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**Thermal safety assessment through the concept of structure-reactivity:
application to vegetable oils valorization**

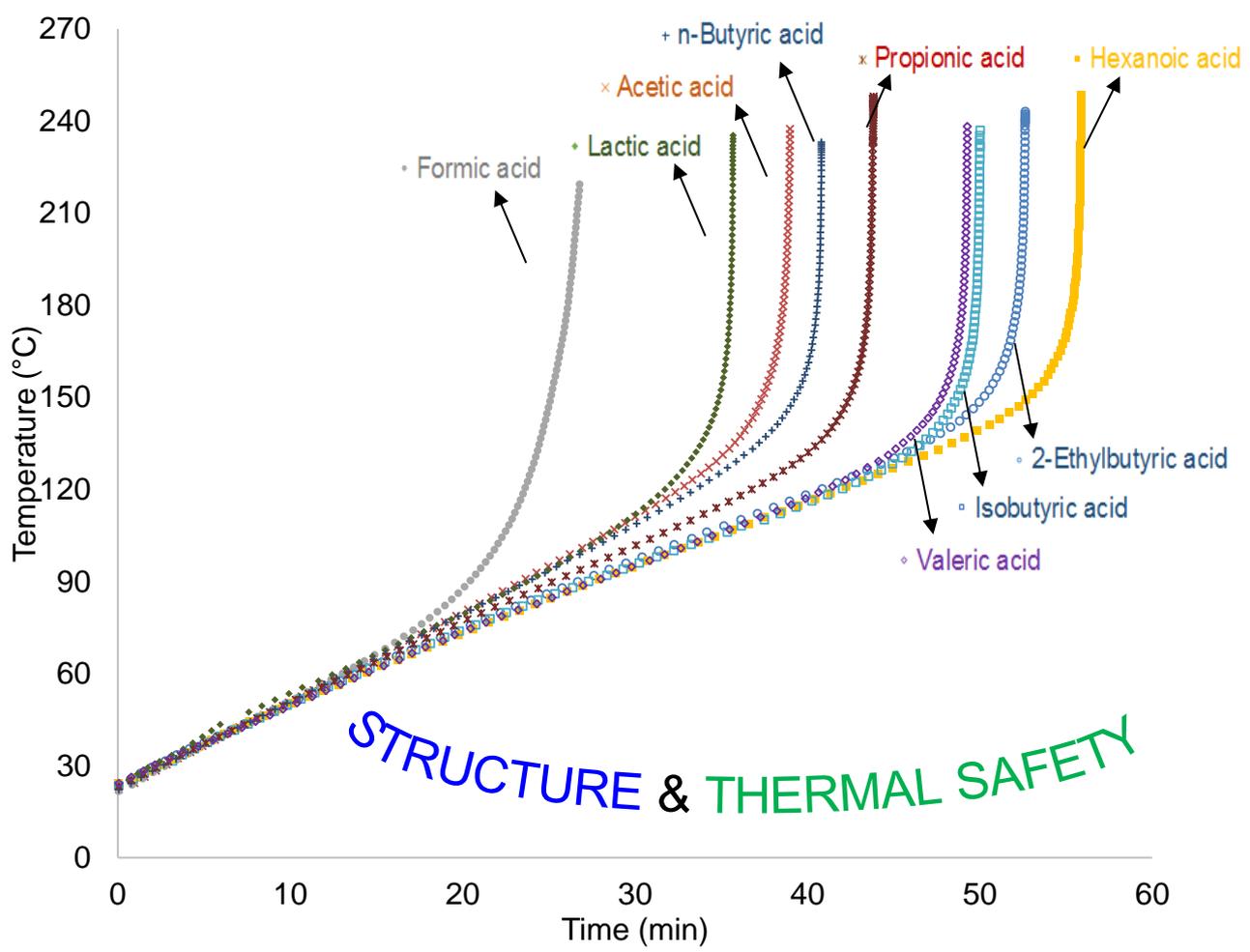
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TOC graphic



Abstract

The concept of linear free-energy relationships, and more particularly the Taft equation, was extended to a multiphase system with several reactions and reaction centers: epoxidation of vegetable oils and free fatty acids. Epoxidation of vegetable oils and free fatty acids by different percarboxylic acids produced *in situ* is an exothermic reaction system which can lead to a thermal runaway. The safety criterion Time-to-Maximum-Rate under adiabatic conditions (TMR_{ad}) linked to the kinetics of the system, was determined with the advanced reactive system screening tool (ARSST). We have demonstrated that TMR_{ad} values for the epoxidation of vegetable oils and free fatty acids by using different carboxylic acids follow the Taft equation. The epoxidation reaction series by different carboxylic acids was found to be more sensitive to the polar effect than steric effect. It was demonstrated, that by knowing the carboxylic acid used for the epoxidation, it is possible to predict the values of TMR_{ad} .

Keywords: Linear free-energy relationship, epoxidation of vegetable oils, time-to-maximum rate under adiabatic conditions, Taft equation, calorimeter.

1. Introduction

During the twenty-first century, our society should see the shift from the use of fossil to renewable raw materials in chemical industries. The use of biomass as renewable materials at industrial-scale has already started in some processes such as the production of biodiesel from vegetable oils, the production of levulinic acid from lignocellulosic materials (Biofine process) and the production of ethanol from sugars. Several challenges limit the production of chemicals or fuels from biomass, such as collection networks, food versus fuel issues or process valorization.¹ The chemical composition of biomass depends on the species, plant part, crop location or the season. This variation and the complexity of biomass structure make the development of biomass valorization processes challenging. The development of kinetic and thermodynamic models for these complex chemical systems can be cumbersome. Thus, optimization of production and thermal risk assessment, which are linked to the knowledge of kinetics and thermodynamics, are time-consuming stages. The use of the concept of structure-reactivity can accelerate these stages.²⁻⁴ This manuscript proposes to study the correlation between the chemical structure of biomass and thermal risk criterion.

