

Stereoselective Synthesis and Corrosion Inhibition Behaviour of Allyldihydrocarveols on Steel in Molar Hydrochloric Acid

S. Kharchouf¹, L. Majidi^{1,*}, M. Znini¹, J. Costa², B. Hammouti³, J. Paolini²

¹Université My Ismail, Laboratoire des Substances Naturelles & Synthèse et Dynamique Moléculaire, Faculté des Sciences et Techniques, Errachidia, Morocco.

²Université de Corse, UMR CNRS 6134, Laboratoire de Chimie des Produits Naturels, Faculté des Sciences et Techniques, Corse, France.

³LCAE-URAC18, Faculté des Sciences, Université Mohammed Premier ; 60000 Oujda, Morocco.

*E-mail: lmajidi@yahoo.fr

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The addition of allylic Grignard reagents to dihydrocarvone gives rise to allyldihydrocarveol **P1-P3**. The reaction is completely stereoselective. Allyldihydrocarveols **P1-P3** are tested as corrosion inhibitors of steel in 1M HCl using weight loss measurements. The results show that the addition of Allyldihydrocarveols decreases weakly the corrosion rate and increases the inhibition efficiency to reaches 77 %, 70% and 67% for **P1**, **P2** and **P3** at 3 g/L, respectively. The inhibitor adsorption process in mild steel/(**P1-P3**)/hydrochloric acid system was studied at different temperatures (313–333 K) by means of weight loss measurements. The adsorption of Allyldihydrocarveols **P1-P3** on steel surface obeyed Langmuir's adsorption isotherm. The corresponding kinetic parameters were determined and discussed.

Keywords: Corrosion Inhibition, Steel, dihydrocarvone, Allyldihydrocarveols, Adsorption

1. INTRODUCTION

Mild steel is extensively used in industry especially for structural applications, but its susceptibility to rusting in humid air and its high dissolution rate in acid mediums are the major obstacles for its use on larger scale [1]. Thus, considerable efforts are made to stop or delay to the maximum the attack of this metal in various corrosive media.

The corrosion inhibitors are one of the largest products within water treatment chemicals market, and the global corrosion inhibitor market is expected to grow from ca. \$ 5 billion in 2010 to ca. \$6 billion in 2015 [2]. The corrosion inhibitors can be either inorganic or organic materials, and

Hinton reviewed corrosion inhibitors containing rare earth metals, the interested readers are referred to the review [3]. Since some of inorganic inhibitors, e.g. chromate compounds, are carcinogenic and lead to DNA damage and have high risk of environmental pollution [4,5], the use of organic inhibitors is more demanded. Indeed, the synthesis of new natural derivatives products offers various molecular structures containing several heteroatoms and substituents. Their adsorption is generally explained by the formation of an adsorptive film of a physical and/or chemical character on the metal surface. We previously reported that pulegone and epoxy-pulegone [6], menthol derivatives [7], 2-Allyl-*p*-mentha-6,8-dien-2-ols [8] and Epoxy-allylpulegols [9] have been found to be very efficient corrosion inhibitors for steel in acid media.

In continuation of our work on development of natural products as acid inhibitors [10], we have firstly synthesized three dihydrocarveol derivatives (P1, P2 and P3) from dihydrocarvone (Fig.1) and secondly investigated the corrosion inhibitor of steel in 1 M hydrochloric acid in the presence of these compounds using Weight loss measurements.

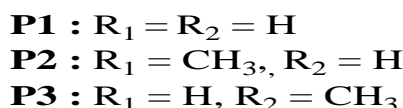
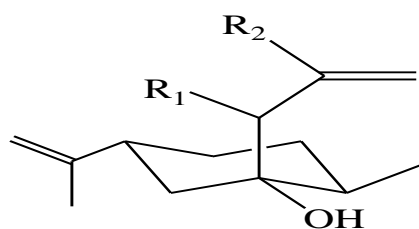


Figure 1. Chemical structure of Allyldihydrocarveols P1-P3

2. EXPERIMENTAL PART

2.1. Synthesis of Allyldihydrocarveols (P1-P3)

Infrared (IR) spectra were recorded on Shimadzu IR-470. 1H NMR spectra were determined on a Brüker AC250 (250 MHz) spectrometer with Me_4Si as the internal standard. ^{13}C NMR spectra of $CDCl_3$ solution were recorded on Brüker AC250 (60 MHz).

