretching vibration peak of olefin C=C[9]. In addition, 1740 cm-1 corresponds to the stretching vibration of carbonyl-C=O, which indicates that this type of material undergoes oxidation reaction to generate carbonyl during use, and the carbonyl absorption peak can be used as a characteristic peak to characterize its heat resistance [10]. In the infrared spectrum of epoxy resin material, 1460 cm-1 is the characteristic absorption peak of benzene ring, indicating that the epoxy resin material contains benzene ring structure; 2960 cm-1-2850 cm-1 is the contraction vibration peak of CH bond; 1734 cm -1 is the

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characteristic absorption peak of C=O; the wavelength of 3435.49 cm-1 is the hydroxyl absorption peak of epoxy resin [11]; the epoxy group in the epoxy resin reacts with the amine group in the curing agent, and after ring-opening A large amount of -OH and -NH will be generated, and 3356 cm-1-3480 cm-1 are the stretching vibration absorption peaks of -OH and -NH. The infrared spectrum of the silicone rubber material is the CH stretching vibration absorption peak of Si-CH3 at 2967 cm-1, the symmetric and antisymmetric characteristic peaks of Si-O-Si at 1006 cm-1 and 1068 cm-1, 1258 cm-1 is the CH symmetrical swing absorption peak in Si-CH3.

3.2 Sample contact angle analysis

It can be seen from the contact angles of the three materials in Fig. 2 that the three materials are generally hydrophobic. The maximum contact angle of the silicone rubber material in the figure is 112.8°, which is 20.3° higher than that of the XLPE insulating sleeve and 29.3° higher than that of the epoxy resin insulating board. It can be concluded that the hydrophobicity of silicone rubber is better among the three insulating materials. The epoxy resin insulating material has poor hydrophobic performance, which indicates that the silicone rubber material is more suitable for components with high hydrophobic performance requirements in high-voltage switchgear, and epoxy resin materials are more suitable for components with low hydrophobic performance requirements.

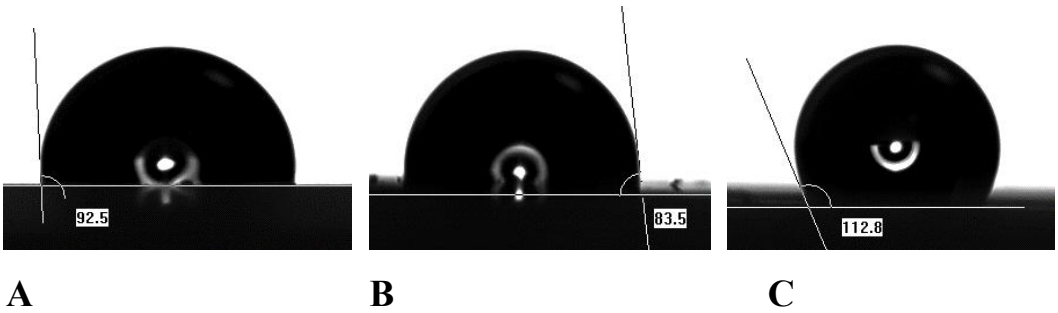

Figure 2. Hydrophobic properties of three insulating materials
A: Cross-linked polyethylene; B: Epoxy resin; C: Silicone rubber

3.3 Thermal conductivity analysis of samples

Table 1. Thermal conductivity of three materials

Material	XLPE	Epoxy	Silicone Rubber
Experimental temperature/K	292.86	294.71	292.94
Thermal conductivity (W/m•K)	0.395	0.836	0.394

It can be obtained from Table 1 that the thermal conductivity of epoxy resin is higher than that of the other two insulating materials. Zhang Xiaoxing et al. [12] found that when the temperature is >450 K, the epoxy resin is already in a high elastic state, which is the upper limit of the use temperature of epoxy resin materials. When the temperature reaches 500 K, the equipment is likely to be in a fault state. It is found that the thermal conductivity of pure epoxy resin at room temperature is 0.21384 W/(m•K) by simulation and 0.208 W/(m•K) by experimental test. The

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thermal conductivity of the three insulating materials in this study is greater than 0.21384 W/(m•K), among which the thermal conductivity of epoxy resin material is as high as 0.836 W/(m•K), which is higher than that of cross-linked polyethylene insulating sleeve and organic The thermal conductivity of silicone rubber materials is high, indicating that the epoxy resin material has better heat dissipation capacity, and is more suitable for components with high thermal conductivity requirements inside the high-voltage switchgear.

