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Kinetics Study of Degradation and Stabilizing Effect of Organic Thermal Stabilizers (EDTA, 1,2 Propane Diol, Benzoic Acid, and Phenol) for Rigid Polyvinyl Chloride

Mohamad Taghi Taghizadeh* and Farvardin Fakhimi

Physical Chemistry Department, Faculty of Chemistry, Tabriz University, Post Code-5166/15731
Tabriz, I.R. Iran

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ABSTRACT

The kinetic of the thermal degradation of rigid polyvinyl chloride (PVC) under nitrogen atmosphere was studied by bromometry titration at various temperatures (160-190°C) in the presence of ethylene diamine tetra acetic acid (EDTA), 1,2 propane diol, benzoic acid, and phenol as thermal stabilizers. The rate of dehydrochlorination at 1% degradation (R_{DH}) and the time required for dehydrochlorination to attain 1% conversion (t_{DH}) were used to assess the effect of the additives on the thermal susceptibility of PVC. It was found that the values of the R_{DH} were relatively lower and the t_{DH} were considerably higher than the value obtained in the absence of the additives. The degradation rate coefficients were determined from the rate of dehydrochlorinating. The following rate expressions R= k[PVC]$^{0.77}$[benzoic acid]$^{-0.40}$, R= k[PVC]$^{0.71}$[1,2 propane diol]$^{-1.78}$, R= K[PVC]$^{0.67}$[EDTA]$^{-2.18}$, and R= k[PVC]$^{0.88}$[phenol]$^{-0.28}$ were obtained. The activation energies determined from the temperature dependence of the rate coefficients of the polymer's degradation. The activation energies of the PVC degradation in the presence of EDTA, 1,2 propane diol, benzoic acid, phenol, and also in the absence of stabilizer were obtained 28, 27.5, 26.8, 26, and 24.5 kcalmol^{-1}, respectively. The results show that the order of increasing stabilizing effet was EDTA >1,2 propane diol>benzoic acid> phenol. The results also, reveal greater stabilizing efficiencies of the investigated materials compared to non stabilizer.

Key Words:
polyvinyl chloride;
thermal degradation;
dehydrochlorination;
organic thermal stabilizers;
kinetic;
activation energy.

INTRODUCTION

Polyvinyl chloride (PVC) is an important polymer. But one of the problems associated with the processing and using of PVC is its low thermal stability. It is an unstable polymer when exposed to high temperatures during its moulding and applications. Thermal degradation of PVC occurs by an autocatalytic dehydrochlorination reaction with the subsequent formation of conjugated double bonds [1-4]. This results in an unacceptable discoloration of the polymer and a change

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(*)To whom correspondence should be addressed.
E-mail: mttaghizadeh@tabrizu.ac.ir

in physical and mechanical properties together with a decrease or an increase in molecular weight as a result of chain scission or cross-linking of the polymer molecules, respectively [5-7].

The mechanisms of the two basic steps involved in the degradation, namely initiation through labile structures and propagation or building up to polyenes, have been taken particular attention. Most authors agree that initiation is due to the presence of a few abnormal structures such as allylic chlorine [8], tertiary hydrogen and chlorine atoms [9], terminal end groups such as double bonds [10], oxygen containing groups [11], or peroxide residues [12], head- to- head structures [13], and steric order of the monomer units in the polymeric chain (tacticity) [14]. This instability requires the polymer stabilization for all technical applications practically. A wide variety of stabilizers are used industrially to improve the thermal stability of the polymer. Several workers have reported on the degradation and stabilization of PVC [14-25].

Additives as thermal stabilizer for PVC include metal salts of organic acids, organometallic compounds, esters or mercaptides of dialkyl tin [26-29], inhibitors of radical chain reactions [12], zinc and barium carboxylate [30]. They can react with the evolved hydrogen chloride gas, thus retarding its deleterious catalytic action [25]. More recently, interests have been led to the use of epoxides and mercaptans as thermal stabilizers [24].

