



# Application of linear free-energy relationships to perhydrolysis of different carboxylic acids over homogeneous and heterogeneous catalysts

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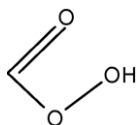
## ABSTRACT

This paper describes the application of LFER to understand the mechanism of the perhydrolysis of carboxylic acids over homogeneous and heterogeneous catalysts. Several experiments were carried out with different linear carboxylic acids: formic, acetic, propionic and butyric acids; using sulfuric acid and Amberlite IR-120 as catalyst and different reaction temperatures. From the experiments, the apparent rate constants decrease in the following order:  $k_{app}(\text{PFA}) > k_{app}(\text{PAA}) > k_{app}(\text{PPA}) > k_{app}(\text{PBA})$ , in both catalytic system. Furthermore, it was found that this reaction follows Taft and Charton correlations, which implies that the steric effect of the substituent governs that reaction and the mechanism is similar between the different carboxylic acids. Comparison between homogeneous and heterogeneous catalytic system was carried out based on the analysis of the kinetic expression.

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## 1. Introduction

Peroxy-carboxylic acids, and mainly peroxyacetic acid, are well-known industrial chemicals. They are usually classified as eco-friendly chemical, because their decompositions do not produce toxic compounds, and their impacts on environment are harmless. They are used for their oxidative properties due to their “exotic” functional group



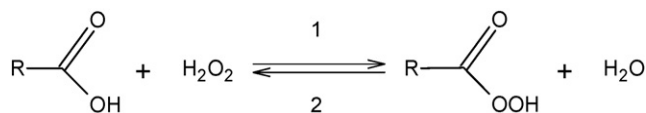
Those peroxy-carboxylic acids are widely used in several production technologies, as well as disinfecting and antimicrobial agents (destruction of organophosphorus as paraoxon, control legionella bacteria) in alimentary or pharmaceutical industry; as a bleaching agent of wood pulp in paper industry, instead of chlorine dioxide (which is not eco-friendly); and in fine chemistry for Baeyer–Villiger reaction or epoxidation of olefins. In industry, peroxyacetic acid is the main product used.

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The nature of the substituent influences not only the oxidizing capacity of the functional group  $-\text{CO}_3\text{H}$ , but also the solubility and volatility of the whole molecule. For instance, Goud et al. [1] studied the epoxidation of jatropa oil with peroxyacetic and peroxyformic acid, where the peroxy-carboxylic acid synthesis occurs in the aqueous phase and the epoxidation in the organic phase. In this paper, the influence of the substituent (R) of the carboxylic acid on the synthesis of the corresponding peroxy-carboxylic acid is investigated (i.e., the influence of R on  $-\text{CO}_2\text{H}$ ).

Several routes of peroxy-carboxylic acids synthesis are available, oxygenation of the parent aldehyde [2] or carboxylic acid [3]. In order to use a clean oxidation process, aqueous hydrogen peroxide is usually selected to oxidize carboxylic acids in liquid phase, as



The kinetics of the reaction is enhanced by an acid catalyst. In industry [4,5], the process is still catalyzed by a homogeneous catalyst (e.g., sulfuric acid) leading to several drawbacks (corrosion, catalyst separation, and threat for the environment). The use of a heterogeneous catalyst can surmount those problems.

In this work, the influence of the carbon chain length of the carboxylic acid on the perhydrolysis reaction is described. Experiments were carried out with the following carboxylic acids: formic, acetic, propionic and butanoic acid. Two different temperatures (30 and

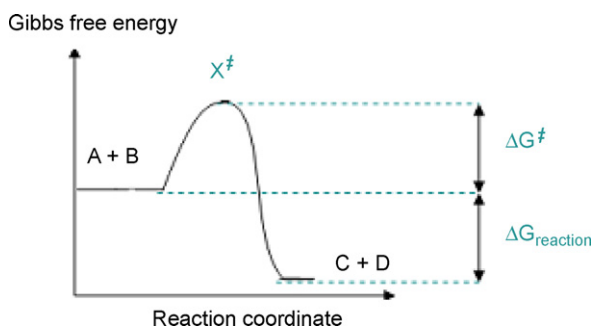


Fig. 1. Potential energy diagram for reaction  $A + B = C + D$ .

45 °C) and two different catalytic systems (homogeneous and heterogeneous) were applied. Our main purpose is to give a qualitative study of those effects on the kinetics of the reaction. Thus, the comparison of those experiments was based on the apparent kinetic rate constants.

## 2. Linear free-energy relations

Let us consider, the following reversible reaction:



For visualization of the concept of linear free-energy relationship (LFER), the potential energy diagram for this reaction is plotted in Fig. 1 ( $X^\ddagger$  is the activated complex).

The basic assumption of the concept is the existence of a relation between rate and equilibrium constant [6,7]:

$$k = \text{const} \times K^\alpha \quad (2)$$

Eq. (2) is equivalent to a linear relation between Gibbs energy of activation ( $\Delta G^\ddagger$ ) and Gibbs energy of the reaction ( $\Delta G_R$ ):

$$(\Delta G^\ddagger) = \alpha(\Delta G_R) + \text{const} \quad (3)$$

This approach can be established only for congeneric series of compounds, i.e., sets of compounds that share the same “functional group or reaction center” Y (e.g., -SH, -COOH, -CO) and only have variations in the substituents R attached to this functional group. Thus, this concept implies that there is a quantitative relationship between the structural features of a molecule and its reactivity. Eq. (3) is widely applied [8], although the theoretical explanation is still debated [9].

The pioneering research on this topic related to physical organic chemistry was done by Hammett, who quantified the effects of substituents in *m*- and *p*- position in benzene structure on ester hydrolysis. Taft [10] and Charton [11,12] expanded this approach to aliphatic series. Several applications of these relations can be explored such as understanding of the mechanism, prediction of the rate and equilibrium constants.

There are two different family of LFER: Hammett equation, which describes the behavior of *meta*- and *para*-substituted aromatic compounds; and Taft equation, which describes the behavior of aliphatic derivatives and *ortho*-substituted aromatic compounds. The main reason of these two different families is due to that the reaction center is close to the substituent in case of *o*-substituted aromatic and aliphatic compounds. Whereas, in case of *m*- and *p*-substituted aromatic compounds the reaction center and substituent are distant and strongly held by the benzene group.