3.4 DSC curve analysis of samples

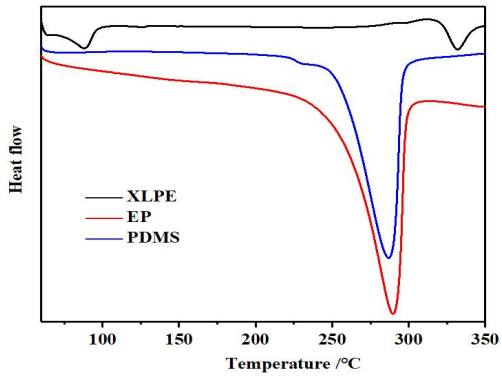

Figure 3. DSC diagram of three materials

It can be seen from Figure 3 that under the same heating rate, the endothermic peak of cross-linked polyethylene is very small, but the endothermic peaks of epoxy resin and silicone rubber are obvious, and both reach the peak around 290 ℃. . It shows that under the same heating rate, the heat resistance of cross-linked polyethylene is better. Compared with cross-linked polyethylene, the heat resistance of epoxy resin and silicone rubber is relatively poor.

3.5 Thermal gravimetric TG analysis of samples

The thermal weight loss of the three materials is shown in Figure 4 below. It can be seen from Figure 4A that the three materials do not decompose when the temperature is lower than 217 ℃. In the temperature range of 217-275 ℃, the cross-linked polyethylene material does not decompose, but the epoxy resin and silicone rubber begin to decompose slowly. , and entered the first decomposition section as shown in Figure 4C and Figure 4D; in the temperature range of 300-400 °C, the cross-linked polyethylene slowly decomposed and entered the first decomposition section as shown in Figure 4B; In the temperature range of -500 ℃, cross-linked polyethylene decomposes rapidly, while epoxy resin decomposes slower than cross-linked polyethylene in the temperature range of 275-450 ℃, and after 450 ℃, the decomposition curve of epoxy resin tends to be flat, Decomposition no longer occurs. In the temperature range of 275-380 ℃, the silicone rubber decomposes slowly, but after 380 ℃, the silicone rubber decomposes rapidly until 540 ℃, and it tends to be flat.

The above experimental results prove that the three materials can be used for a long time at around 217 ℃. If the switchgear instrument is used in the temperature range of 217 ℃-275 ℃, the parts made of cross-linked polyethylene material should be selected as far as possible for the switch.

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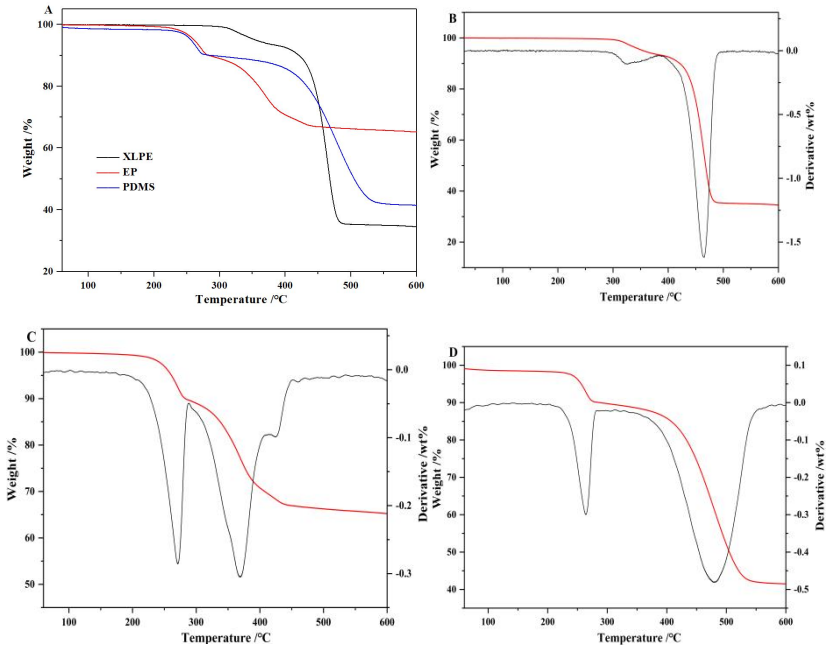