2.2. General procedure for the addition of allylic Grignard reagents to dihydrocarvone: Obtention of dihydroallylcarveols P1-P3

Magnesium (1,1g) was recovered by anhydrous ether (15 ml) and was activated by 1,2-dibromoethane. Upon cessation of gas evolution, the reaction flask was cooled with ice, and a solution of allylic chloride (25 mmol) and dihydrocarvone (15 mmol) in 60 ml of anhydrous ether was added

dropwise. The reaction mixture was stirred in an ice bath for 08 h and then poured onto diluted sulphuric acid solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed to neutrality and dried (Na_2SO_4). The solvent was evaporated and the residual oil was purified by chromatography (silica gel flash, hexane).

Compound P1: $\text{C}_{13}\text{H}_{22}\text{O}$: Rdt = 76%. IR (film): 3450, 3080, 1635, 1045 cm^{-1} . $^1\text{H NMR}$ (CDCl_3): 0.98 (3H, d, J = 6.5 Hz), 1.70 (3H, s), 4.62 (2H, s), 5.05 (1H, m), 5.75 (2H, m). $^{13}\text{C NMR}$ (CDCl_3): 18.8 (q), 24.7 (q), 27.5(t), 30.5(t), 39.8(d), 41.1(t), 42.6(t), 45.8(d), 73.8 (s), 108.8 (t), 110.2 (t), 144.5 (d), 150.4 (s).

Compound P2: $\text{C}_{14}\text{H}_{24}\text{O}$: Rdt = 75%. IR (film): 3450, 3080, 1635 cm^{-1} . $^1\text{H NMR}$ (CDCl_3): 0.86 (3H, d, J = 6.5Hz), 1.09 (3H, d, J = 6.5Hz), 1.72 (3H, s), 4.69 (2H, s), 5.05 (1H, m), 5.75 (2H, m). $^{13}\text{C NMR}$ (CDCl_3): 13.3 (q), 14.6 (q), 21.3 (q), 30.6 (t), 32.0(t), 36.7(t), 36.8(d), 39.9(d), 44.9(d), 74.8 (s), 105.5 (t), 115.4 (t), 140.3 (d), 150.5 (s).

Compound P3: $\text{C}_{14}\text{H}_{24}\text{O}$: Rdt = 70%. IR (film): 3460, 3085, 1645 cm^{-1} . $^1\text{H NMR}$ (CDCl_3): 0.95 (3H, d, J = 6.5Hz), 1.72 (3H, s), 1.69 (3H, s), 4.60 (2H, s), 4.70 (2H, m). $^{13}\text{C NMR}$ (CDCl_3): 12.7 (q), 19.8 (q), 24.0 (q), 30.2 (t), 30.7(t), 37.6(t), 41.7(t), 42.0(d), 42.1(d), 74.1 (s), 108.5 (t), 114.8 (t), 142.9 (s), 149.4 (s).

2.3. Weight loss measurements

2.3.1. Preparation of materials

The material used in this study was mild steel (2 cm x 2 cm x 0.05 cm) with a chemical composition (in wt.%) of 0.09% P; 0.38% Si; 0.01% Al; 0.05% Mn; 0.21% C; 0.05% S and the remainder iron (Fe). For all the experiments, the mild steel samples were pre-treated prior to the experiments by grinding with emery paper SiC (grades 400, 600 and 1200), then washed thoroughly with double-distilled water, degreased with AR grade ethanol, and finally dried at room temperature before use.

The aggressive solution (1M HCl) was prepared by dilution of Analytical Grade 37% HCl with double-distilled water.

2.3.2. Effect of concentration of inhibitors

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 100 mL with and without the addition of different concentrations of inhibitors ranging from 1 to 3 g/L. The immersion time for the weight loss was 1 h at 333 K. After the corrosion test, the specimens of steel were carefully washed in double-distilled water, dried and then weighed. The rinse removed loose segments of the film of the corroded samples. Duplicate experiments were performed in each case and the mean value of the weight loss is reported using an analytical balance (precision ± 0.1 mg). Weight loss allowed us to calculate the mean corrosion rate as expressed in $\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$.

The corrosion rate (W) and inhibition efficiency E_w (%) were calculated according to the Eqs. (1) and (2) respectively:

$$W = \frac{\Delta m}{S.t} \quad (1)$$

$$E_w \% = \frac{W_0 - W_{\text{inh}}}{W_{\text{corr}}} \times 100 \quad (2)$$

where Δm (mg) is the specimen weight before and after immersion in the tested solution, W_0 and W_{inh} are the values of corrosion weight losses ($\text{mg}/\text{cm}^2 \cdot \text{h}$) of mild steel in uninhibited and inhibited solutions, respectively, S is the area of the mild steel specimen (cm^2) and t is the exposure time (h).