Although the application of these equations for reactions homogeneously catalyzed is widespread in the literature, only few examples are found [13–16] for heterogeneously catalyzed reactions.

From the literature [10], three different effects of the substituent on the reaction center influence the rates or equilibria of a reaction:

- Polar interactions, which are associated with coulombic forces. The main contributors are inductive effect and the through-space electronic effect.
- Resonance interactions, which are due to the delocalization of electrons through  $\pi$  bond.
- Steric interactions, which result from van der Waals type forces.

Obviously, for reactions in solution, potential energies of solvation must also be considered. For that reason, experiments in this study were carried out in the same environment.

### 2.1. The Hammett equation

Even if the study of *m*- or *p*-substituted aromatic compounds is not treated in the experimental part, a brief description of Hammett equation is presented for the sake of clarity.

Within reaction series of the *m*- and *p*-substituted side-chain derivatives of benzene, the effect of structure on rates and equilibria is nearly always determined by a basic single factor, the polar effect of the substituent. Substituents are held rigidly at such large distances from the reaction center that no change in steric interactions occurs between the reactant and the transition state (in the rate case), or the product state (in the equilibrium case). Hammett established the following semi-empirical relationship:

$$\log \left( \frac{k}{k_0} \right) = \rho\sigma + \psi \quad (4)$$

where

- $\sigma$  is a substituent constant independent of the nature of the reaction. It is a quantitative measure of the polar effect in any reaction of a given *m*- or *p*- substituent relative to hydrogen atom. Hammett selected as the standard reaction for obtaining this constant the ionization of substituted benzoic acids ( $K^*$ ) in water at 25 °C:

$$\log \left( \frac{K^*}{K_0^*} \right) = \sigma \quad (5)$$

- $\rho$  is a proportionality constant, dependent upon the nature of the reaction and the conditions. It is a measure of the susceptibility of a given reaction series to polar constituent.
- $\psi$  is a parameter, which takes into account the resonance effects. This parameter is equal to zero if there is no resonance between the substituent in *m*- or *p*- and the rest of the molecule.
- The subscript zero in Eq. (4) refers to the unsubstituted benzene derivative.

Groups, which are electron withdrawing relative to hydrogen, are defined as having positive  $\sigma$  values, a reaction series in which rates or equilibria are facilitated by electron withdrawal will have a positive  $\rho$  value.

### 2.2. The Taft equation

Reactivity is greatly complicated in reaction series in which substituents are introduced close to the reaction center. This situation prevails in reactions involving *ortho*-substituted benzene derivatives and most aliphatic derivatives. For this reason, Taft [10] developed a different equation to explain the behavior of those compounds.

To illustrate that concept, Taft investigated the hydrolysis of esters or acid esterification. According to his conclusions, the effect of structure on equilibrium in this reaction is negligible, but both

the forward and reverse rates show very wide variations with the structure. Based on Hammett equation model, it was found that the three different effects should be taken into account, and, thus the following semi-empirical relation was developed:

$$\log \left( \frac{k}{k_0} \right) = \rho^* \sigma^* + \delta E_s + \psi \quad (6)$$

$\Psi$  is a parameter which takes into account the resonance effect between the substituent and the reaction center.

In contrast to Hammett polarity case, the relationship between the ionization of aliphatic carboxylic acids and the rate of hydrolysis or esterification is not linear. To evaluate the polar effects of substituent R on the rates of hydrolysis of esters RCOOR', Taft proposed the following relation:

$$\sigma^* = \frac{1}{2.48} \left[ \log \left( \frac{k}{k_0} \right)_B - \log \left( \frac{k}{k_0} \right)_A \right] \quad (7)$$

where

- $\sigma^*$  is a substituent constant dependent only upon the net polar effect of the substituent (corresponding to the rate constant  $k$ ) relative to that for the standard of comparison ( $k_0$ , R=CH<sub>3</sub>). These values are defined as measures of the inductive electron-withdrawing power of an atom or group of atoms in a molecule.
- Subscripts B and A refer to alkaline and acidic reactions, respectively, i.e., both involving the same ester, solvent and temperature.
- The factor 2.48 is a constant introduced in an attempt to put the polar effects obtained in this manner on about the same scale as for the Hammett  $\sigma$  values.

$\rho^*$  is a constant giving the susceptibility of a given reaction series to polar substituents. Its value depends upon the nature of the reaction center Y, the attacking reagent and the experimental conditions (solvent, temperature).

Except for unsaturated substituent conjugated with the carbonyl group, or for substituent which gives rise to changes in attractive interaction between reactant and transition states, e.g., internal hydrogen bonding, it has been assumed that the non-polar ( $\log(k/k_0)$ )<sub>A</sub> values are near-quantitative measures of the net potential- and kinetic-energy steric effects. Again, the strongest argument in favor of this assumption is its ability to describe experimental results. In equation, this assumption is given by

$$\log \left( \frac{k}{k_0} \right)_A = E_s \quad \text{and} \quad \log \left( \frac{k}{k_0} \right)_B = 2.48 \sigma^* + E_s \quad (8)$$

$E_s$  is a near-quantitative measure of the total steric effect associated with a given substituent relative to the standard of comparison. The standard of comparison in each case is the CH<sub>3</sub> group, whereas the reference group is the substituent H in the case of Hammett approach,  $\delta$  is a reaction constant, independent of the nature of the substituents. The value of  $\delta$  gives a measure of the relative susceptibility of the reaction series to the steric requirements of the substituents.

MacPhee et al. [17] have revisited the Taft  $E_s$  scale, by choosing as reference reaction the acid catalyzed esterification of carboxylic acids in methanol at 40 °C. In this paper, we have chosen to use this modified scale. However, for Taft  $\sigma^*$  values the original scale was applied.