Metal chlorides are considered as strong catalysis for the subsequent dehydrochlorination process [26, 27]. For this reason, stabilizers of an organic nature have been used [28, 31, 32]. Ethylen diamine tetra acetic acid (EDTA) and other aliphatic and aromatic compounds are organic materials that in their structures possess many basic functional groups and highly conjugated structures. They are capable of acting as efficient radical traps, and consequently, may intervene with the radical degradation process of PVC. For this reason, it has been found various organic compounds as thermal stabilizers of rigid PVC. The temperature effect on the PVC stabilization kinetic has been studied over a temperatures range of 160-190°C. The rates of dehydrochlorination and the temperature effect on it at constant concentration of stabilizers were determined and the rate equations were established.

EXPERIMENTAL

Materials

Polyvinyl chloride suspension (M_r =Molecular mass= 48000 g/mol, k-value= 55-57), from Fluka was purified by solving in THF/acetone mixture and precipitated, with constant stirring, in a large excess of methanol. The precipitated polymer was filtered off after 24 h, washed with methanol and air-dried [29]. EDTA, 1,2 propane diol, benzoic acid, and phenol from Merck were used in this investigation.

Preparation of PVC Samples

Samples of PVC for heat degradation were prepared by thoroughly mixing 0.2 g of PVC powder and 0.006 g of the stabilizer in a mortar for each experiment and transferred into a degradation tube. The tube was connected to a source of nitrogen maintained at a flow rate of 180 mL/min. The degradation tube was then immersed in a thermostat oil bath controlled [17, 18].

Evaluation of Stabilizing Efficiency

The amount of evolved HCl was established by titration after various periods of time. The extent of dehydrochlorination (conversion %) was calculated from the ratio of evolved HCl to the amount available in the polymer [29].

RESULTS AND DISCUSSION

Temperature Effect on the Rate of Dehydrochlorination in Degradation of PVC

The extents of degradation of PVC in the presence of EDTA at various temperatures are shown in Figure 1. It can be seen that the extent of dehydrochlorination at temperatures between 160-180°C is linear. The rates of dehydrochlorination at 1% conversion (R_{DH}), were of the same order of magnitude but at 190°C the initial rate of evolution of HCl was relatively slow and gradually increased after about 45 min. Similar trends were observed in the degradation of PVC in the presence of other compounds. It has been suggested that the time required for the evolution of HCl to attain a steady rate provides an estimate of induction period [27, 29]. It may be used to assess relative effectiveness of stabilization. Figure 1 shows that the values of R_{DH} increase

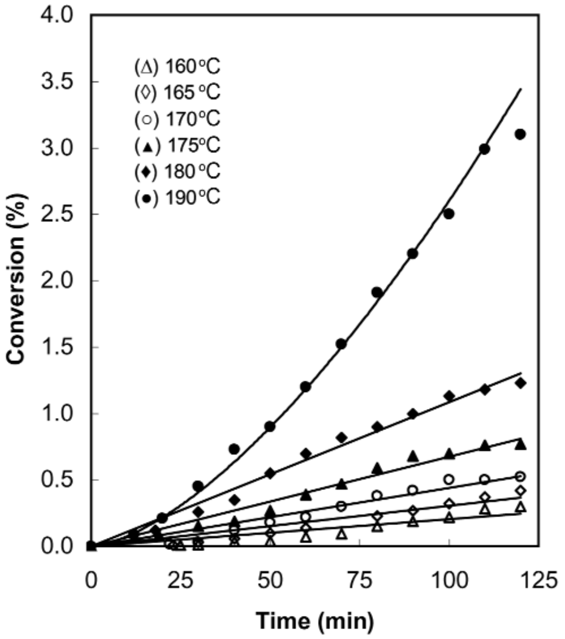

Figure 1. Conversion (%) of PVC in the presence of 0.006 g EDTA stabilizer at different temperatures.

with increase in temperature. The values of the required time for dehydrochlorination to attain 1% conversion, t_{DH}, are shown in Table 1.