2.3.3. Effect of temperature

The effect of temperature on the inhibited acid–metal reaction is very complex, because many changes occur on the metal surface such as rapid etching, desorption of inhibitor and the inhibitor itself may undergo decomposition [11]. The change of the corrosion rate with the temperature was studied in 1M HCl during 1 h of immersion, both in the absence and presence of inhibitors at a concentration corresponding to the maximum inhibition efficiency. For this purpose, gravimetric experiments were performed at different temperatures (313–333 K).

To calculate activation thermodynamic parameters of the corrosion process, Arrhenius Eq. (3) and transition state Eq. (4) were used [12]:

$$W = A \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

$$W = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a^\ddagger}{R}\right) \exp\left(-\frac{\Delta H_a^\ddagger}{RT}\right) \quad (4)$$

where E_a is the apparent activation corrosion energy, R is the universal gas constant, A is the Arrhenius pre-exponential factor, h is the Plank's constant, N is the Avogadro's number, ΔS_a^\ddagger is the entropy of activation and ΔH_a^\ddagger is the enthalpy of activation.

2.4. Adsorption isotherm

The type of the adsorption isotherm can provide additional information about the properties of the tested compounds. In order to obtain the adsorption isotherm, the degree of surface coverage (θ) of the inhibitors must be calculated with several adsorption isotherms, including Langmuir, Frumkin, and Temkin. The Langmuir isotherm (C/θ vs C) assumes that there is no interaction between adsorbed molecules on the surface. The Frumkin adsorption isotherm (θ vs C) assumes that there is some interaction between the adsorbates, and the Temkin adsorption isotherm (θ vs $\lg C$) represents the effect

of multiple layer coverage [13]. In this study, the degree of surface coverage values (θ) for various concentrations of the inhibitors in acidic media have been evaluated from the Weight loss measurements.

3. RESULTS AND DISCUSSION

3.1. Synthesis of Allyldihydrocarveols P1-P3

We were the first, to accomplish stereoselective synthesis of allyldihydrocarveols from dihydrocarvone and allylmagnesium chloride in ether. Condensation of allylic Grignard reagents on dihydrocarvone P leads to allyldihydrocarveols P1–P3 in good yields (Fig. 2). These homoallylic alcohols contain the allylic moiety in the axial position, and the hydroxyl group, in the equatorial position of the cyclohexane ring which adopts a chair conformation. The reaction, in all cases, is stereoselective and the allylation of dihydrocarvone takes place on the “si face”.

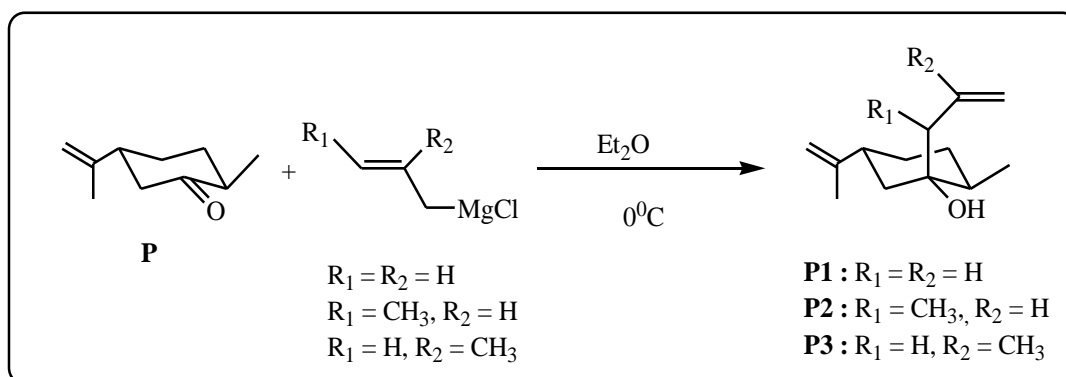


Figure 2. From dihydrocarvone P to Allyldihydrocarveols P1-P3

The ^{13}C NMR spectrum of each homoallylic alcohols P1-P3 after a purification by chromatography on silica gel was consistent with the presence of only one diastereoisomer per Grignard reagent. Their IR spectra lack carbonyl absorption but contain band at 1635 cm^{-1} , 3080 cm^{-1} , and 3450 cm^{-1} , typical of stretching vibration of C=C bond, the vinylic protons of the allylic moieties ($\text{C}=\text{CH}_2$) and associated hydroxyl group, respectively. In the ^1H NMR spectra of these compounds we observed signals from protons of both p-menthane fragment and massifs due to protons of allylic moieties (experimental section).