### 2.3. Charton relationship

Charton [11,12] has proposed a modified Taft correlation, based on the van der Waals radii of the substituents. Indeed, the parameter  $E_s$  is linearly proportional to van der Waals radii, and, therefore it is the true measure of the steric effect. The second important conclusion was that the rates of acid-catalyzed esterification are

**Table 1**  
Experimental matrix.

Reaction temperature	30–45 °C
Rotation speed	250 rpm
[CA] <sub>0</sub>	5.8–9.0 mol l <sup>-1</sup>
[H <sub>2</sub> O <sub>2</sub> ] <sub>0</sub>	4.3–7.5 mol l <sup>-1</sup>
[H <sub>2</sub> O] <sub>0</sub>	17–28.2 mol l <sup>-1</sup>
[H <sub>2</sub> SO <sub>4</sub> ] <sub>0</sub>	0.10–0.15 mol l <sup>-1</sup>
Amberlite loading on dry basis	50.8–73.6 g l <sup>-1</sup>

solely a function of steric effects at least for the substituent studied. Thus, the following equation was established:

$$\log k = \psi v_X + h \quad (9)$$

where  $v_X$  is a steric parameter defined by the relationship  $v_X = r_{v_X} - r_{v_H} = r_{v_X} - 1.2$ ;  $r_{v_X}$  is the van der Waals radius of the substituent X, and  $r_{v_H}$  is the van der Waals radius of the hydrogen atom.

According to MacPhee et al. [17], the scope of Eq. (9) cannot be extended to groups, which impose steric hindrance.

## 3. Experimental conditions

### 3.1. Apparatus and experimental procedures

All experiments were performed in a 250 ml jacketed glass reactor vessel. The reactor was equipped with a mechanical agitator and a temperature probe. Water was pumped through the outer jacket of the vessel to control the temperature of the reaction mixture. A pitched blade impeller (PTFE coated) was used to ensure a vigorous mixing (agitation speed was adjusted at 250 rpm) during the reaction.

A reflux condenser was attached to the top of the reactor (adjusted at 0 °C) to avoid loss of liquid phase compounds. In case that decomposition of peroxycarboxylic acid (PCA) or H<sub>2</sub>O<sub>2</sub> appeared, a carrier gas (Helium, AGA, 99.996%) was introduced to the reactor through one of the necks in order to avoid accumulation of oxygen in the gas phase.

To prevent contamination induced by alkaline and metal components, which initiate the catalytic decomposition of peroxycarboxylic acid and hydrogen peroxide, all parts of the reactor system being in contact with the reaction solution were washed with hydrochloric acid followed by another washing, with a phosphate free detergent solution.

At the first stage, carboxylic acids (propionic acid: Acros, 99 wt.%, acetic acid: J.T. Baker 99–100 wt.%, butanoic acid: Fluka 98 wt.% and formic acid: J.T. Baker 98 wt.%) and the catalyst (sulfuric acid: J.T. Baker 95–97 wt.% and Amberlite IR-120 Aldrich) were mixed together in the reactor. When the reaction desired temperature was reached, preheated hydrogen peroxide solution (Merck, 30 wt.%) was added through a dropping funnel. At the time “zero” the required amount was introduced into the reactor. The experimental matrix is summarized in Table 1.

All experiments in one series were carried out at the same conditions regarding the temperature and agitation speed. However, due to the difference of molecular masses of the different acids, it is not their initial concentrations which were kept constant but their molar amounts. In other words, the initial number of moles of water, carboxylic acid, number of acid sites and hydrogen peroxide were kept constant in a reaction series (cf. Table 2).

Two series were carried out with sulfuric acid at 30 °C and 45 °C, and two series with a heterogeneous catalyst at 30 °C and 45 °C.

**Table 2**  
Initial number of moles.

$n_0$ (CA)	1.1–1.2 mol
$n_0$ (H <sub>2</sub> O <sub>2</sub> )	0.8–1.1 mol
$n_0$ (H <sub>2</sub> O)	3.5–4.1 mol
$n_0$ (H <sub>2</sub> SO <sub>4</sub> )	0.02 mol
$n_0$ (H <sup>+</sup> ) from resin	0.04–0.05 mol

### 3.2. Analytical methods

Samples were withdrawn from the reaction mixture by a plastic syringe (to avoid contamination of the solution by trace of metals) and were analyzed by the Greenspan and Mackellar method [18]. The concentration of hydrogen peroxide was determined by titration using a standard solution of ammonium cerium sulfate (0.1N). The concentrations of carboxylic and peroxy-carboxylic acids were determined by titration with an automatic titrator (Metrohm 751 GPD Titrino) using a standard solution of sodium hydroxide (0.2N).

### 3.3. Catalyst properties and characterization

The properties of the Amberlite IR-120 are summarized in Table 3. It is a cation exchange resin with a styrene-divinyl benzene matrix bearing sulfonic acid groups, which were used in the form of beads.

The Amberlite IR-120 catalyst was pre-treated before using, i.e., it was dried at 99 °C for 48 h.

The concentration of acid sites of catalyst was determined by titration [19]. Around 0.5 g of the catalyst sample was added to about 50 ml of NaCl solution (200 g/l) and stirred. The ion exchange between H<sup>+</sup> and Na<sup>+</sup> was allowed to proceed for 24 h. The mixture

**Table 3**  
Properties of Amberlite IR-120 given by the manufacturer.

Amberlite IR-120	
Polymer type	Gel
Cross-linking (%)	8
Moisture content (% mass)	45
Capacity by dry weight (mequiv./g)	4.4
Native particle size range (mm)	0.3–1.2

was then titrated with 0.1N NaOH solution. To have a complementary method to determine the capacity of the resins, an elementary analysis of sulfur content was carried out by a ThermoQuest Flash EA1112 Series elemental.