The results in Table 1 show that EDTA exerts stabilizing effect on the degradation of PVC. The values of t_{DH} ranged from 50 min at 190°C to 200 min at 160°C. When compared with the values obtained for degradation in the absence of stabilizers, these results indicate that these stabilizers have a deleterious effect on the stability of PVC, reducing t_{DH} (Table 1) and increasing the R_{DH} value. It can be seen from Figure 1 that, at 190°C, the degradation can be divided into two stages, viz. an initial low rate of evolution of HCl (up to about 45 min) followed by a higher rate. The weaker stabilization effect of compounds on the degradation of PVC at 190°C, indicated by the relatively high R_{DH} value, may be explained in terms of volatilization of materials from the polymer matrix. The attendant reduction in the additive content of the polymer, and/or its decomposition at this temperature may lead to produce materials which could accentuate dehydrochlorination or have implications on its accurate estimation.

A similar trend was reported for the degradation of PVC in cashew nut shell liquid, in the presence of rubber seed oil [33,34], jatropha seed oil [35], and khaya seed oil [36]. From Table 1, it seems that EDTA is more effective than the other additives. Therefore it would be expected that the stabilizing effect of these compounds on the degradation of PVC should increase with increase in carboxylic group or alcohol group [22]. The results in Table 1 are consistent with this suggestion.

Effect of the Stabilizer Concentration on the Efficiency of Stabilization

Data of the dehydrochlorination of rigid PVC (0.2g) stabilized by EDTA in different concentrations (0.002-0.008g) are shown in Figure 2. They indicate that the rate of dehydrochlorination decrease with the increasing of [EDTA]/[PVC] ratio. The data of other compounds show that, the stabilizing efficiency of these stabilizers is greater in the presence of stabilizers with concentration of 3 g per 100 g PVC.

Dehydroclorination (conversion%) of rigid PVC at 180°C for other stabilizers is linear vs. time too. The data for non-stabilized blank sample and those of the samples stabilized with various stabilizers are also given for comparison in Figure 3. Experimental values of rate dehydrochlorination, R, of rigid PVC with other stabilizers and the length of the induction period, T_s,

Table 1. The values of t_{DH} in the presence and absence of stabilizers.

Temperature (°C)	t_{DH}				
	EDTA	1,2 Propane diol	Benzoic acid	Phenol	Non
160	200	180	130	70	55
165	180	160	90	50	25
170	160	140	70	30	17
175	130	120	60	28	15
180	120	110	50	22	8
190	50	40	30	15	1

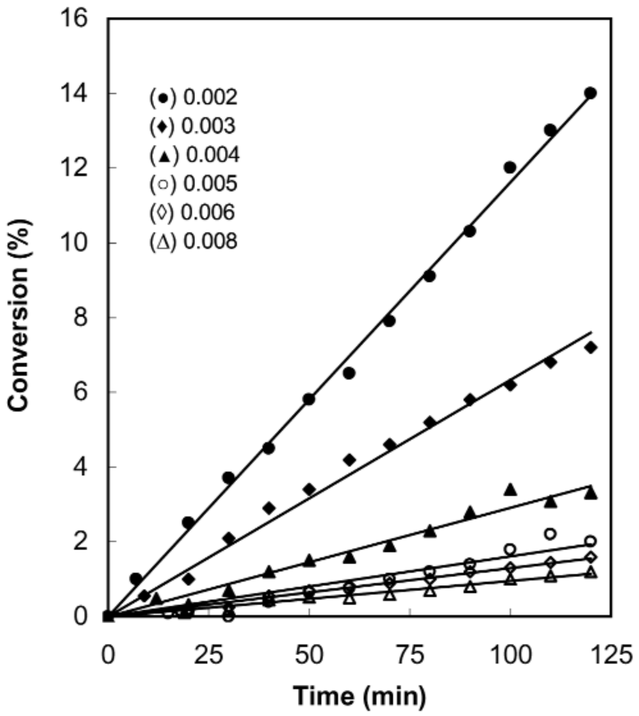

Figure 2. Conversion (%) of PVC at 180°C with 0.2 g of PVC and various amounts of EDTA (g).