Biomass structures are composed of similar building blocks: amino-acids for proteins, simple sugars for polysaccharides, aromatic compounds for lignin and fatty acids for oils. If the kinetics and thermodynamics of transformation for the single building blocks were known, would it be possible to predict the kinetics and thermodynamics of the biomass structure? For example, linseed oil is mainly composed of triglycerides of oleic, linoleic and linolenic acids, which are unsaturated acids (Table 1). If the kinetics (rate constant) and thermodynamics (reaction enthalpy) for the hydrogenation of each of

these three free fatty acids (single building blocks) are known, can we predict the kinetics or thermodynamics for the hydrogenation of linseed oil?

Through systematic structure evaluation of reactants, one can predict the kinetic behavior of a reaction or the physicochemical properties of chemicals. This is the principle of structure-reactivity research. One should distinguish QSAR (quantitative structure–activity relationship)/QSPR (quantitative structure–property relationship) to predict physicochemical properties of a compound and LFER (linear free-energy relationship) to predict kinetic or thermodynamic constants of a chemical reaction based on reactant structure. QSPR/QSAR approach can be used to predict thermal stability of chemicals,⁵ or to predict the chemical toxicology of a compound based on their chemical structure.⁶⁻⁸ LFER is used for congeneric series of compounds, compounds sharing the same reaction center like –SH, –COOH, –CO, etc., and where their substituents/radicals R attached to this functional group vary. It has been demonstrated that the LFER such as Charton or Taft equations can be used to predict the kinetic behavior of some reactions.⁹⁻¹⁷ The concept of LFER has also been used to estimate the solvent effect on propagation rate coefficients¹⁸ or to predict the sorption of compounds.¹⁹

Daoutidis et al.,²⁰ have pointed out that the contribution of LFER to biomass transformation for the determination of kinetic and thermodynamic constants can be important.

Biomass transformation involves several consecutive or parallel reactions, different reaction centers located in the same molecules and multiphase reaction system. Can we apply the concept of LFER, which was derived for single reactions with one reaction

center, to complex biomass valorization system? To reply to this question, this concept was applied to the epoxidation of vegetable oils and free fatty acids.

Epoxidized vegetable oils or their ring-opening products can be used as plasticizer,²²⁻²³ lubricant²⁴⁻²⁸ or for the green production of polyurethanes.²⁹⁻³⁵ These modified vegetable oils are preferred than their petroleum-derived counterparts because they are renewable, biodegradable and non-toxic.²⁷ However, this reaction system presents some safety issues due to the fact that the reaction system is exothermic.³⁶⁻³⁹

Köckritz and Martin⁴⁰ have reviewed the different processes for the production of epoxidized vegetable oils or free fatty acids. The use of oxygen or hydrogen peroxide is more eco-friendly, but there are not efficient and inexpensive catalysts.⁴¹⁻⁴⁷ Enzymatic catalysis is more and more developed to improve the selectivity.⁴⁸⁻⁵⁵

Currently, epoxidation by percarboxylic acids (also known as peroxy acid, peracid or peroxy-carboxylic acid) produced *in situ* is most commonly utilized. This reaction system is known as the Prileschajew oxidation.²¹ It is a liquid-liquid reaction system with consecutive and parallel exothermic reactions. The percarboxylic acid, produced *in situ*, epoxidizes the unsaturated groups of the vegetable oils or free fatty acids. Different carboxylic acids can be used to perform this reaction. In this manuscript, the concept of LFER was applied to the epoxidation reaction by the Prileschajew oxidation using different carboxylic acids. The values of TMR_{ad} were used for the different epoxidations instead of rate constants.

Chemical processes using biomass are considered greener but they can present some risks.⁵⁶ One aspect of process safety is thermal risk assessment, which requires the knowledge of probability criteria such as TMR_{ad} and severity criteria such as adiabatic temperature rise ΔT_{ad} .⁵⁷ The determination of such criteria requires time and

calorimetric data.⁵⁸ By taking into account structure complexity, diversity and composition variation for biomass, it can be an onerous task to determine these criteria for each biomass.

Taft equation is a LFER that takes into account the influence of steric, polar and resonance effects for a series of reaction. For example, the influence of polar effect was found to be dominant in the sulfation of different alcohols,¹¹ bromination of different ketones,¹¹ esterification of carboxylic acid by different primary alcohols.^{13, 15} Steric effect was found to be dominant for the perhydrolysis reaction¹⁴ or the esterification of different carboxylic acids by 1-propanol.¹⁵ For these studies, the authors have determined the rate constants of different single reactions with one reaction center. To the best of our knowledge, there are no studies involving the use of safety criteria like TMR_{ad} to Taft equation or the use of Taft equation to complex system, i.e., multiphase systems with several reactions and reaction centers. This manuscript proposes to fill this gap.

The criterion TMR_{ad} is linked to the kinetics of the reaction system. If this criterion follows the Taft equation, thus it could be possible to extend this investigation to predict the kinetic or thermodynamic behavior of biomass macromolecules transformation by knowing the behavior of their building blocks. This study can be seen as a first brick in this field.

The values of TMR_{ad} for the epoxidation of vegetable oils or free fatty acids by different percarboxylic acids produced *in situ* were determined by using an adiabatic reactor, namely Advanced Reactive System Screening Tool (ARSST). Subsequently, the influence of steric and polar effects on TMR_{ad} values was evaluated by using the Taft equation.

2. Results and discussion

-Kinetics of vegetable oils epoxidation

Figure 1 presents the detailed epoxidation reaction scheme. This liquid-liquid reaction system consists of several consecutive and parallel exothermic reactions.