The stereochemistry at the carbinol center of alcohols P1-P3 was initially assigned based on the relative chemical shifts of the carbinol centers in the ^{13}C NMR spectra. The signal for the carbinol carbon appears at lower fields for an equatorial than axial hydroxyl group (see experimental section) [14]. The carbinol signal further downfield should belong to the axial-addition product. These data are consistent with our previous results [15] that the addition of allylic and aryllic magnesium chloride to cycloalkenone is stereoselective: the attack occurs from the axial side of the enone.

3.2. Gravimetric results

3.2.1. Effect of concentration

The effect of allyldihydrocarveols P1-P3 on the corrosion rates of steel were determined in aerated 1M hydrochloric acid solution at various concentrations for 1h at 333K. The values of corrosion rate (W_{inh}) and the corresponding inhibition efficiency (E_w %) are given in Table 1 and Fig. 3.

Table 1. Influence of Allyldihydrocarveols P1-P3 concentration on the steel corrosion in 1M HCl at 333 K during 1 hour of immersion.

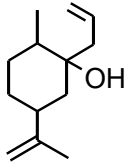
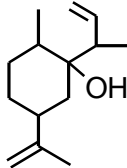
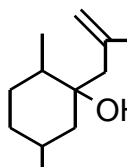
Inhibitors	C (g/l)	C (10^{-2} mol/L)	W_{inh} (mg/cm ² h)	E %
Blank	0	0	12.68	-
 P1	1	0.52	5.58	56
	1.5	0.78	4.56	64
	2	1.03	3.67	71
	2.5	1.29	3.42	73
	3	1.55	2.92	77
 P2	1	0.48	6.47	49
	1.5	0.72	5.70	55
	2	0.96	4.82	62
	2.5	1.20	4.31	66
	3	1.44	3.80	70
 P3	1	0.48	7.23	43
	1.5	0.72	6.21	51
	2	0.96	5.45	57
	2.5	1.20	4.94	61
	3	1.44	4.18	67

Fig. 3 showed clearly that the corrosion rate (W_{inh}) decreased and the inhibition efficiency increased with increasing concentration of three homoallylic alcohols P1-P3 at 333 K, i.e. the corrosion inhibition enhances with the inhibitor concentration. Table 1 showed also that the maximum values of the inhibition efficiency (E_w) are 77%, 70% and 67% for P1, P2 and P3 at 3 g/L, respectively, which indicates that these three compounds P1-P3 act as good inhibitors for steel in 1M HCl. This behaviour is due to the fact that the adsorption coverage of inhibitors on metal surface increases with the inhibitor concentrations resulting in the blocking of the reaction sites, and protection of the mild steel surface from the attack of the corrosion active ions in the acid medium. This adsorption is influenced by the nature and surface charge of metal, the type of aggressive electrolyte and the chemical structure of inhibitors [16].