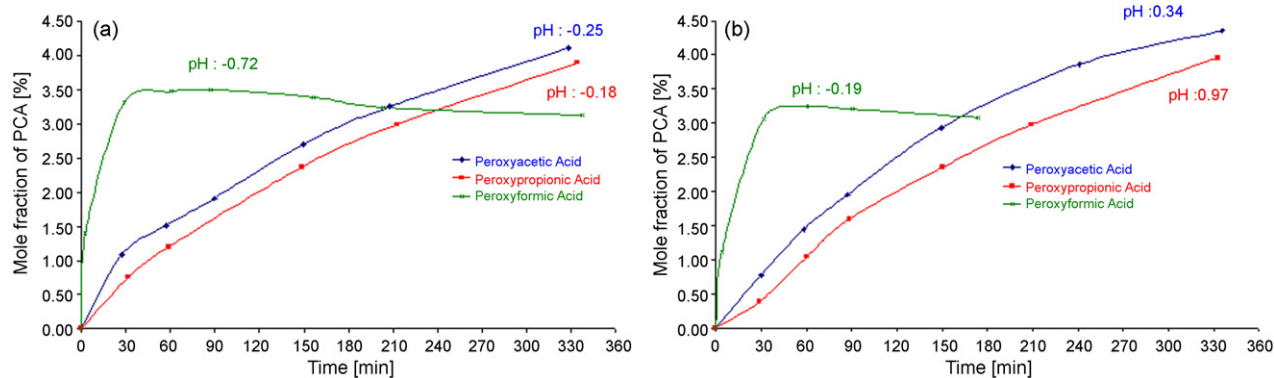
## 4. Results and discussion

### 4.1. Catalyst characterization

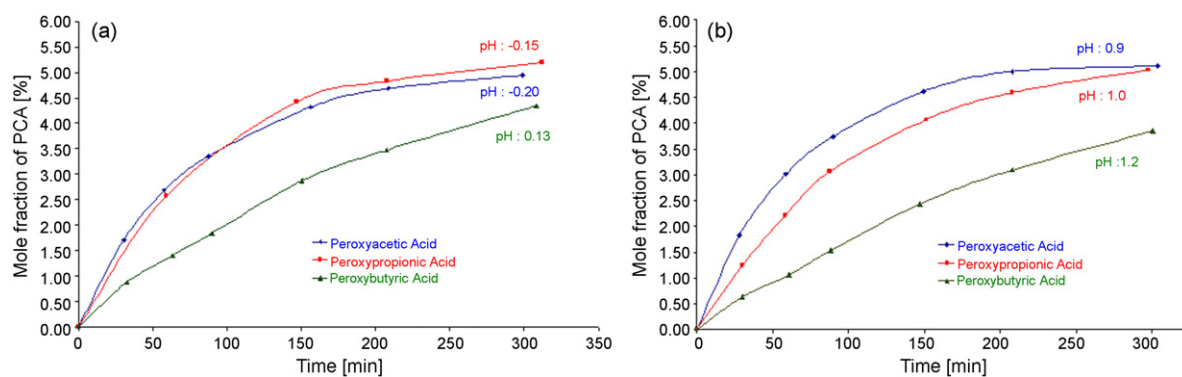
The exchange capacity of the resin, determined by the titration method, is equal to 4.7 mequiv./g (on dry basis). The unit mequiv./g states for milli-equivalent per gram, which represents the number of moles of sulfonic group per gram of resins. This value is an average value of three different sets of experiments.

By assuming that all the sulfur determined by the elementary analysis corresponds to –SO<sub>3</sub>H group, the average capacity value was calculated to be equal to 4.4 mequiv./g (on dry basis).

By using titration method, Musante et al. have found a capacity equal to 4.5 mequiv./g (on dry basis) [20]. The exact value of Amberlite IR-120 capacity is difficult to determine, due to experimental errors, sensitivity of the elementary analysis and the non-ideality of the titration mixture. Moreover, the behavior of those resins in our



**Fig. 2.** Mole fraction of PCA versus time at 30 °C with sulfuric acid concentration at 0.11–0.15 M (a) and with pre-treated Amberlite IR-120 at an apparent concentration of 0.25–0.32 M (b).



**Fig. 3.** Mole fraction of PCA versus time at 45 °C with sulfuric acid concentration at 0.10–0.11 M (a) and with pre-treated Amberlite IR-120 at an apparent concentration of 0.22–0.28 M (b).



reaction mixture might be different. Then, it is reasonable to assume that the capacity value fluctuates between 4.4–4.7 mequiv./g (on dry basis).

#### 4.2. Use of linear free-energy relations

From the literature [20–23], the rate of formation of peroxy-carboxylic acid is expressed by the following relation:

$$\frac{d[\text{PCA}]}{dt} = k \left( [\text{CA}][\text{H}_2\text{O}_2] - \frac{1}{K_{\text{eq}}} [\text{PCA}][\text{H}_2\text{O}] \right) \quad (10)$$

A detailed kinetic equation has been developed [21] by taking into account the effect of water and catalyst concentrations. However, the main goal of the current study is to check if the perhydrolysis of linear carboxylic acids follows the LFER, and investigate the sensitivity of the LFER parameters towards the reaction temperature and the nature of the catalyst. The apparent rate constant  $k_{\text{app}}$  was obtained by plotting the rate of formation of peroxy-carboxylic acids versus the product concentration of carboxylic acid and hydrogen peroxide:

$$\frac{d[\text{PCA}]}{dt} = k_{\text{app}}[\text{CA}][\text{H}_2\text{O}_2] \quad (11)$$

Figs. 2 and 3 show the mole fraction of peroxy-carboxylic acids as a function of time at 30 °C and 45 °C with the homogeneous and the heterogeneous catalyst.

In case of heterogeneous catalysis, the apparent  $[\text{H}^+]$  concentration (the number of Brønsted sites of the solid catalyst present per liter of reaction mixture) was used. This value was calculated on the basis of the cation exchange capacity by dry weight (mequiv./g) provided by the acidity measurements.

Synthesis of peroxyformic acid was carried out only at 30 °C because of safety concerns. As can be seen from Fig. 2, peroxyformic acid is not stable. Mošovský et al. [24], have studied the synthesis of peroxyformic acid using sulfuric acid, and also noticed occurrence of this compound decomposition. For that reason, the apparent rate constant for the synthesis of peroxyformic acid was calculated before the decomposition phase starts.

No decomposition was observed for other peroxy-carboxylic acids, which is in line with our previous study [25] and literature data [26].

Synthesis of peroxybutyric acid was carried out at 45 °C because below this temperature butyric acid is not soluble in water.

Table 4 shows the apparent rate constants for the perhydrolysis of different carboxylic acids. As can be noticed, the apparent rate constants decrease in the following order:  $k_{\text{app}}$  (PFA) >  $k_{\text{app}}$  (PAA) >  $k_{\text{app}}$  (PPA) >  $k_{\text{app}}$  (PBA). Even if the apparent concentration of active site  $[\text{H}^+]$  is twofold of the sulfuric acid concentration, the apparent rate constant for the homogeneous catalyst is higher than

**Table 4**

Apparent rate constants ( $1 \text{ mol}^{-1} \text{ s}^{-1}$ ).