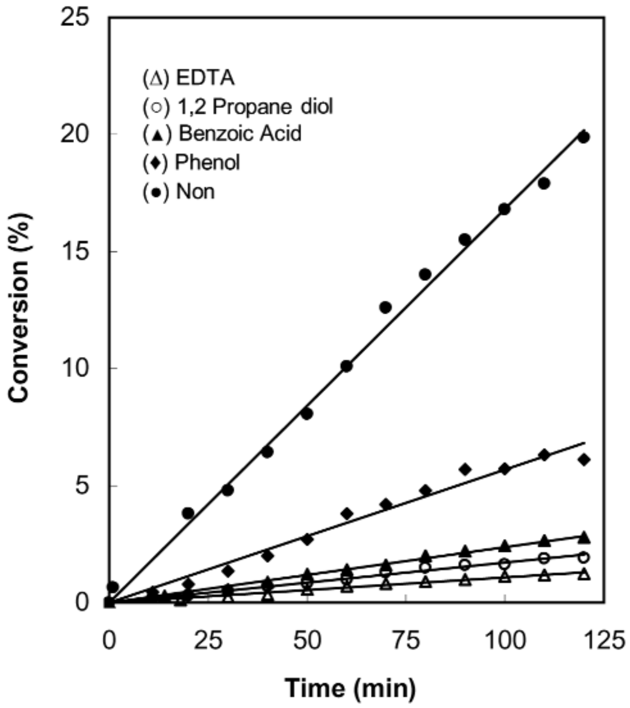

Figure 3. Conversion (%) of PVC at 180°C for different stabilizers.

are given in Table 2.

Effect of the PVC Concentration on Degradation PVC in Constant Concentration of Stabilizer

Data of dehydrochlorination of PVC with various amounts, in constant amount of stabilizer (0.006g) is shown in Figure 4. These data indicate that the rate of dehydrochlorination decrease with increasing the ratio of [EDTA] / [PVC].

Degradation of PVC with Different Amount in the Absence of Stabilizer

Data of dehydrochlorination of rigid PVC with different amount in the absence of stabilizer are shown in Figure 5. The obtained rates of dehydrochlorination of PVC were (7.71, 10.57, 13.21, 17.03, 20.18, and 26.18) × 10^{-2} (conversion%/min) for the amounts of 0.10, 0.15, 0.20, 0.25, 0.30, and 0.35 g PVC, respec-

Table 2. Dehydrochlorination data at 180°C for rigid PVC containing various stabilizers systems.

Stabilizer system	T_S(min)	R×10^2 (%conversion/min)
EDTA	18	0.93
1,2 Propane diol	17	2.02
Benzoic acid	14	5.78
Phenol	11	13.55

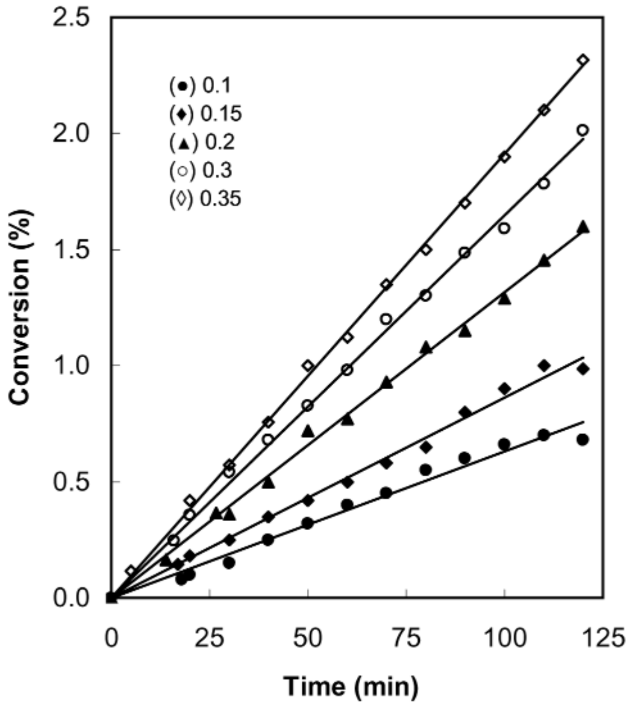

Figure 4. Conversion (%) of PVC at 180°C for various amounts of PVC at constant amount of EDTA.