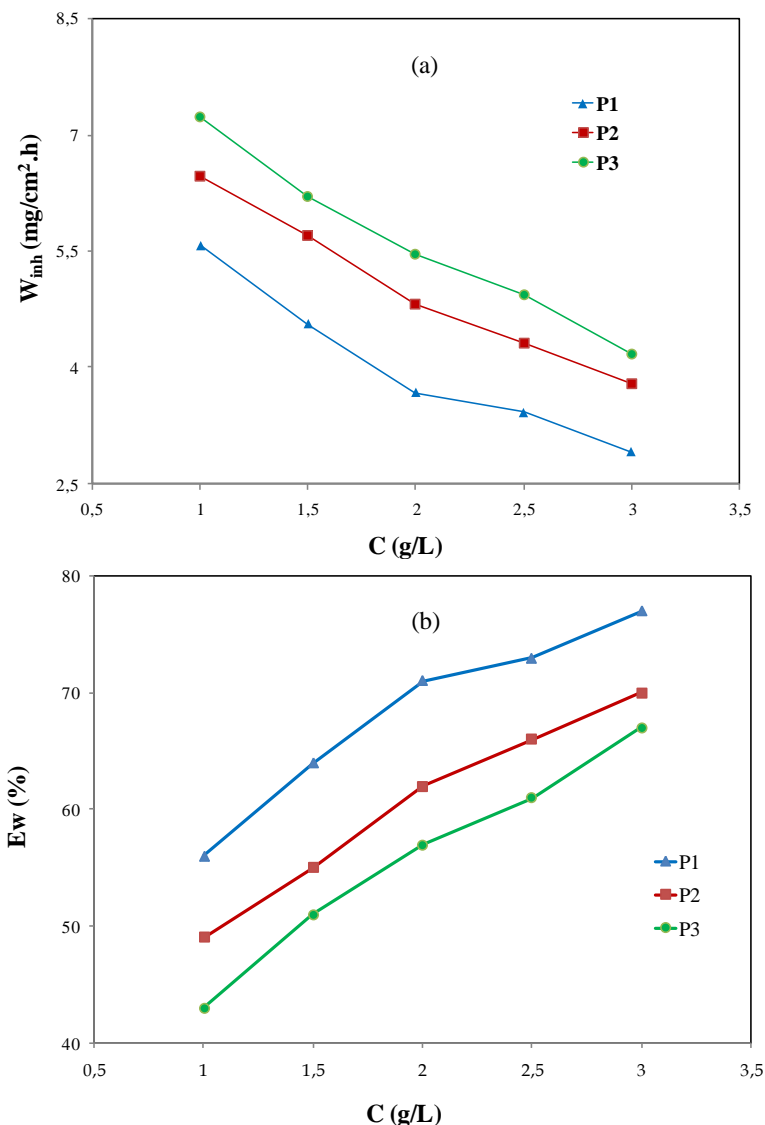


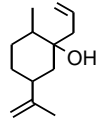
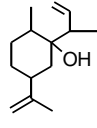
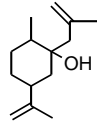
Figure 3. Variation of corrosion rate (W_{inh}) (a) and inhibition efficiency (E_w) of corrosion (b) of mild steel in 1 M HCl in the presence of allyldihydrocarveols P1-P3 at various concentrations at 333 K.

3.2.2. Effect of temperature and activation parameters E_a , ΔS_a° , ΔH_a°

The corrosion rate of steel with temperature was studied in molar HCl both in the absence and presence of inhibitor at a maximal concentration (3g/L) in the temperature range 313-333K using weight loss measurements, the corresponding results are summarised in table 2 and Fig. 4.

It is clear that the corrosion rate (W) is more increased with the rise of temperature for uninhibited acid solution, whereas, the presence of inhibitor leads to decrease of the corrosion rate. In contrast, the inhibitory action of allyldihydrocarveols is slightly increased at elevated temperature. Hence, we note that the efficiency depends on the temperature and decreases with the rise of temperature from 318 to 3353 K. This can be explained by the increase of the strength of the adsorption process and the inhibitory effect of inhibitors is reinforced at elevated temperature.

Table 2. Effect of temperature (313-333 K) on the corrosion inhibition of steel in 1M HCl by Allyldihydrocarveols P1-P3 at 1 hour of immersion.

	T K	W_{inh} (mg/cm ² h)	W_0 (mg/cm ² h)	E %
 P1	313	1.34	4.48	70
	323	1.93	7.42	74
	333	2.92	12.68	77
 P2	313	1.70	4.48	62
	323	2.37	7.42	68
	333	3.80	12.68	70
 P3	313	1.79	4.48	60
	323	2.67	7.42	64
	333	4.18	12.67	67