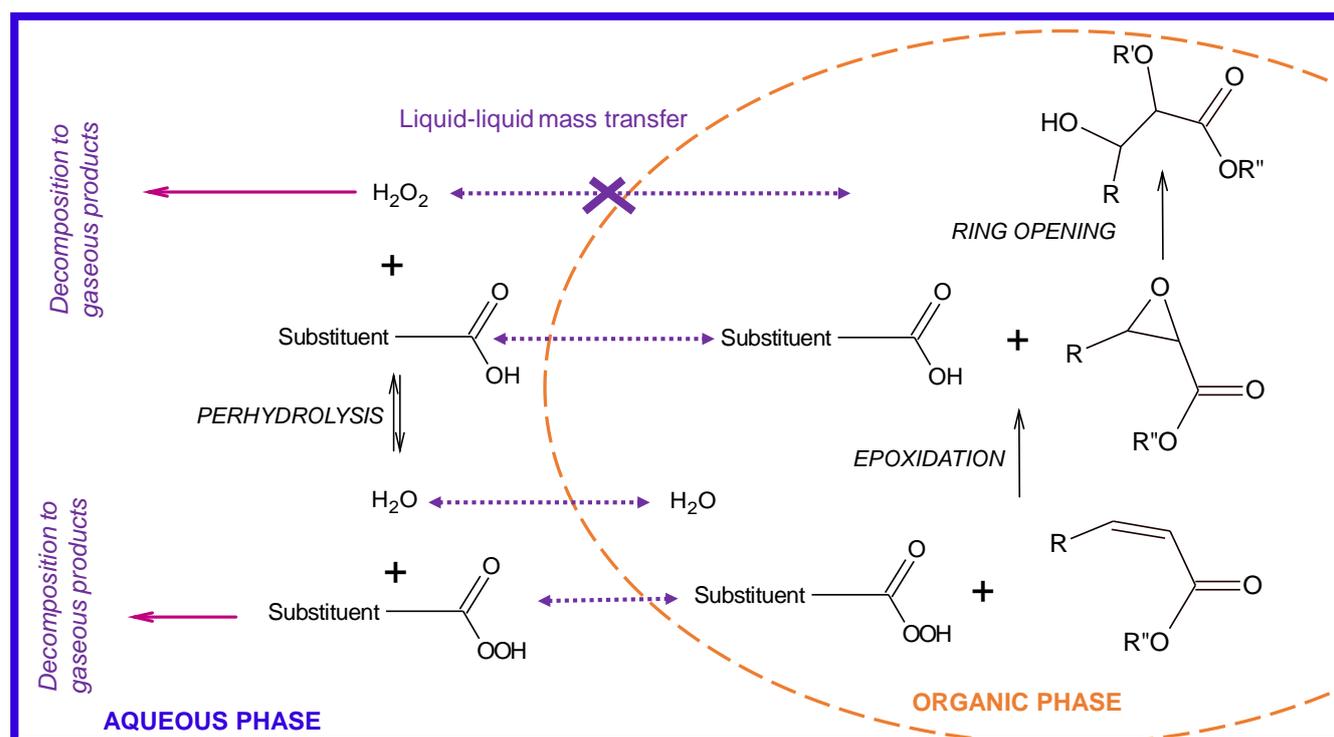


Figure 1. Reaction scheme for epoxidation.

In a first step, perhydrolysis reaction producing percarboxylic acid occurs in the aqueous phase. The percarboxylic acid migrates to the organic phase to epoxidize unsaturated groups on vegetable oils or free fatty acids. Side reactions can also occur such as decomposition of hydrogen peroxide or percarboxylic acid according to the nature of the percarboxylic acid,⁵⁹⁻⁶¹ temperature or pH. Ring-opening reactions could also occur during the epoxidation process. The importance of the ring-opening depends on temperature and pH but also if vegetable oils or free fatty acids are used.

Different kinetic models have been proposed to describe this reaction system: a rigorous two-phase models,⁶²⁻⁶⁵ a pseudo-homogeneous model,⁶⁶⁻⁷² or by just considering the organic phase.⁷³⁻⁸¹ When this reaction is studied under non-isothermal conditions, it is compulsory to couple the mass and energy balance.^{62, 71-72, 82-83} Our group have demonstrated that the heat-flow rate of this reaction system is governed by the formation of the percarboxylic acid.³⁹ The reactivity of the percarboxylic acid is influenced by the nature of the substituent/radical. The latter could also impact on the heat flow rate released during the epoxidation process and the safety criteria.

The reaction temperature used for the epoxidation system is usually between 60 and 80°C.⁸⁴ The determination of TMR_{ad} at these reaction temperatures can be done by knowing the intrinsic kinetic and thermodynamic constants of the epoxidation system with the different carboxylic and vegetable oils/free fatty acids. However, the determination of all these constants is time-consuming. For that reason, ARSST calorimeter was used to rapidly determine TMR_{ad} values at 60 and 80°C for the different epoxidation system. The determination of TMR_{ad} values, based on zero-order approach (eq S3), is explained in details in SII.

Epoxidation by different percarboxylic acids of several vegetable oils and free fatty acids was tested (Table 1). The unsaturated fatty acids on the triglyceride of vegetable oils are usually: oleic, linoleic and linolenic acids. We have selected different vegetable oils with different composition of these fatty acids: olive oil which is rich with oleic acid, cottonseed oil which is composed in majority of linoleic acid and linseed oil which is composed primarily of linolenic acid. The degree of unsaturation is characterized by the iodine number. The more the values of iodine number are high, the more the vegetable oil/free fatty acid is unsaturated.

Table 1. Composition of different vegetable oils and free fatty acids.

	Weight percentage of fatty acid moiety						Iodine value
	Palmitic C16:0	Palmitoleic C16:1	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3	
Olive oil	9.2	0.8	3.4	80.4	4.5	0.6	81
Cottonseed oil	28.7	-	0.9	13	57.4	-	105
Linseed oil	5.1	0.3	2.5	18.9	18.1	55.1	178
Oleic acid	-	-	-	100	-	-	92
Linoleic acid	-	-	-	-	100	-	177-183

The kinetics of epoxidation of vegetable oils and free fatty acids are different.⁷¹⁻⁷² Indeed, the ring-opening reaction is more prominent during the epoxidation of free fatty acid compared to vegetable oil. For that reason, we have pursued our investigation to include the epoxidation of oleic and linoleic acids.

The description of the ARSST units and experimental protocol are described in the experimental section. ARSST unit is a pressurized near-adiabatic system using an open cell. The cell is surrounded by an electrical heater. The fact that the system is under high pressure allows to increase the boiling point limiting the evaporation phenomenon. From ARSST experiments, it is possible to estimate the time to maximum rate under adiabatic conditions TMR_{ad} .