Figure 4. A: TG diagram of three materials; B: TG-DTG diagram of cross-linked polyethylene; C: TG-DTG diagram of epoxy resin; D: TG-DTG diagram of silicone rubber

3.6 Sample kinetic studies

The thermogravimetric analysis of typical epoxy resin, cross-linked polyethylene and silicone rubber commonly used in high-voltage switchgear was carried out at heating rates of 5 ℃•min-1, 10 ℃•min-1, and 15 ℃•min-1, respectively. The pyrolysis was carried out at 20 ℃•min-1, and the effect of different heating rates on the pyrolysis of the above three types of insulating materials under N2 atmosphere was investigated. The TG spectra at different temperatures are as follows:

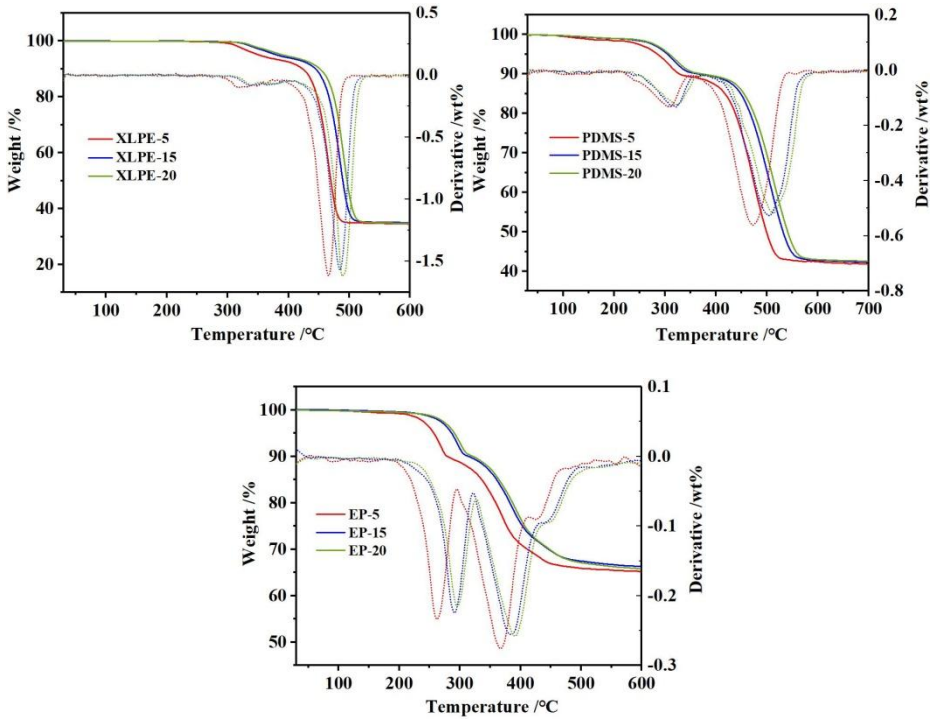

Figure 5. TG spectra of three materials at different temperatures

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When describing the problem of reaction kinetics, a sample with mass m0 undergoes a decomposition reaction at a programmed temperature, and at a certain time t mass becomes m, its decomposition rate can be expressed in two different forms: differential and integral. f (α) is the differential formal function related to the reaction mechanism, and g (α) is the integral formal function related to the reaction mechanism:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

$$g(\alpha) = kt \tag{2}$$

In the formula: t is the time, α is the decomposition degree, which can be expressed as α = (m0-m)/(m0-m∞)*100 %, m∞ is the residual mass that cannot be decomposed; dα/dt is the decomposition rate; k is the Arrhenius reaction rate constant.