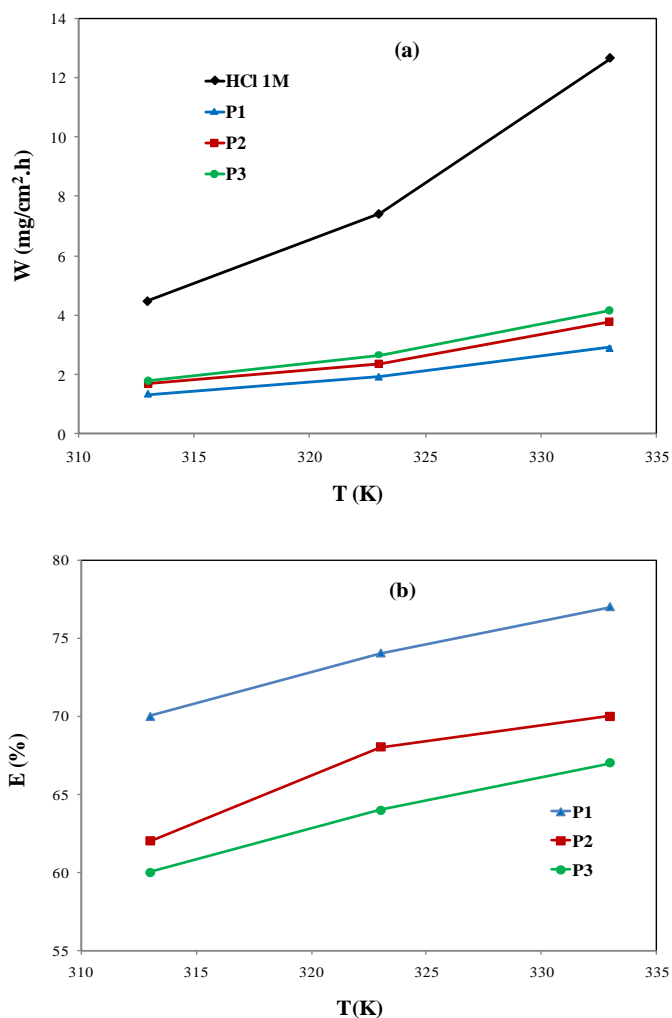


Figure 4. Variation of corrosion rate (W) (a) and inhibition efficiency (E_w) of corrosion (b) of mild steel in 1 M HCl at different temperatures in the absence and presence of P1-P3.

The apparent activation energy (E_a) was determined from the slopes of $\ln(W)$ vs $1/T$ graph according to Arrhenius plots depicted in Fig. 5, and the entropy of activation ΔS°_a and the enthalpy of activation ΔH°_a were determined from the plot of $\ln(W/T)$ vs $1/T$ graph depicted in Fig. 6. Straight lines are obtained with a slope of $(\Delta H^\circ_a/R)$ and an intercept of $(\ln R/Nh + \Delta S^\circ_a/R)$ from which their values of these kinetic parameters are calculated and are listed in Table 3.

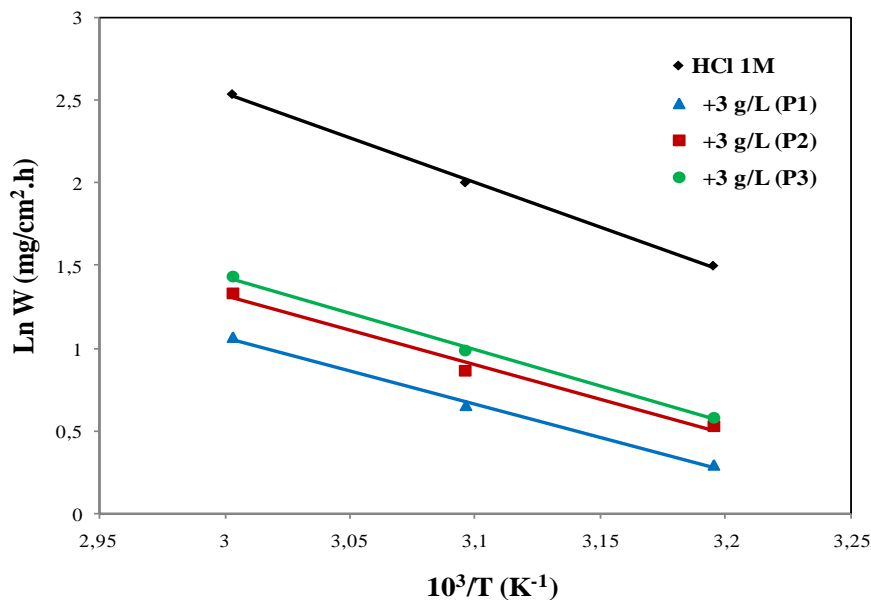


Figure 5. Arrhenius plots for mild steel corrosion rates (W) in 1M HCl in the absence and presence of 3 g/L of Allyldihydrocarveols P1-P3.

