A Study of PVC Stabilization with Epoxides Using Dynamic pH Determinations

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Synopsis

The activation energy (E_a) for the dehydrochlorination of PVC and PVC stabilized with an epoxide was determined by a method involving dynamic pH measurements. The E_a increase was 5 kcal/mole between unformulated PVC (E_a = 22.6 kcal/mole) and any of the other formulations (E_a = 27.7–28.6 kcal/mole). On the basis of this and data contained in the literature, research alternatives for the stabilization mechanism are proposed using model compounds.

INTRODUCTION

The degradation of poly(vinyl chloride) (PVC) has been studied by various researchers, and these studies have been reviewed.[1-3] It is known that thermal degradation takes place in an inert atmosphere through dehydrochlorination and crosslinking[4] and that some of the most precise techniques for following the dehydrochlorination are those which involve the quantification of evolved HCl using potentiometric methods.[5] The most accepted dehydrochlorination mechanism[3] is by free radicals with the formation of polyenes of five to ten conjugated double bonds.[6] However, the initiation sites of the reaction are still in question. Model compound analogs of low molecular weight PVC require activation energies of about 50 kcal/mole for pyrolysis temperatures of 350–400°C.[6] In contrast, activation energies of 7.3–36 kcal/mole have been reported[7] for the dehydrochlorination of PVC at temperatures between 140° and 260°C. Van Hoang[12] reports temperatures of decomposition in solution of such model compounds as 4-chloro-2-hexene in the order of 60°C, for which reason structural abnormalities such as double bond and branching points have been proposed as initiation sites.

The stabilization of PVC using organometallic salts (Cd, Zn: etc.) and the synergistic action of such stabilizers as phosphites and metal stearates has been widely studied,[8-12] and mechanisms that explain the synergism between epoxy derivatives and Cd and Zn salts[8] have been proposed. The esterification reaction of 4-chloro-2-hexene as a PVC model and the cyclohexene oxide as an epoxy derivative model, when heated in solution,[12] are also reported as an S_{n1} mechanism. E_a values for the dehydrochlorination of PVC formulated with epoxy derivatives have not been reported.

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EXPERIMENTAL

Materials and Sample Preparation

Commercial PVC Primex 250-12* resin with $\overline{M}_n$ = 87,100 and polydispersity $\overline{M}_w/\overline{M}_n$ = 1.51 (data received from José Luis Angulo, M.Sc., CIQA) was used as a stabilizer with commercial Epoxol 7-4* (soya oil epoxidate, oxirane number 7.2). The samples were prepared by mixing the PVC with the additive in concentrations of 0%, 2.5%, 5.0%, and 7.5% in a mortar. These were used in the dynamic pH determinations.

Dynamic pH Determinations

Gases from the outlet of a Perkin-Elmer DSC-1B were bubbled through a potentiometer cell containing distilled water the pH of which was adjusted to 7 with dilute KOH. The potentiometer (Beckman Expandomatic SS-2) was connected to the calorimeter recorder and calibrated with buffer solutions of pH 7 and 4 while the calorimeter was calibrated with In, Sn, and Pb standards. A 1-mg sample was placed in the calorimeter, and high-purity nitrogen was
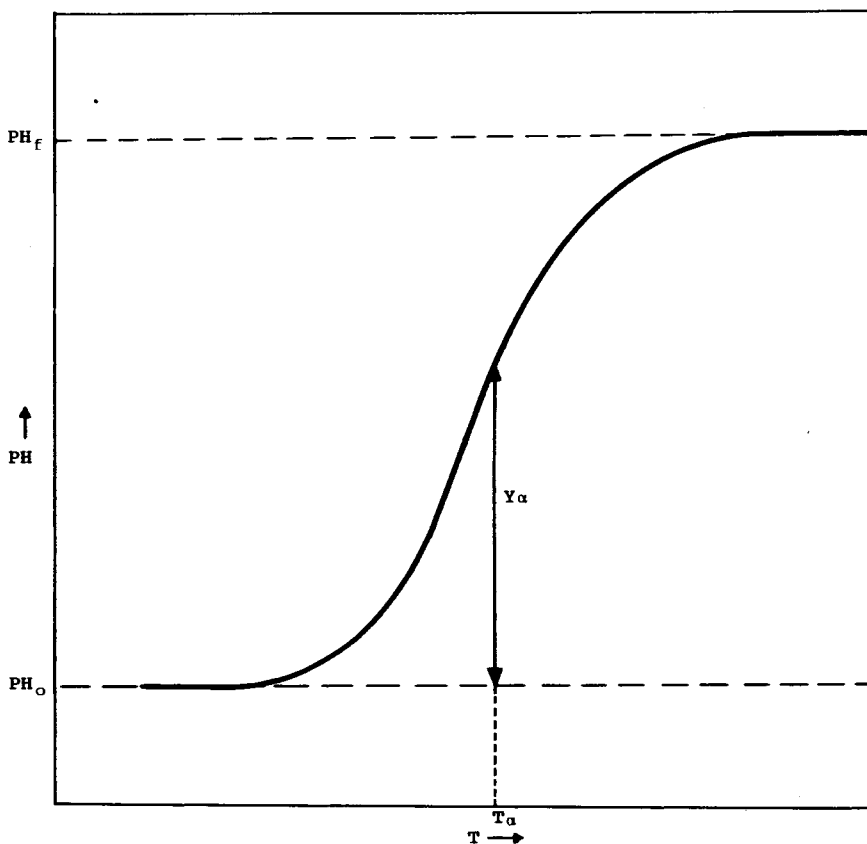

Fig. 1. Typical dynamic pH determination curve for PVC dehydrochlorination.