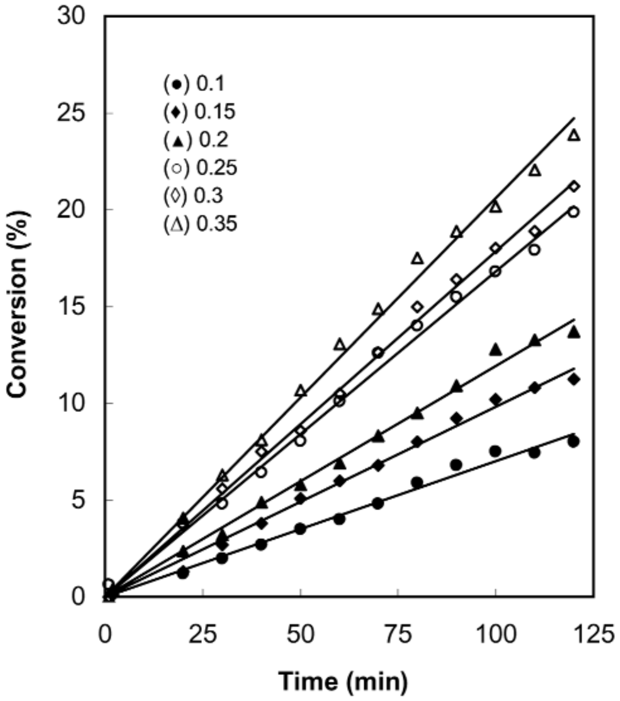

Figure 5. Conversion (%) of PVC at 180°C for various amounts of PVC in the absence of stabilizer.

tively. The results show that the rate of dehydrochlorination in this case is greater than that in the presence of stabilizer. It is observed that with increasing the amount of PVC, the rate of dehydrochlorination increases.

Kinetics of Dehydrochlorination of PVC

Determination of reation order with respect to stabilizer at constant amount of PVC

The rate of dehydrochlorination depends on the concentration of stabilizer and polymer as following:

$R = k[PVC]^{\alpha}[S]^{\beta}$ and $R = k'[S]^{\beta}$

The plot of Ln (R) vs. Ln[S] is linear and for EDTA is plotted in Figure 6. The slope of the line is -2.18, which suggests that the order of the reaction with respect to EDTA is -2.18. Experimental values of dehydrochlorination for all stabilizers are given in Table 3.

The data show how the rate of dehydrochlorination are effected strongly by the type of stabilizer (-OH, -COOH, and-NH_2 groups). The introduction of -OH, -COOH, -NH_2 groups into the phenyl rings of the stabilizer result in an appreciable improvement in the rate of dehydrochlorination. From the data of Table 3 the reaction order with respect to EDTA, 1, 2 propane diol, benzoic acid, and phenol were determined -2.18, -1.78, -0.40, and -0.28, respectively. These results show that all stabilizers are of negative order. The more negative reaction order shows that the more PVC is stabilized. It is clear that EDTA and 1,2 propane diol exhibited a greater stabilizing efficiency relative to the others.

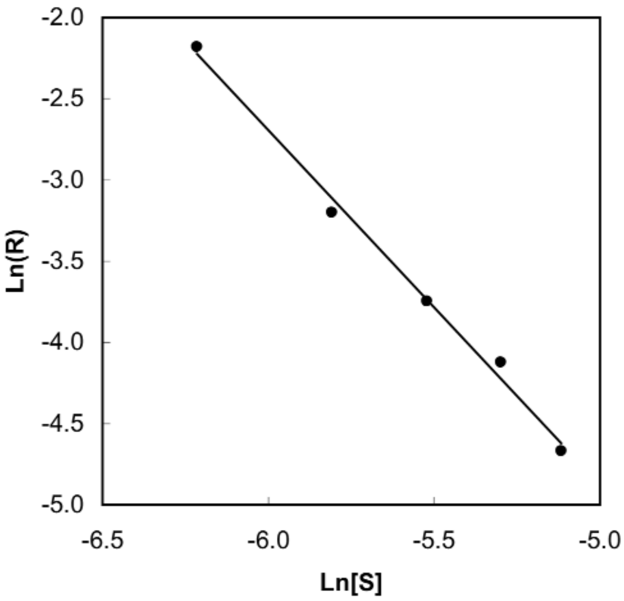

Figure 6. Ln(R) vs. Ln[S] for EDTA stabilizer at 180°C.