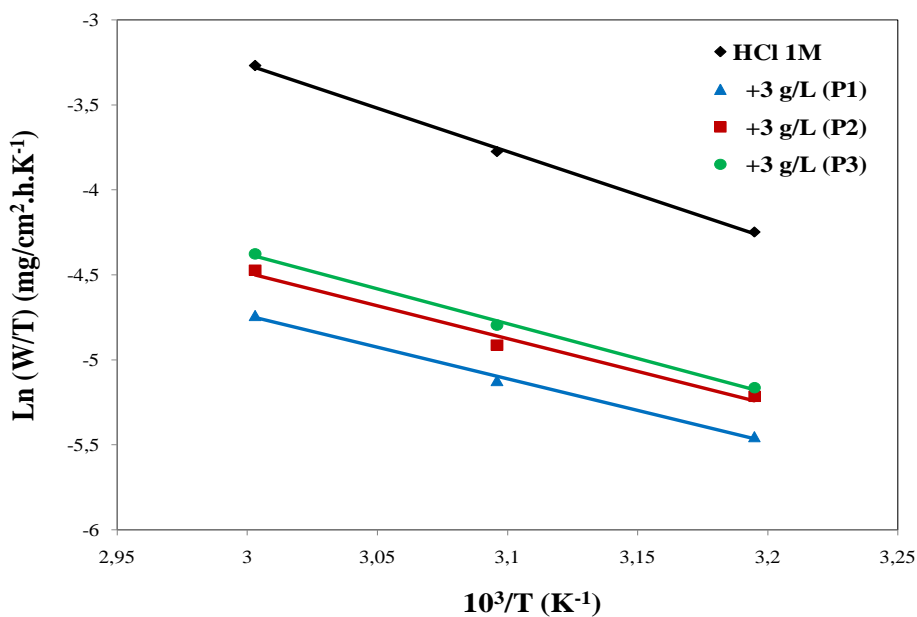


Figure 6. Transition-state plots for mild steel corrosion rates (W) in 1M HCl in the absence and presence of 3 g/L of Allyldihydrocarveols P1-P3.

Table 3. Corrosion kinetic parameters for mild steel in 1M HCl in the absence and presence of 3g/L of Allyldihydrocarveols P1-P3.

Inhibitors	A ($\text{mg.cm}^{-2}.\text{h}^{-1}$)	E_a (kJmol^{-1})	ΔH_a° (KJ.mol^{-1})	$E_a - \Delta H_a^\circ$ (KJ.mol^{-1})	ΔS_a° ($\text{J.mol}^{-1}.\text{K}^{-1}$)
HCl 1M	$1.40 \cdot 10^8$	45.09	42.40	2.69	-97.34
P1	$5.24 \cdot 10^5$	33.56	30.87	2.69	-144.14
P2	$1.05 \cdot 10^6$	34.80	32.11	2.69	-138.35
P3	$2.37 \cdot 10^6$	36.75	34.06	2.69	-131.60

The calculated values of activation energies from the slopes are 45.09 kJmol^{-1} for free acid and 33.56 , 34.80 and 36.75 kJmol^{-1} with the addition of 3 g/L of P1, P2 and P3, respectively. It was found that, E_a values for uninhibited system are higher than E_a for inhibited systems. Due to this decrease in the activation energy the dissolution reaction of mild steel decreases in 1M HCl medium. The tendency of variation in pre-exponential factor (A) is similar to that in apparent activation energy. The experimental fact that the activation energy is lower in the presence of inhibitors is explained in different ways in the literature. The increase of inhibition efficiency (E_w), accompanied by the decrease in activation energy (E_a) within temperature in the presence of Allyldihydrocarveols P1-P3 can be attributed to an appreciable increase in the adsorption of these inhibitors. This result may be interpreted as chemical adsorption on the mild steel surface [17,18].

Moreover, inspection of the data of Table 3 reveals that the ΔH_a° values for dissolution reaction of mild steel in 1M HCl in the presence of 3 g/L of compounds P1-P3 are lower than that uninhibited system. The positive signs of ΔH_a° reflect the endothermic nature of the mild steel dissolution process suggesting that the dissolution of mild steel is slow in the presence of inhibitors [19]. The average difference value of the $E_a - \Delta H_a$ is 2.69 kJ mol^{-1} , which is approximately equal to the average value of RT (2.69 kJ mol^{-1}) at the average temperature (323 K) of the domain studied. This result agrees that the corrosion process is a unimolecular reaction as described by the known of perfect gas [20].

On the other hand, the entropy of activation (ΔS_a°) in the absence and the presence of Allyldihydrocarveols P1-P3 has large and negative values. This indicates that the activated complex in the rate determining step represents an association rather than dissociation, meaning that a decrease in disordering takes place on going from reactants to the activated complex [21].

3.3. Adsorption isotherm and energy of adsorption, ΔG_{ads}^0

The dependence of the fraction of the surface covered θ obtained by the ratio $E\%/100$ as function of the inhibitors concentration (C_{inh}) was graphically fitted for various adsorption isotherms.