	Sulfuric acid		Pre-treated Amberlite IR-120	
	30	45	30	45
FA	2.00E–04	–	1.00E–04	–
AA	1.06E–05	1.95E–05	7.00E–06	2.23E–05
PA	7.29E–06	1.64E–05	1.16E–06	1.59E–05
BA	Non-soluble	1.28E–05	Non-soluble	5.00E–06

**Table 5**

Polar and steric parameters for LFER.

Substituent	$E_s$	$\sigma^*$	$\nu_x$
H–	1.12	0.49	0.00
CH <sub>3</sub> –	0.00	0.00	0.52
CH <sub>3</sub> –CH <sub>2</sub> –	–0.08	–0.10	0.56
CH <sub>3</sub> –CH <sub>2</sub> –CH <sub>2</sub> –	–0.31	–0.12	0.68

for the heterogeneous counterpart.

Those apparent rate constants were used in Eqs. (6) and (9) to determine the parameters dependent upon the nature of the perhydrolysis reaction ( $\rho^*$ ,  $\delta$ ,  $\psi$  and  $h$ ). The constant parameters such as steric parameter of Taft ( $E_s$ ), Charton parameter ( $\nu_x$ ), and polar  $\sigma^*$  are displayed in Table 5.

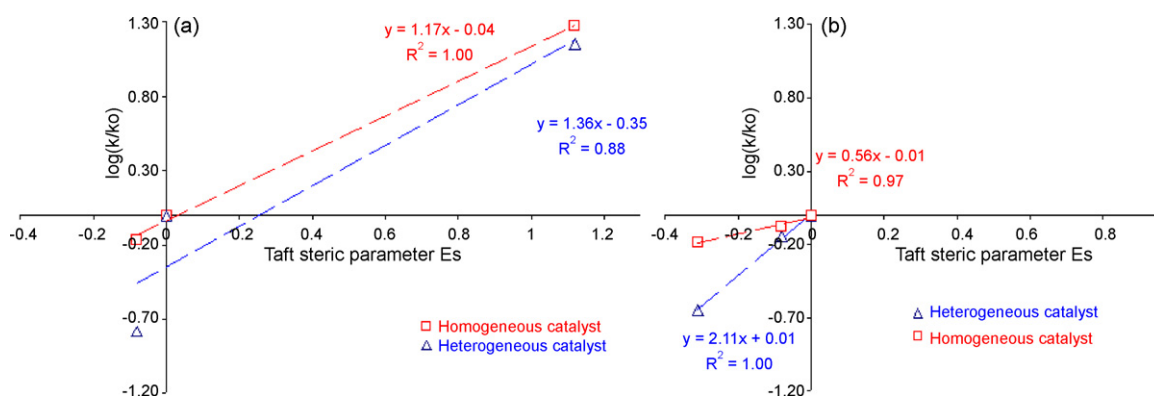
From Table 5, one can notice that a high value of  $E_s$  implies a low steric hindrance; the substituent CH<sub>3</sub>– is defined as a reference. In the case of the steric factor  $\nu_x$ , it is the opposite, i.e., a high value of  $\nu_x$  implies a high steric hindrance; and the substituent H– is defined as a reference. A high value of the polar parameter  $\sigma^*$  implies a high polar effect of the substituent, CH<sub>3</sub>– is chosen as a reference. For instance, the value of  $\sigma^*$  for Cl– substituent is equal to 2.96. Note that the polar part is negligible for linear carbon chain substituent.

##### 4.2.1. Use of Taft equation

Several assumptions can be done for the cases investigated here. First of all, there is no resonance effect between the functional group and the substituent for the carboxylic acids used in the experiments. The different polar parameters  $\sigma^*$  can be negligible because their values are low, and the experiments were carried out in acidic media. Indeed, Taft-Ingold and Charton have noticed that polar effect is negligible for experiments carried out in an acidic media [10]. Then, Eq. (6) becomes:

$$\log \left( \frac{k}{k_0} \right) = \delta E_s \quad (12)$$

Fig. 4 represents the application of Taft equation to the perhydrolysis of different carboxylic acids with sulfuric acid and pre-treated Amberlite IR-120 at 30 °C and 45 °C.



**Fig. 4.** Taft equation (Eq. (12)) for perhydrolysis of different carboxylic acids with  $\text{H}_2\text{SO}_4$  and Amberlite IR-120 at 30 °C (a) and 45 °C (b).

**Table 6**  
Value of coefficient  $\delta$ .

	Coefficient $\delta$	
	$T = 30^\circ\text{C}$	$T = 45^\circ\text{C}$
Homogeneous catalyst	1.17	0.56
Heterogeneous catalyst	1.36	2.11

For the sake of clarity, the values of the coefficient  $\delta$  are summarized in Table 6.

At a first glance, Fig. 4 shows that perhydrolysis of carboxylic acids, catalyzed by an acid catalyst, follows the Taft equation by considering only the steric part. It can be concluded that the mechanism of formation of linear carboxylic acid is the same, i.e., there is no difference between the formation of peroxyacetic and peroxybutanoic acid.

In case of homogeneous catalysis, the apparent rate constant  $k_{\text{app}}$  can be split into two different parts associated with: hydroxonium ions from the dissociation of sulfuric acid and from the dissociation of carboxylic acid, respectively;  $k_{\text{app}} = f(\text{H}_2\text{SO}_4, \text{CA})$ .

In case of heterogeneous catalysis, kinetics is more complex because an adsorption phenomenon appears. Then, the apparent rate constant  $k_{\text{app}}$  depends on: hydroxonium ions concentration from the dissociation of carboxylic acid, active site concentration of the catalysts and the adsorption term of the different species  $K_{\text{ads}}$ ;  $k_{\text{app}} = f(\text{CA}, \text{Amberlite}, K_{\text{ads}})$ .

The active site of Amberlite IR-120 is the functional group  $-\text{SO}_3\text{H}$ , which is structurally close to sulfuric acid. The apparent rate constant is proportional to the active site concentration in case of the heterogeneous catalyst and to hydroxonium ions concentration in case of the homogeneous catalyst. However, in case of heterogeneous catalyst, the rate constant and the adsorption term are related

by  $k_{\text{het}} \propto (1/1 + K_{\text{ads}})$ . Thus, the main difference between the two catalytic systems is the adsorption term, which could explain the change of the slope  $\delta$  between systems catalyzed homogeneously and heterogeneously. A more detailed kinetic expression will be given below.