Determination of reaction order with respect to PVC in the absence of stabilizer

Results of dehydrochlorination of rigid PVC with various amount of PVC in the absence of stabilizer are given in Table 3 and depicted in Figure 5. The results indicate that the rate of dehydrochlorination increases with the increasing of the amount of PVC. In these con-

Table 3. Effect of stabilizers concentration on the rate of dehydrochlorination of rigid PVC at 180°C with 0.2 g PVC.

[S]	R ×10^2 (%conversion/min)			
	EDTA	1,2 Propane diol	Benzoic acid	Phenol
0.006	0.93	2.02	5.78	13.55
0.005	1.61	2.60	6.26	14.11
0.004	2.36	4.39	6.72	14.89
0.003	4.07	7.28	7.42	16.09
0.002	11.29	13.76	9.07	18.43

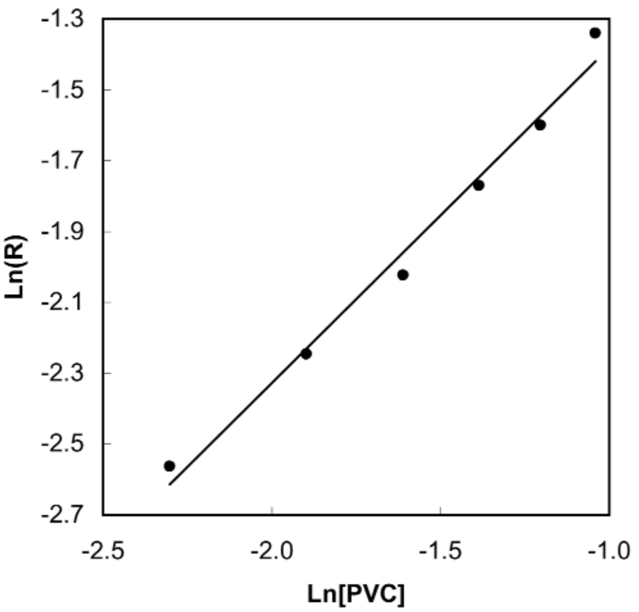

Figure 7. Ln](R) vs. Ln[PVC] in absence of stabilizer at 180°C.

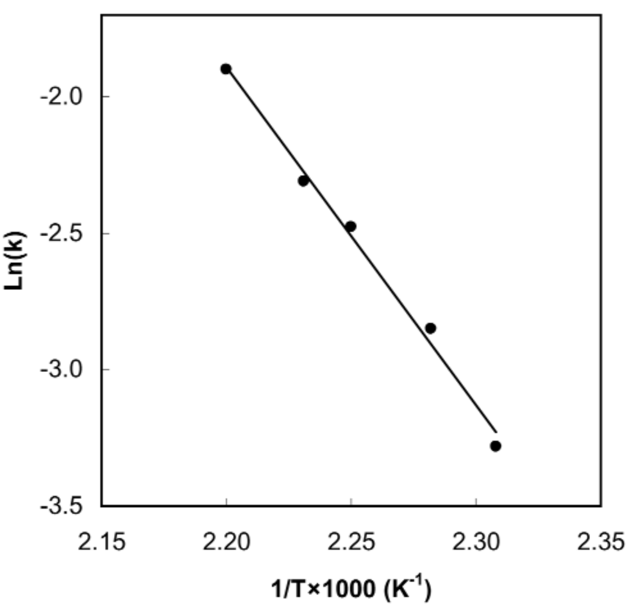

Figure 8. Ln (k) vs. 1/T for degraded PVC.

ditions the rate equation is as follows:

$R = k'[PVC]^{\alpha}$

The plot of Ln(R) vs. Ln[PVC] is linear and presented in Figure 7. The slope of the line is 0.95 nearly equal to unit [32].