$$k = A\exp(-E/RT) \tag{3}$$

In the formula: E is the activation energy of the reaction; A is the frequency factor; R is the gas constant, and T is the absolute temperature.

he specific form of the function f(α) depends on the type of reaction or the reaction mechanism. It can be assumed that the function f(α) is independent of temperature T and time t, but only related to the degree of reaction α.

Therefore, by combining (1) and (3), we can obtain the relation:

$$d\alpha/dt = A\,exp(-E/RT)\,f(\alpha) \tag{4}$$

For a non-isothermal case: T=T0+βt. T0 is the initial temperature of the reaction system, and β is the heating rate. Then the decomposition rate can be expressed in the following two different forms: differential and integral:

$$\frac{d\alpha}{dt} = \frac{d\alpha}{\beta dT} = A\exp(\frac{-E_a}{RT})f(\alpha) \tag{5}$$

$$g(\alpha) = \frac{A}{\beta}\int_0^T \exp(\frac{-E_a}{RT})dT = \frac{AE_a}{\beta R}p(x) \tag{6}$$

Equations (5) and (6) are kinetic equations, but the equations are complex and need to be simplified by transformation methods such as modeless. There are many isotransformation methods for pattern functions, including: Kissinger method, Flynn-Wall-Ozawa method, Coats-Redfern and Friedman method, etc.

The selection of the appropriate kinetic mechanism function is mainly based on the following criteria:

(1)The apparent activation energy E calculated by the Coats-Redfern method and the Kissinger method should be as consistent as possible;

(2) The linear correlation coefficient r given by the Coats-Redfern method linear regression should be as large as possible;

(3)The decomposition form corresponding to the selected mechanism function should be consistent with the state of the sample.

Using the TG spectrum, the Coast-redfern integral method was used to calculate the activation energy, that is, the relationship between ln[F(α)/T 2] and 1/T was drawn through the

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thermogravimetric diagram, and the slope of the curve was obtained, and then the activation energy of the reaction was obtained.

The specific form of the function f(α) depends on the type of reaction or the reaction mechanism. It can be assumed that the function f(α) is independent of temperature T and time t, but only related to the degree of reaction α. For simple reactions f(α) desirable

$$f(\alpha)=(1-\alpha)^n \tag{7}$$

The kinetics of weight loss in solid state pyrolysis can be expressed by equation (7), let Φ = dT/dt.

Joint equations (4) and (7) can be obtained:

$$\frac{da}{dt}=\frac{A}{\Phi}\exp\left(-\frac{E}{RT}\right)(1-a)^n \tag{8}$$

In equation (8), when n=1, the approximate solution is obtained by the Coats-Redfern integration method:

$$\ln\left[-\frac{\ln(1-a)}{T^2}\right]=\ln\left[\frac{AR}{\Phi E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT} \tag{9}$$

When n≠1, equation (8) is:

$$\ln\left[\frac{1-(1-a)^{(1-n)}}{T^2(1-n)}\right]=\ln\left[\frac{AR}{\Phi E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT} \tag{10}$$

Toop activation energy and calculation method are used, and the general reaction order is n=0.5, 1 or 2, etc. Due to the large value of E, 2RT/E is approximately zero.

A straight line was obtained by kinetic fitting at different heating rates. According to the slope and intercept of the straight line, the apparent activation energy E and pre-exponential factor A of the pyrolysis reaction of the insulating material at different temperatures can be obtained.