Experiments carried out at  $30^\circ\text{C}$  show that the slopes of the curves appear to be parallel. The accuracy of the calculated apparent rate constant for the perhydrolysis of formic acid is lower than the other rate constants. Experiments carried out at  $45^\circ\text{C}$  show that the slopes  $\delta$  in case of homogeneous and heterogeneous catalysts are different. This difference might be certainly due to the adsorption term.

Table 6 demonstrates that the values of  $\delta$  are dependent of the reaction temperature, and the nature of the catalyst at  $45^\circ\text{C}$ . The value of  $\delta$  is positive, as in the case of the acid catalyzed hydrolysis of ethyl esters in aqueous acetone at  $24.8^\circ\text{C}$ , where the value of the slope  $\delta$  is equal to 1.038 [17].

By comparing the slope  $\delta$  from Table 6, one can notice that its value increases when heterogeneous catalysts are used instead of a homogeneous catalyst.

In order to check if the assumption that polar effect is negligible, the steric effect of Eq. (6) is neglected. Then, it becomes:

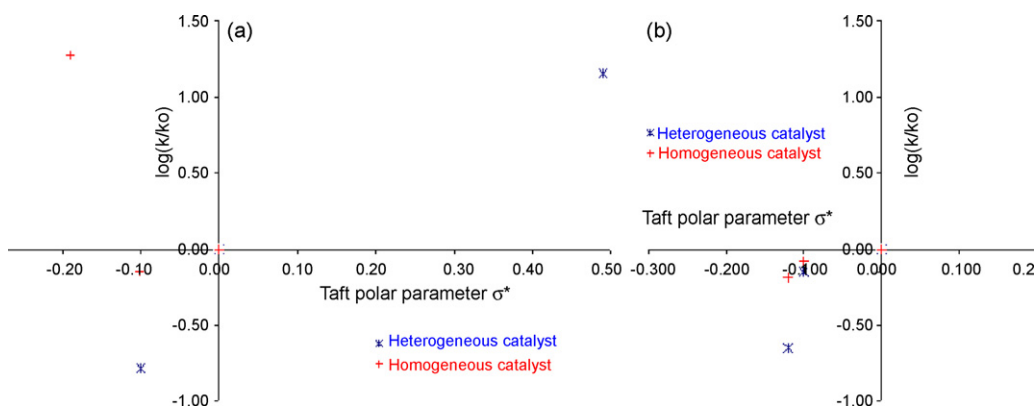
$$\log\left(\frac{k}{k_0}\right) = \rho^* \sigma^* \quad (13)$$

The results of this equation are shown in Fig. 5.

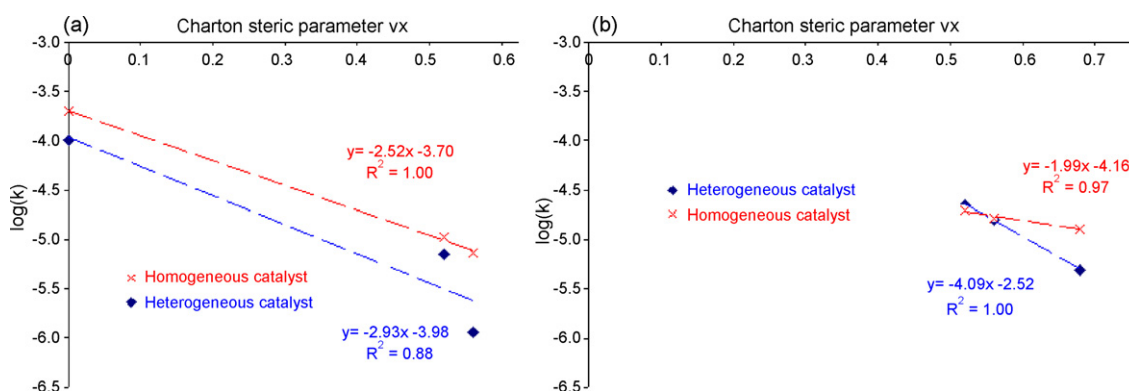
Fig. 5 confirms that there is no linear relation between the logarithm of the rate constant and the polar parameters.

#### 4.2.2. Use of Charton equation

The Charton correlation takes into account only the steric effect of the substituent on the reaction center. The application of Eq. (9) to



**Fig. 5.** Taft equation (Eq. (13)) for perhydrolysis of different carboxylic acids with  $\text{H}_2\text{SO}_4$  and Amberlite IR-120 at  $30^\circ\text{C}$  (a) and  $45^\circ\text{C}$  (b).



**Fig. 6.** Charton equation (Eq. (9)) for perhydrolysis of different carboxylic acids with  $\text{H}_2\text{SO}_4$  and Amberlite IR-120 at  $30^\circ\text{C}$  (a) and  $45^\circ\text{C}$  (b).

**Table 7**  
Coefficients  $\psi$  and  $h$  from Fig. 6.

	Coefficient $\psi$		$h$	
	$T=30^\circ\text{C}$	$T=45^\circ\text{C}$	$T=30^\circ\text{C}$	$T=45^\circ\text{C}$
Homogeneous catalyst	-2.52	-1.09	-3.7	-4.16
Heterogeneous catalyst	-2.93	-4.09	-3.98	-2.52

the perhydrolysis of different carboxylic acids is displayed in Fig. 6. From this figure, it is evident that the apparent rate constant for this reaction follows Charton relation, thus the polar effects are negligible for the perhydrolysis of linear carboxylic acids. The slopes for experiments carried out at  $30^\circ\text{C}$  are parallel. This parallelism is not due to the polar effect.