Time to maximum rate under adiabatic conditions is the time to reach the maximum value of the derivate $\left(\frac{dT_P}{dt}\right)$. The accurate determination of this value by numerical

methods is cumbersome and time-consuming, because it requires the knowledge of intrinsic kinetic and thermodynamic constants for the whole system including secondary reactions.³⁸ For that reason, the zero-order approximation was used. Besides its simplicity, this kinetic approach gives the worst-case scenario, *i.e.*, shorter TMR_{ad}. Then, one can express TMR_{ad} by:³⁸

$$\text{TMR}_{\text{ad}}(T_P) = \frac{m_R \cdot \hat{C}_{\text{PR}} \cdot R \cdot T_P^2}{q_r(T_P) \cdot E_a} \quad (1)$$

where T_P is the process temperature, m_R is the reaction mass, \hat{C}_{PR} is the heat-capacity of the reaction mixture, R is the gas constant, E_a is the activation energy and $q_r(T_P)$ is the heat-flow rate due to chemical reactions at the process temperature T_P . The derivation of eq 1 is explained in SI1.

The values of TMR_{ad} at 60 and 80°C were determined by extrapolation based on the ARSST experimental data.

-Taft equation: application to TMR_{ad}

We have chosen different carboxylic acids (Table 2) to perform the epoxidation. The reader should keep in mind that the oxidizing compound is the percarboxylic acid produced *in situ* from the corresponding carboxylic acid. As mentioned in the introduction, Taft equation is a linear free energy relationship (LFER) assuming a linear relation between kinetic and thermodynamic constants. In other words, such relation could predict the value of kinetic constant based on the structure of the reactants. The original Taft equation is expressed as:

$$\log\left(\frac{k}{k_0}\right) = \rho^* \cdot \sigma^* + \delta \cdot E_s + \psi \quad (2)$$

where σ^* is a near-quantitative measure of the polar effect of a substituent/radical, E_s is a near-quantitative measure of the steric effect of a substituent/radical, ρ^* and δ give the influence of a reaction series to polar and steric effects, respectively. The term ψ represents the resonance effect between the substituent/radical and the reaction center.

The different carboxylic acids used for this study do not present any resonance effects.

Thus, eq 2 can be simplified to:

$$\log\left(\frac{k}{k_0}\right) = \delta \cdot E_s + \rho^* \cdot \sigma^* \quad (3)$$

The term k_0 is the reference rate constant of the epoxidation by using acetic acid.

Table 2 presents the different values of E_s and σ^* found from different sources.^{9-12, 85-87}

Table 2. Steric and polar Taft parameters. ^{9-12, 85-87}

Radical	σ^*	E_s	Corresponding carboxylic acids
H-	0.49	1.24	Formic acid
CH ₃ -	0	0	Acetic acid
CH ₃ -CH ₂ -	-0.1	-0.07	Propionic acid
CH ₃ -CH ₂ -CH ₂ -	-0.115	-0.36	Butanoic acid
CH ₃ -CH ₂ -CH ₂ -CH ₂ -	-0.13	-0.39	Valeric acid
iPr-	-0.2	-0.47	IsoButanoic acid
CH ₃ -CH(OH)-CH ₂ -	0.12	0.08	Lactic acid
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -	-0.25	-0.4	Hexanoic acid
(CH ₃ -CH ₂) ₂ -CH-	-0.225	-1.98	2-Ethylbutyric acid

The steric Taft parameter E_s increases in the following order: Formic>Lactic>Acetic>Propionic>nButyric>Valeric>Hexanoic>isoButyric>2-Ethylbutyric. As the steric hindrance increases, the value of E_s becomes negative. The polar Taft parameter σ^* increases in the following order:

Formic>Lactic>Acetic>Propionic>nButyric>Valeric>isoButyric>2-Ethylbutyric>Hexanoic. The value of σ^* is negative for electron withdrawing groups and positive for electron releasing group.

The variation of Taft steric and polar parameters for the different carboxylic acids is relatively similar except for isobutyric, 2-ethylbutyric and hexanoic acid. To determine the importance of these effects on TMR_{ad} during the epoxidation process, we have derived a correlation between these parameters.

As mentioned previously, the determination of the different intrinsic kinetic and thermodynamic constants is time-consuming for complex chemical system. In process

safety, the zero-order approach is commonly accepted.⁵⁷ Thus, the heat-flow rate due to chemical reactions can be expressed as:

$$q_r(T_p) = k(T_p) \cdot \Delta H_R \cdot V_R \quad (4)$$

where, V_R is the volume of reaction mixture, $k(T_p)$ and ΔH_R stand for the rate constant at temperature T_p and reaction enthalpy assuming a zero-order reaction.

Eq 1 can be rewritten as

$$\text{TMR}_{\text{ad}}(T_p) = \frac{m_R \cdot \hat{C}_{\text{PR}} \cdot R \cdot T_p^2}{k(T_p) \cdot \Delta H_R \cdot V_R \cdot E_a} \quad (5)$$

which is equivalent to

$$k(T_p) = \frac{m_R \cdot \hat{C}_{\text{PR}} \cdot R \cdot T_p^2}{\text{TMR}_{\text{ad}}(T_p) \cdot \Delta H_R \cdot V_R \cdot E_a} \quad (6)$$

Thus, eq 3 becomes

$$\log\left(\frac{k(T_p)}{k_0(T_p)}\right) = \log\left(\frac{\frac{m_R \cdot \hat{C}_{\text{PR}} \cdot R \cdot T_p^2}{V_R} \cdot \frac{1}{\text{TMR}_{\text{ad}}(T_p) \cdot \Delta H_R \cdot E_a}}{\frac{m_{R0} \cdot \hat{C}_{\text{PR0}} \cdot R \cdot T_p^2}{V_{R0}} \cdot \frac{1}{\text{TMR}_{\text{ad0}}(T_p) \cdot \Delta H_{R0} \cdot E_{a0}}}\right) \quad (7)$$

The terms $\frac{m_R \cdot \hat{C}_{\text{PR}} \cdot R \cdot T_p^2}{V_R}$ and $\frac{m_{R0} \cdot \hat{C}_{\text{PR0}} \cdot R \cdot T_p^2}{V_{R0}}$ can be assumed to be similar, thus eq 7

becomes

$$\begin{aligned} \log\left(\frac{k(T_p)}{k_0(T_p)}\right) &= \log\left(\frac{\text{TMR}_{\text{ad0}}(T_p) \cdot \Delta H_{R0} \cdot E_{a0}}{\text{TMR}_{\text{ad}}(T_p) \cdot \Delta H_R \cdot E_a}\right) = \delta \cdot E_s + \rho^* \cdot \sigma^* \\ \Leftrightarrow \log\left(\frac{\text{TMR}_{\text{ad}}(T_p)}{\text{TMR}_{\text{ad0}}(T_p)}\right) &= \log\left(\frac{\Delta H_{R0} \cdot E_{a0}}{\Delta H_R \cdot E_a}\right) - \delta \cdot E_s - \rho^* \cdot \sigma^* \end{aligned} \quad (8)$$

The term $\log\left(\frac{\Delta H_{R0} \cdot E_{a0}}{\Delta H_R \cdot E_a}\right)$ was supposed to be constant.