Determination of reaction order with respect to PVC at constant amount of stabilizer

Data of dehydrochlorination of rigid PVC with various amount of PVC in the presence of stabilizer are given in Table 4. The results clearly reveal the greater rate of dehydrochlorination of phenol and benzoic acid relative to the EDTA and 1, 2 propane diol. It is clear that EDTA exhibited a greater stabilizing efficiency relative to the other stabilizers. From the data of Table 4 the reaction order with respect to PVC were determined 0.67, 0.71, 0.77, 0.88 and 0.95 in presence of EDTA, 1, 2 propane diol, benzoic acid, phenol, and non stabilizer, respectively. These results show that low values of reaction order obtained for stabilizers that exert a stabilizing effect on degradation of PVC. Therefore, under the experimental conditions four suitable rate equations were proposed as follow:

Table 4. Effect of various amount of PVC at constant concentration of stabilizer on the rate of dehydrochlorination of PVC at 180°C with 0.006 g of stabilizer.

PVC	R×102 (%conversion/min)			
(g)	EDTA	1,2 Propane diol	Benzoic acid	Phenol
0.10	0.60	1.02	7.25	7.25
0.15	0.93	1.41	9.00	10.36
0.20	1.00	1.79	12.03	13.71
0.30	1.30	2.32	16.69	18.56
0.35	1.60	2.47	18.22	22.53

$R = k[PVC]^{0.67}[EDTA]^{-2.18}$
$R = k[PVC]^{0.71}[\text{Propane diol}]^{-1.78}$
$R = k[PVC]^{0.77}[\text{Benzoic acid}]^{-0.4}$
$R = k[PVC]^{0.88}[\text{Phenol}]^{-0.28}$

Calculation of activation energy

The dehydrochlorination of PVC was carried out at different temperatures in constant conditions (Figure 1). It was observed that the dehydrochlorination of PVC increases with increasing temperature. The degradation rate coefficients were determined from the rate of dehydrochloriantion. The effect of temperature on the rate coefficients of dehydrochlorination are given in Table 5.

According to the Arrhenius equation, Ln (k) vs. 1/T yields a straight line which the activation energy deter-

Table 5. The effect of temperature on the rate coefficients of dehydrochlorination.

Temperature (K)	k (mol.g^{-1}min^{-1})				
	EDTA	1,2 Propane diol	Benzoic acid	Phenol	Non
160	0.003	0.004	0.008	0.01	0.03
163	0.004	0.005	0.013	0.02	0.05
170	0.006	0.008	0.021	0.03	0.08
175	0.008	0.011	0.024	0.04	0.09
180	0.014	0.018	0.039	0.06	0.14

mined from its slope, and the case of non stabilizer is shown in Figure 8. The activation energies of the degradation of the PVC in the presence of EDTA, 1,2 propane diol, benzoic acid, phenol, and non stabilizer were obtained 28, 27.5, 26.8, 26, and 24.5 k cal mol^{-1}, respectively. The calculated activation energies and the data of Table 5 show that the variation of the rate coefficients and activation energies of dehydrochlorination of PVC, the degradation rate coefficients are lower and the activation energies are higher at the presence of stabilizers, compared to the absence of stabilizer. This daringly indicates that the polymer with stabilizer is more stable than the polymer alone. This indicates also that the addition of stabilizer to PVC augments the stability and the order of increasing stabilizing agent is EDTA>1, 2 propane diol > benzoic acid > phenol.

CONCLUSION

In this work, we studied degradation and stability of PVC in absence and presence of different stabilizers at various temperatures. The length of the induction period, T_s, the rate of dehydrochlorination at 1% degradation (R_{DH}), and the time required for dehydrochlorination to attain 1% conversion (t_{DH}) were used to compare the stability efficiency. Our results indicate that the stability efficiency of stabilizers is in the order of EDTA>1,2 propane diol >benzoic acid >phenol. The results indicate also that the optimum stability efficiency obtained when the ratio of [S]/[PVC] is equal to 0.006 g/ 0.2 g. From the kinetics study, suitable rate equation is proposed for each stabilizers. The calculated activation energies for the thermal degradation of PVC in presence of EDTA, 1,2 propane diol, benzoic acid, phenol, and non stabilizer were 28.05, 27.5, 26.83, 26.09, and 24.52 kcal.mol^{-1}, respectively.

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