Fig. 7 shows that the relationship between C_{inh}/θ and C_{inh} , at 333 K , yields a straight line with correlation coefficient (R^2) was almost equal to unity and the slopes were very close to unity. This behaviour suggests that the adsorption of Allyldihydrocarveols P1-P3 on mild metal surface followed the Langmuir adsorption isotherm suggesting that P1-P3 molecules are adsorbed over the metal surface

forming a barrier, which prevents the contact of the metal with electrolyte [22]. This isotherm may be written in the following form:

$$\frac{C_{inh}}{\theta} = \frac{1}{b} + C_{inh} \tag{5}$$

where C_{inh} is the inhibitor concentration; θ is the fraction of the surface covered, b is the equilibrium constant of the adsorption process which is related to the standard Gibbs energy of adsorption, ΔG_{ads}^0 , according to [20]:

$$b = \frac{1}{55,5} \cdot \exp\left(-\frac{\Delta G_{ads}^0}{R.T}\right) \tag{6}$$

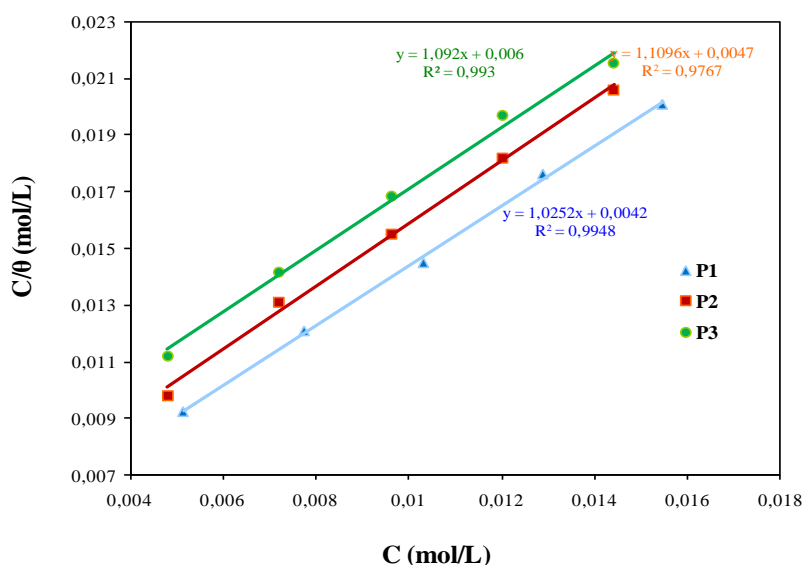


Figure 7. Langmuir’s isotherm adsorption model of Allyldihydrocarveols P1-P3 on the mild steel surface in 1 M HCl at 333 K.

where R is the universal gas constant, T is the thermodynamic temperature, and the value of 55.5 is the concentration of water in the solution in mol/L. The b values and ΔG_{ads}^0 were calculated and are presented in Table 4.

Table 4. The values of equilibrium constant (b) and ΔG_{ads}^0 of Allyldihydrocarveols P1-P3 on mild steel surface in 1M HCl at 333 K.

Inhibitors	b (L/mol)	$-\Delta G_{ads}^0$ (kJmol ⁻¹)
P1	238	26.29
P2	212.76	25.98
P3	166.67	25.30

The standard free energy of adsorption ΔG_{ads}^0 , which can characterize the interaction of adsorption molecules and metal surface, was calculated. The large negative values of ΔG_{ads}^0 ensure the spontaneity of the adsorption process and the stability of the adsorbed layer on the mild steel surface [23] as well as a strong interaction between the Allyldihydrocarveols P1-P3 molecules and the metal surface [24].

Generally, values of ΔG_{ads}^0 up to -20 kJ mol^{-1} , the types of adsorption was regarded as physisorption, the inhibition acted due to the electrostatic interactions between the charged molecules and the charged metal, while the values around -40 kJ mol^{-1} or smaller were associated with chemisorption as a result of sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) [15]. Here, the calculated ΔG_{ads}^0 values are ranging between -25.30 and $-26.29 \text{ kJ mol}^{-1}$, indicating that the adsorption mechanism of Allyldihydrocarveols P1-P3 on mild steel in 1 M HCl solution at the studied temperatures is both electrostatic-adsorption (ionic) and chemisorption (molecular) [25], with predominance of physical adsorption regarding the nature of molecules studied.

4. CONCLUSION

From the overall experimental results, the following conclusions can be deduced:

- ✓ The condensation of allylic Grignard on dihydrocarvone leads stereoselectively to allyldihydrocarveols P1-P3 in good yields;
- ✓ Allyldihydrocarveols P1-P3 compounds acts as good inhibitors for the corrosion of mild steel in HCl medium;
- ✓ The inhibition efficiency increases with temperature and the Allyldihydrocarveols P1-P3 concentration to attain 77 %, 70% and 67% for P1, P2 and P3 at 3 g/L, respectively;
- ✓ The value of adsorption parameters show that P1-P3 were adsorbed on mild steel surface by a spontaneous process and this adsorption fits a Langmuir isotherm model.

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