For a series of epoxidation, we obtain a system of algebraic equations by applying eq 8.

This system of equation was solved out by multiple linear regression to estimate ρ^* and δ for different epoxidation system. This approach allows to verify if the term

$\log\left(\frac{\Delta H_{R0} \cdot E_{a0}}{\Delta H_R \cdot E_a}\right)$ can be assumed constant.

For the sake of clarity, the determination of TMR_{ad} from ARSST equipment is explained in supporting information (SI1).⁸⁸⁻⁸⁹ The influence of the stirring rate and electrical heating (SI2) on TMR_{ad} was verified to determine the optimum conditions. Stirring rate was fixed to avoid mass transfer limitation (Figure S3). By performing reaction on a long time, one can notice the presence of decomposition due to the excess of hydrogen peroxide (SI3). In a previous paper of our group,³⁸ we have also noticed that in presence of excess of hydrogen peroxide, its decomposition occurs after the reactions of the epoxidation system.

-Preliminary experiments

The evolution of reaction temperature during the epoxidation of cottonseed oil by different percarboxylic acids under near-adiabatic conditions is displayed in Figure 2.

Figure 2 shows that the reactivity increases in the following order:

Formic>Lactic>Acetic>n-Butyric>Propionic>Valeric>isoButyric>2-

EthylButyric>Hexanoic. This trend is similar to the variation of the Taft steric and polar parameters.

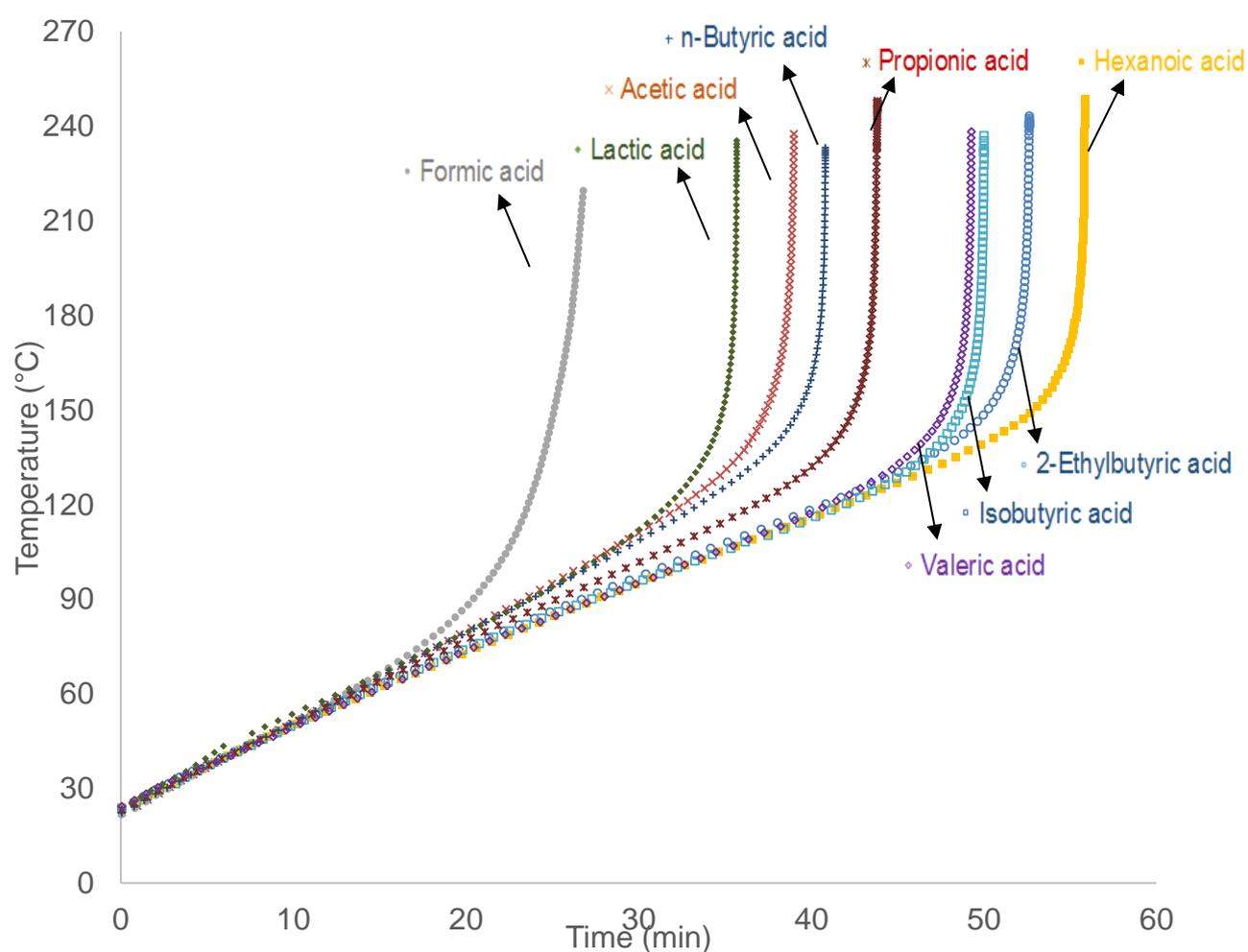


Figure 2. Evolution of temperature during the epoxidation of cottonseed oil by different percarboxylic acids produced *in situ* under near-adiabatic conditions and with temperature ramps of 2.3-2.9°C/min.