$$r_{\text{tot}} = \left( \frac{k_{\text{het}}[-\text{SO}_3\text{H}]_0}{(1 + K_{\text{ads,CA}}^{\text{C}}[\text{RCOOH}] + K_{\text{ads,PCA}}^{\text{C}}[\text{RCO}_3\text{H}] + K_{\text{ads,water}}^{\text{C}}[\text{H}_2\text{O}])} + \frac{k_{\text{hom}} \times \sqrt{K_{\text{RCOOH}}^{\text{C}}[\text{RCOOH}][\text{H}_2\text{O}]}}{[\text{H}_2\text{O}]} \right) \times \left( [\text{RCOOH}][\text{H}_2\text{O}_2] - \frac{1}{K^{\text{C}}}[\text{RCO}_3\text{H}][\text{H}_2\text{O}] \right) \quad (17)$$

$$k_{\text{app}}^{\text{het}} = \left( \frac{k_{\text{int}}^{\text{het}}[-\text{SO}_3\text{H}]_0}{(1 + K_{\text{ads,CA}}^{\text{C}}[\text{RCOOH}] + K_{\text{ads,PCA}}^{\text{C}}[\text{RCO}_3\text{H}] + K_{\text{ads,water}}^{\text{C}}[\text{H}_2\text{O}])} + \frac{k_{\text{int}}^{\text{hom}} \times \sqrt{K_{\text{RCOOH}}^{\text{C}}[\text{RCOOH}][\text{H}_2\text{O}]}}{[\text{H}_2\text{O}]} \right) \quad (18)$$

For the sake of clarity, the values of the coefficient  $\psi$  and  $h$  are summarized in Table 7.

Liu et al. [15] have studied the esterification of acetic, propionic, butyric and hexanoic acid with methanol using sulfuric acid, and SAC-13 which is a Nafion/silica composite solid acid (fiber form) at  $60^\circ\text{C}$ . The mechanism for esterification and perhydrolysis of carboxylic acids is quite similar, therefore a qualitative comparison is possible. At the same time, the turnover frequencies were used in [15] instead of the apparent rate constant in Eq. (9), which should not, however, change qualitatively the results.

In the case of esterification, a negative value for the slope  $\psi$  was found as well with the curves, which describe homogeneous and heterogeneous catalyst systems being, however, parallel to each other.

The parallelism of the curves for perhydrolysis of carboxylic acids with homogeneous and heterogeneous catalysts (Taft or Charton correlation) is not clear. If it is genuine, further kinetic analysis is required, which is presented below.

#### 4.2.3. Kinetic equation

In a previous paper [21], the rate of formation of peroxy-carboxylic acids using sulfuric acid is expressed:

$$r_{\text{tot}} = k \times \frac{[\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]} \times \left( [\text{RCOOH}] \times [\text{H}_2\text{O}_2] - \frac{1}{K^{\text{C}}} \times [\text{RCO}_3\text{H}] \times [\text{H}_2\text{O}] \right) \quad (14)$$

The hydroxonium ions concentration was determined based on the electroneutrality principle:

$$[\text{H}_3\text{O}^+] = \frac{1}{2} \times [\text{H}_2\text{SO}_4]_0 + \sqrt{\frac{[\text{H}_2\text{SO}_4]_0^2}{4} + 2 \times K_{\text{II}}^{\text{C}} \times [\text{H}_2\text{SO}_4]_0 \times [\text{H}_2\text{O}] + K_{\text{III}}^{\text{C}} \times [\text{H}_2\text{O}] \times [\text{CH}_3\text{CH}_2\text{COOH}]} \quad (15)$$

Then, the apparent rate constant  $k_{\text{app}}$  is

$$k_{\text{app}}^{\text{hom}} = k_{\text{int}}^{\text{hom}} \frac{[\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]} \quad (16)$$

where  $k_{\text{int}}^{\text{hom}}$  is the intrinsic rate constant for the homogeneous system.

In case of experiments carried out with Amberlite IR-120, an Eley-Rideal mechanism can be applied, which implies that only one reactant, is adsorbed on the surface. Due to a similarity with esterification reaction and the fact that it is the protonation of the carbonyl group which is a key step; only carboxylic acid is assumed to be adsorbed.

The protolysis of carboxylic acid and the adsorption of water on the active sites should be taken into account in the reaction rate (Eq. (17)):

Then, the apparent rate constant  $k_{\text{app}}$  is

$$k_{\text{app}}^{\text{het}} = \left( \frac{k_{\text{int}}^{\text{het}}[-\text{SO}_3\text{H}]_0}{(1 + K_{\text{ads,CA}}^{\text{C}}[\text{RCOOH}] + K_{\text{ads,PCA}}^{\text{C}}[\text{RCO}_3\text{H}] + K_{\text{ads,water}}^{\text{C}}[\text{H}_2\text{O}])} + \frac{k_{\text{int}}^{\text{hom}} \times \sqrt{K_{\text{RCOOH}}^{\text{C}}[\text{RCOOH}][\text{H}_2\text{O}]}}{[\text{H}_2\text{O}]} \right) \quad (18)$$

where  $k_{\text{int}}^{\text{hom}}$  and  $k_{\text{int}}^{\text{het}}$  represent the intrinsic rate constants.

Note that Eq. (6) in principle should be used for an elementary reaction. By using Eqs. (16) and (18), Eq. (12) becomes:

- In case of the homogeneous catalyst:

$$\log \left( \frac{k_{\text{app}}^{\text{hom}}(\text{CA})}{k_{\text{app}}^{\text{hom}}(\text{AA})} \right) = \log \left( \frac{k_{\text{int}}^{\text{hom}}(\text{CA})}{k_{\text{int}}^{\text{hom}}(\text{AA})} \right) + \log \frac{[\text{H}_3\text{O}^+]_{\text{CA}}}{[\text{H}_3\text{O}^+]_{\text{AA}}} + \text{const} = \delta_{\text{hom}} \cdot E_s \quad (19)$$

If the water concentration is the same or similar in both cases, then the last term of Eq. (19) can be neglected. If the protolysis of the carboxylic acid is similar to the protolysis of acetic acid, then, the second term can be neglected, as well. Therefore, Eq. (19) becomes:

$$\log \left( \frac{k_{\text{app}}^{\text{hom}}(\text{CA})}{k_{\text{app}}^{\text{hom}}(\text{AA})} \right) = \log \left( \frac{k_{\text{int}}^{\text{hom}}(\text{CA})}{k_{\text{int}}^{\text{hom}}(\text{AA})} \right) = \log \left( \frac{A_{\text{CA}}}{A_{\text{AA}}} \right) + \frac{1}{2.3RT} (\Delta G_{\text{AA}}^\ddagger - \Delta G_{\text{CA}}^\ddagger) = \delta_{\text{hom}} \cdot E_s \quad (20)$$

By using the Arrhenius relationship, the intrinsic rate constant is expressed by:  $k_{\text{int}} = A \exp(-\Delta G^\ddagger/RT)$ , where  $A$  is the pre-exponential factor,  $R$  is the gas constant,  $\Delta G^\ddagger$  is the Gibbs energy of activation.