The fitting diagrams of the three insulating materials are obtained as follows:

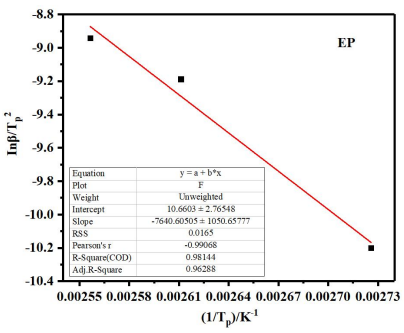

Figure 6. The relation between EP thermal decomposition ln[g(α)/T^2] and 1/T

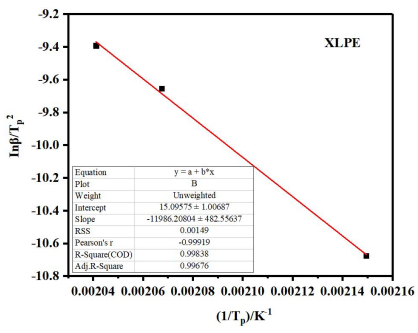

Figure 7. The relation between XLPE thermal decomposition ln[g(α)/T^2] and 1/T

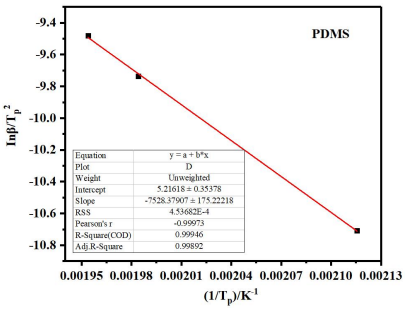

Figure 8. The relation between PDMS thermal decomposition $\ln[g(\alpha)/T^2]$ and 1/T

According to the fitted curve, the activation energies and pre-exponential factors of the three insulating materials are calculated as follows:

Epoxy resin: The curve equation obtained by fitting is y=10.6603-7640.60505x, the slope is -7640.60505, the intercept is 10.6603, and the fitted correlation coefficient R2 is 0.98144, thus the activation energy E=63.53kJ•mol- 1. Pre-exponential factor A=3.2×105•s-1.

Cross-linked polyethylene: The curve equation obtained by fitting is y=15.09575-11986.20804x, the slope is -11986.20804, the intercept is 15.09575, and the fitted correlation coefficient R2 is 0.99838, thus the activation energy E=99.66kJ·mol can be obtained -1, the pre-exponential factor A=4.3×107•s-1.

Silicone rubber: The curve equation obtained by fitting is y=5.21618-7528.37907x, the slope is -7528.37907, the intercept is 5.21618, and the fitted correlation coefficient R2 is 0.99946, thus the activation energy E=62.59 kJ•mol- 1, the pre-exponential factor A=1386.9•s-1.

4. Conclusion

(1)Silicone rubber has better hydrophobicity and is more suitable for parts with high hydrophobic performance requirements, and epoxy resin materials are more suitable for parts with low hydrophobic performance requirements.

(2)The thermal conductivity of the three insulating materials is greater than 0.21384 W/(m•K), among which the thermal conductivity of epoxy resin material is as high as 0.836 W/(m•K), which is higher than that of cross-linked polyethylene insulating sleeve and silicone rubber. The thermal conductivity of the materials are all high, indicating that the epoxy resin material has better heat dissipation capacity, and is more suitable for the use of components with high thermal conductivity requirements inside the high-voltage switchgear.

(3)Under the same heating rate, the heat resistance of cross-linked polyethylene is better. Compared with cross-linked polyethylene, the heat resistance of epoxy resin and silicone rubber is relatively poor. The three materials can be used for a long time at around 217 ℃. If the switchgear instrument is used in the temperature range of 217-275 ℃, the parts made of cross-linked polyethylene material should be selected as far as possible for the switchgear.

(4)The activation energies of epoxy resin, cross-linked polyethylene and silicone rubber are: 63.53 kJ•mol-1, 99.66 kJ•mol-1, 62.59 kJ•mol-1 respectively; the pre-exponential factors are: 3.2×105 •s-1, 4.3×107•s-1, 1386.9•s-1.

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