The evolution of the pressure during the epoxidation of cottonseed oil in the ARSST unit is displayed in Table 3. The initial pressure in the containment was ca. 36 bar of nitrogen. The difference in pressure was measured as the difference between the final pressure, after the first exothermic peak, and the initial pressure at 30°C. Thus, this difference in pressure represents the pressure increase due to the production of non-condensable products. As illustrated in Figure 1, peroxide species can undergo decomposition to produce oxygen, carbon dioxide, carbon monoxide, etc.⁵⁹⁻⁶¹ By using the zero-order approach, it is possible to extrapolate the values of TMR_{ad} from ARSST experiments without taking into account secondary reactions.

Table 3 shows that the use of performic acid produces more non-condensable products due to its higher instability.^{14, 61} One can consider that the production of non-condensable products is relatively low for the epoxidation by the other percarboxylic acids.

Table 3. Variation of pressure at final and initial stage at 30°C for the epoxidation of cottonseed oil.

	Final pressure (bar)-Initial pressure (bar)
Formic acid	1.56
Acetic acid	0.62
Propionic acid	0.66
n-Butyric acid	0.75
Valeric acid	0.52
iso-Butyric acid	0.88
Lactic acid	0.91
Hexanoic acid	0.64
2-EthylButyric acid	0.64

Figure 3 shows the evolution of TMR_{ad} at a process temperature of 60°C for the epoxidation of cottonseed oil. One can notice that the values of TMR_{ad} at 60°C for the epoxidation of cottonseed oil by performic, peracetic, perpropionic and n-perbutanoic acid are shorter. Thus, epoxidation carried out by these acids should be done cautiously by limiting the accumulation of heat-flow rate, i.e., use of continuous or semi-continuous reactor.

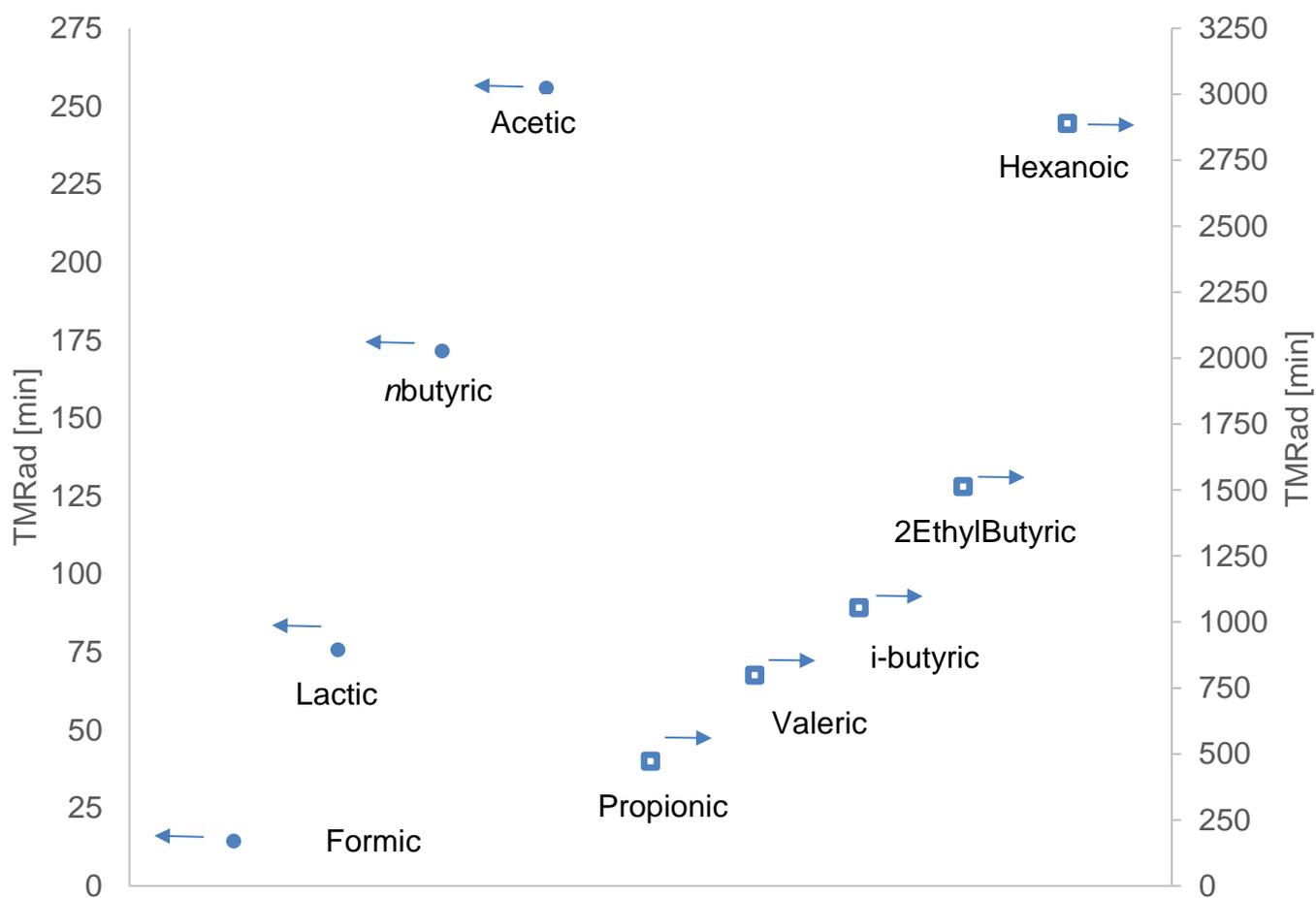


Figure 3. TMR_{ad} at $60^{\circ}C$ for the epoxidation of cottonseed oil.

-Taft equation

The values of TMR_{ad} at 60 and $80^{\circ}C$ for the different vegetable oils are represented in SI4. The standard deviations for TMR_{ad} at 60 and $80^{\circ}C$ were found to be 8.73% and 4.33%, respectively. In SI4, the reader can also see the number of carboxylic acids tested for the epoxidation experiments.