Eq. (20) shows the linear relation between the Gibbs energy of activation  $\Delta G^\ddagger$  and the apparent rate constant. One should keep

in mind that this relation is valid only in case where the protolysis of a carboxylic acid is similar to acetic acid and the substituent has only a steric effect on the functional group.

- In a case of a heterogeneous catalyst, one gets:

$$\log \left( \frac{k_{\text{app}}^{\text{het}}(\text{CA})}{k_{\text{app}}^{\text{het}}(\text{AA})} \right) = \log \left( \frac{(k_{\text{int}}^{\text{het}}[-\text{SO}_3\text{H}]_0)/(1 + K_{\text{ads,CA}}^{\text{C}}[\text{RCOOH}] + K_{\text{ads,PAA}}^{\text{C}}[\text{RCO}_3\text{H}] + K_{\text{ads,water}}^{\text{C}}[\text{H}_2\text{O}]) + (k_{\text{int}}^{\text{hom}} \times \sqrt{K_{\text{RCOOH}}^{\text{C}}[\text{RCOOH}][\text{H}_2\text{O}]})/[\text{H}_2\text{O}]}{k_{\text{int}}^{\text{het}}[-\text{SO}_3\text{H}]_0/(1 + K_{\text{ads,AA}}^{\text{C}}[\text{AcOH}] + K_{\text{ads,PAA}}^{\text{C}}[\text{AcOOH}] + K_{\text{ads,water}}^{\text{C}}[\text{H}_2\text{O}]) + (k_{\text{int}}^{\text{hom}} \times \sqrt{K_{\text{AcOH}}^{\text{C}}[\text{AcOH}][\text{H}_2\text{O}]})/[\text{H}_2\text{O}]} \right) = \delta_{\text{het}} \cdot E_s \quad (21)$$

By neglecting the homogeneous part in Eq. (21) and by assuming that the concentration of the active sites is the same for both systems, one arrives at

$$\log \left( \frac{k_{\text{app}}^{\text{het}}(\text{CA})}{k_{\text{app}}^{\text{het}}(\text{AA})} \right) = \log \left( \frac{k_{\text{int}}^{\text{het}}(\text{CA})}{k_{\text{int}}^{\text{het}}(\text{AA})} \right) + \log \left( \frac{1 + K_{\text{ads,AA}}^{\text{C}}[\text{AcOH}] + K_{\text{ads,PAA}}^{\text{C}}[\text{AcOOH}] + K_{\text{ads,water}}^{\text{C}}[\text{H}_2\text{O}]}{1 + K_{\text{ads,CA}}^{\text{C}}[\text{RCOOH}] + K_{\text{ads,PAA}}^{\text{C}}[\text{RCO}_3\text{H}] + K_{\text{ads,water}}^{\text{C}}[\text{H}_2\text{O}]} \right) \quad (22)$$

Applying Arrhenius law for the intrinsic rate constants Eq. (22) becomes

$$\log \left( \frac{k_{\text{app}}^{\text{het}}(\text{CA})}{k_{\text{app}}^{\text{het}}(\text{AA})} \right) = \log \left( \frac{A_{\text{CA}}}{A_{\text{AA}}} \right) + \frac{1}{2.3RT} (\Delta G_{\text{AA}}^{\ddagger} - \Delta G_{\text{CA}}^{\ddagger}) + \log \left( \frac{1 + K_{\text{ads,AA}}^{\text{C}}[\text{AcOH}] + K_{\text{ads,PAA}}^{\text{C}}[\text{AcOOH}] + K_{\text{ads,water}}^{\text{C}}[\text{H}_2\text{O}]}{1 + K_{\text{ads,CA}}^{\text{C}}[\text{RCOOH}] + K_{\text{ads,PAA}}^{\text{C}}[\text{RCO}_3\text{H}] + K_{\text{ads,water}}^{\text{C}}[\text{H}_2\text{O}]} \right) = \delta_{\text{het}} \cdot E_s \quad (23)$$

As can be seen, the adsorption term is taken into account in Eq. (23). However, in case when this term is negligible, e.g., adsorption phenomena are negligible, then the slope of  $\delta_{\text{hom}}$  and  $\delta_{\text{het}}$  can be similar. In case that the adsorption term is constant with the different carboxylic acids, then the logarithm term for the adsorption tends to zero, and, subsequently,  $\delta_{\text{hom}}$  and  $\delta_{\text{het}}$  can be similar.

## 5. Conclusions

The synthesis of different peroxycarboxylic acid was treated in order to establish a relationship between the structure of carboxylic acids and their reactivity. To accomplish this goal Linear Free-Energy Relations were used in the form of Taft and Charton correlations. A comparison between homogeneous and heterogeneous catalyst system is done by using sulfuric acid and a cation exchange resin Amberlite IR-120.

Based on the experiments, the apparent rate constants decreased in the following order:  $k_{\text{app}}(\text{PFA}) > k_{\text{app}}(\text{PAA}) > k_{\text{app}}(\text{PPA}) > k_{\text{app}}(\text{PBA})$  in both catalytic systems, which demonstrates the importance of steric hindrance. The catalytic activity in case of the homogeneous system is higher than in case of the heterogeneous one.

Perhydrolysis of carboxylic acids catalyzed either homogeneously or heterogeneously follows the Taft (based on the steric part) and Charton correlations, which implies that the steric effect of the substituent on the reaction center governs the reaction, but not the polar effect. It was found that the parameters  $\delta$  or  $\psi$  are temperature dependent.

The difference between  $\delta_{\text{hom}}$  and  $\delta_{\text{het}}$  or  $\psi_{\text{hom}}$  and  $\psi_{\text{het}}$  allows to elucidate the importance of the adsorption.

The major problem with experiments carried out with formic acid is the instability of the formed peroxycarboxylic acid, and the importance of the self-catalytic effect of formic acid on the perhydrolysis reaction. These two phenomena prevent very accurate measurements of the apparent rate constant.

Semi-empirically equations used in this study, even if they do not show a clear dependence between the Gibbs energy of activation and the Gibbs energy of reaction, are excellent tools to elucidate the mechanism and predict the reaction rates.

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