We have determined the values of δ , ρ^* and $\log\left(\frac{\Delta H_{R0} \cdot E_{a0}}{\Delta H_R \cdot E_a}\right)$ for the epoxidation of vegetable oils/free fatty acids by different carboxylic acids by solving out eq 8 (Table 4). The determination of the parameters (δ , ρ^* and $\log\left(\frac{\Delta H_{R0} \cdot E_{a0}}{\Delta H_R \cdot E_a}\right)$) for the different epoxidation series was done by using at least six different carboxylic acids (SI4 and SI5). Due to space limitation, the parity plots between $\log\left(\frac{TMR_{ad}(T_P)}{TMR_{ad0}(T_P)}\right)$ are displayed in SI5.

Table 4. Values of coefficient δ , ρ^* and $\log\left(\frac{\Delta H_{R0} \cdot E_{a0}}{\Delta H_R \cdot E_a}\right)$.

Cottonseed oil epoxidation

	Temperature 60°C	Standard error	Temperature 80°C	Standard error
δ	0.01	0.20	0.02	0.16
ρ^*	2.89	0.72	2.10	0.57
H	0.005	0.10	0.01	0.08
R ² (%)	88.89		87.61	

Olive oil epoxidation

	Temperature 60°C	Standard error	Temperature 80°C	Standard error
δ	-0.30	0.19	-0.23	0.13
ρ^*	4.05	0.66	3.14	0.48
H	0.34	0.09	0.23	0.06
R ² (%)	92.04		93.1	

Linseed oil epoxidation

	Temperature 60°C	Standard error	Temperature 80°C	Standard error
δ	-0.26	0.14	-0.21	0.16
ρ^*	3.73	0.55	3.10	0.64
H	0.16	0.08	0.16	0.09
R ² (%)	97.25		94.8	

Oleic acid epoxidation

	Temperature 60°C	Standard error	Temperature 80°C	Standard error
δ	0.09	0.16	0.08	0.09
ρ^*	3.00	0.57	2.26	0.33
H	-0.08	0.08	-0.07	0.05
R ² (%)	95.00		97.09	

Linoleic acid epoxidation

	Temperature 60°C	Standard error	Temperature 80°C	Standard error
δ	0.11	0.10	-0.001	0.10
ρ^*	2.47	0.37	2.28	0.36
H	0.07	0.06	0.09	0.06
R ² (%)	98.33		97.58	

$$H = \log\left(\frac{\Delta H_{R0} \cdot E_{a0}}{\Delta H_R \cdot E_a}\right)$$

In general, there is a good agreement between experimental data and modeling results. In the majority of cases, the slope is close to one and the coefficients of determination are significant. However, the coefficients of determination for the epoxidation of cottonseed oil are relatively lower, due to the deviation for the epoxidation by n-butyric acid (Figure S6).

One can notice that the values of ρ^* , which shows the influence of the polar effect for a reaction series, are higher than the values of δ , which gives the influence of the steric effect for a reaction series. Thus, the steric effect can be assumed negligible for the epoxidation by different percarboxylic acids. This lower impact of steric effect on the reaction series explains the high values for the standard errors for the parameter δ .

The values of ρ^* decrease when temperatures increase. This illustrates that the influence of polar effect on the nucleophile compounds, i.e., percarboxylic acid, slightly decreases when temperature increases.

One can also notice that the term $\log\left(\frac{\Delta H_{R0}.E_{a0}}{\Delta H_R.E_a}\right)$ is relatively low for the different reaction series, involving that the products $\Delta H_R.E_a$ are similar for the different carboxylic acid tested. The values of reaction enthalpy and activation energy do not reflect the intrinsic mechanism, because there were determined by using a zero-order approach. This similarity involves that globally, i.e., by taking into account all the reactions, there is a compensation between the kinetics and thermodynamics for an epoxidation series.

The values of ρ^* cannot be compared directly to other studies because TMR_{ad} and zero-order model were used instead of rate constants by considering intrinsic kinetic model. However, it is possible to compare the values of ρ^* of this study:

ρ^* (Olive oil) > ρ^* (Linseed oil) > ρ^* (Oleic acid) > ρ^* (Cottonseed oil) > ρ^* (Linoleic acid)
at 60°C,

ρ^* (Olive oil) > ρ^* (Linseed oil) > ρ^* (Linoleic acid) > ρ^* (Oleic acid) > ρ^* (Cottonseed oil)
at 80°C.

Epoxidation of olive and linseed oil by different carboxylic acids are more sensitive to polar effect than the other epoxidation system. The values of ρ^* are not the same for the different system, even if the same carboxylic acids are used. The variation of the values of ρ^* is not correlated to the iodine number or the nature/composition of fatty acids. During the epoxidation process, mass transfer plays an important role on the transfer of percarboxylic acid from the aqueous to the organic phase. Several parameters have an influence on mass transfer phenomenon such as viscosity, density and interfacial tension. These parameters are not identical for the different vegetable oils and free fatty acids and can explain the different values of the coefficients ρ^* .

3. Conclusions

Epoxidation of vegetable oils (linseed, cottonseed and olive oils) and free fatty acids (oleic and linoleic acids) by different percarboxylic acids produced *in situ* was studied. The advanced reactive system screening tool (ARSST) unit was used to determine the time-to-maximum-rate under adiabatic conditions (TMR_{ad}) for the epoxidation of the different vegetable oils and free fatty acids at two process temperatures 60 and 80°C. A zero-order kinetic approximation was used to estimate the values of TMR_{ad} .

In this reaction system, the percarboxylic acid produced *in situ* epoxidized the unsaturated groups of the vegetable oils and free fatty acids. We have demonstrated that by changing the nature of the radical of the carboxylic acid, the TMR_{ad} follows Taft relation. Multiple linear regression was used to estimate the values of δ , ρ^* and the term

$$\log\left(\frac{\Delta H_{R0} \cdot E_{a0}}{\Delta H_R \cdot E_a}\right).$$

It was found that the polar effect is the dominant one for an epoxidation reaction series by different carboxylic acids. The values of δ , representing the influence of steric effect on a series, are negligible compared to ρ^* , showing the influence of polar effect. The values of ρ^* were found to be different for the epoxidation of the different vegetable oils or free fatty acids.

This study shows that the concept of Linear Free Energy Relationships (LFER) can be applied to reaction system with several reaction centers, multiphase and several reactions. To have a better understanding of the influence of polar and steric effect on an epoxidation series, one should determine the intrinsic kinetic constants by including the variation of mass transfer parameters taking into account viscosity, density and interfacial surface tension.

Moreover, the Taft steric parameter (E_s) and polar parameter (σ^*) for vegetable oils and free fatty acids should be determined.

4. Experimental section

Advanced Reactive System Screening Tool (ARSST)

Epoxidation experiments were carried out in an ARSST unit, as illustrated by Figure 10. Hydrogen peroxide, water and free fatty acids or vegetable oils were poured in a 10 mL glass reactor, whose ϕ -factor varies between 1.04 to 1.06. This glass reactor was surrounded by a bottom heater, which provides an electrical power, and the whole was wrapped in an aluminum paper. This system was packed by blanket insulation in an insulation sheath. Then, this cell unit was inserted in the 450 mL ARSST system. A thermocouple was inserted in the reaction mixture and the other (TC2) was put in the headspace of the ARSST unit. The system was sealed and the same pressure test was carried out. When the pressure-proof was checked, carboxylic acid was added through the fill tube. The initial pressure of nitrogen in the ARSST unit was ca. 36 bar. Then, the agitation and the heating was started. Table 5 shows the different amounts of chemicals used during the experiments. More detailed data about the initial concentration are provided in SI6.

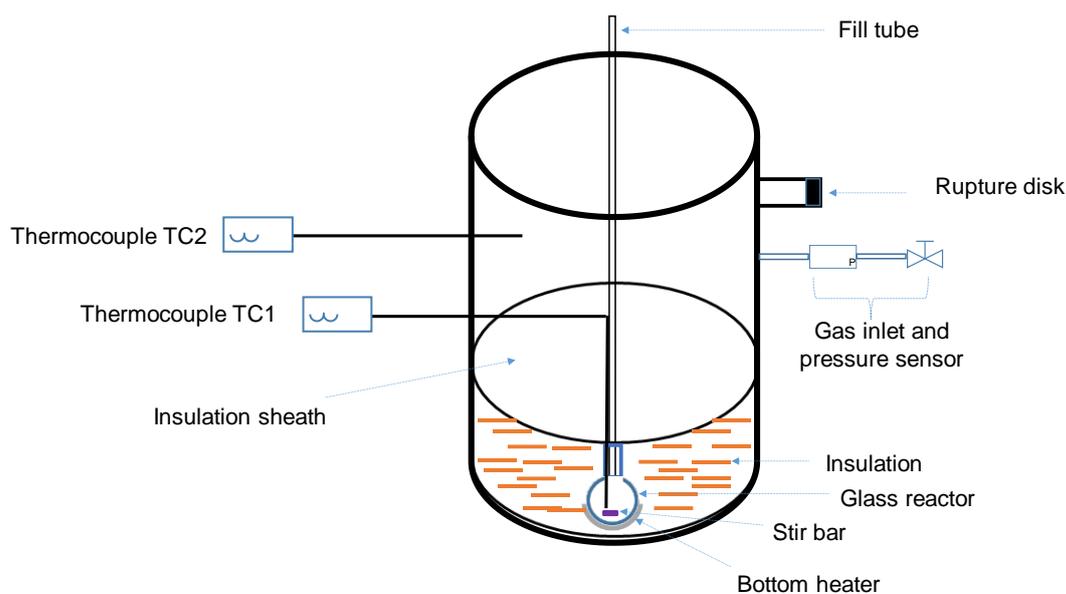


Figure 4. Simplified scheme of ARSST unit.

Table 5. Experimental matrix.

Amount of carboxylic acid (mol)	Amount of hydrogen peroxide (mol)	Amount of water (mol)	Mass of cottonseed oil (gram)	Electrical power (°C/min)
0.022-0.025	0.025-0.027	0.205-0.220	3.120-3.180	2-4

The following chemicals used were: distilled water, hydrogen peroxide (33 wt %, VWR International), formic acid (>99 wt%, VWR International), acetic acid (>99%, Alfa Aesar GmbH & Co.), propionic acid (99 wt%, Acrōs organics), n-butyric acid (99 wt%, Acrōs organics), iso-butyric acid (99 wt%, Acrōs organics), valeric acid (99 wt%, Acrōs organics), n-hexanoic acid (99 wt%, Alfa Aesar GmbH & Co), lactic acid (90 wt%, Fluka), cottonseed oil (ThermoFisher Scientific GmbH), olive oil (Fluka), linseed oil (ThermoFisher Scientific GmbH), linoleic acid (SAFC) and oleic acid (Fluka).

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Supporting information

For the sake of conciseness, we have put in supporting information: the determination of TMR_{ad} based on the zero-order approach, the effect of stirring and electrical heating on TMR_{ad} , experiment with long reaction time, the values of TMR_{ad} at 60 and 80°C and the parity plots.

Nomenclature

E_s Near-quantitative measure of the total steric effect associated with a given radical
 E_a Activation energy [kJ/mol]

H $\log\left(\frac{\Delta H_{R0} \cdot E_{a0}}{\Delta H_R \cdot E_a}\right)$

ΔH_R Reaction enthalpy [J/mol]

k Rate constant

k_0 Reference rate constant for the transformation with acetic acid

m_R Mass of reaction mixture [kg]

$q_r(T_P)$ Reactions heat-flow rate at the process temperature T_P [J/s]

R Gas constant [J/K.mol]

R^2 Coefficient of determination [%]

ΔT_{ad} Adiabatic temperature rise [K]

T_P Process temperature [K]

V_R Volume of reaction mixture [mL]

Greek letters

δ Constant giving the influence of a reaction series to steric effect

ρ^* Constant giving the influence of a reaction series to polar effect

σ^* Measure of the polar effect of the substituent

Subscripts

ad Adiabatic

R Reaction mixture

0 Reference for acetic acid

Abbreviations

ARSST Advanced Reactive System Screening Tool

C18:1 Oleic acid

C18:2 Linoleic acid

LFER Linear Free-Energy Relationship

QSAR Quantitative Structure–Activity Relationship

QSPR Quantitative Structure–Property Relationship

$TMR_{ad}(T_P)$ Time-to-maximum rate under adiabatic conditions at T_P

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