* No endorsement of any commercial product is implied.

TABLE I
Temperatures at which Different Grades of Conversion (α) Appear in PVC Dynamic
Dehydrochlorination Curves at Different Heating Rates (Hr) and Calculated Activation Energy
and Parameter C of Eq. (11)

| α | Temperature, °K | | | | | E_a, kcal/mole | $C, \%$ |
	Hr = 2.5°K/min	5°K/min	10°K/min	20°K/min	40°K/min		
0.005	532.9	597.2	566.2	590.1	609.1	22.75	22.49
0.01	534.5	548.8	568.0	591.9	613.0	22.41	22.11
0.015	535.1	553.1	568.8	593.8	615.3	22.44	22.07
0.02	536.1	551.4	569.4	594.9	616.6	22.11	21.77
0.05	538.7	556.5	571.2	597.2	620.3	22.34	21.86
0.10	541.7	556.7	573.1	600.8	623.9	22.06	21.50
0.15	544.2	559.4	575.6	603.7	627.1	22.09	21.47
0.20	546.1	560.8	578.3	605.6	630.6	21.91	21.24
0.50	564.1	580.7	599.3	624.2	646.0	24.10	22.99
0.75	582	596.6	624.0	647.2	667.2	23.97	21.72

passed through at a rate of 200 ml/min to obtain pH–temperature curves. Each
sample was prepared, and the dynamic dehydrochlorination was determined
four times at each heating rate (2.5°, 5°, 10°, 20°, and 40°K/min).

RESULTS AND DISCUSSION

Figure 1 shows the shape of the pH–temperature curves obtained in these
experiments. Considering the upper part of the curve as the end of the dehy-
drochlorination ($\alpha = 1$), the temperatures at different degrees of conversion can
be determined from these curves ($\alpha = 0.005, 0.01, 0.015, 0.02, 0.05, 0.1, 0.15, 0.2,$
0.5 and 0.75), making the height (Y_α) coincide, in agreement with eq. (1):

$$Y_\alpha = (7 - pH_f + \log \alpha)/K \qquad (1)$$

In eq. (1), α is the degree of conversion, K is the recorder scale in pH units per
centimeter, pH_f is the final pH ($\alpha = 1$), and Y_α is the corresponding height at
α. This equation can easily be deduced, inasmuch as at any particular moment
the hydrochloric acid concentration in the potentiometer cell is given by eq.
(2):

TABLE II
Temperatures at which Different Grades of Conversion (α) Appear in the PVC + 2.5% Epoxol
7-4 Dynamic Dehydrochlorination Curves at Different Heating Rates (Hr) and Calculated
Activation Energy and Parameter C of Eq. (11)

| α | Temperature, °K | | | | | E_a, kcal/mole | $C, \%$ |
	Hr = 2.5°K/min	5°K/min	10°K/min	20°K/min	40°K/min		
0.005	511.4	555.3	564.4	581.7	603.2	29.95	28.41
0.01	539.7	556.2	565.9	596.5	605.8	25.45	29.70
0.015	590.4	557.0	566.9	589.0	607.7	27.56	26.60
0.02	540.9	555.7	567.6	584.5	607	27.82	26.85
0.05	543.1	559.1	569.6	586.4	610.2	27.82	26.77
0.10	545.1	561.3	571.9	589.8	613.9	27.33	26.23
0.15	597.8	563.6	574.1	593.4	615.5	27.78	26.51
0.20	550.0	566.0	575.4	596.4	617.5	27.87	26.51
0.50	564.1	586.4	594.4	620.5	630.0	28.77	26.52
0.75	590.7	603.1	619.1	645.4	653.6	31.03	27.45

TABLE III

Temperatures at which Different Grades of Conversion (α) Appear in the PVC + 5% Epoxol 7-4 Dynamic Dehydrochlorination Curves at Different Heating Rates (Hr) and Calculated Activation Energy and Parameter C of Eq. (11)

	Temperature, °K						
α	Hr = 2.5°K/min	5°K/min	10°K/min	20°K/min	40°K/min	E_a, kcal/mole	C, %
0.005	537.2	557.1	570.1	586.6	607.7	26.51	25.73
0.01	539.2	560.6	573.6	587.8	610.1	26.62	25.70
0.015	540.5	562.5	574.6	588.9	611.4	26.79	26.79
0.02	591.3	562.7	575.3	591.7	612.3	26.74	25.73
0.05	545.7	564.9	577.6	595.5	615.1	27.60	26.35
0.10	551.2	568.7	580.8	598.3	618.1	28.94	27.35
0.15	555.1	571.6	583.2	601.5	620.1	29.96	28.10
0.20	558.1	574.8	586.1	617.1	622.7	30.92	28.37
0.50	573.6	589.9	602.9	634.0	639.7	31.96	28.54
0.75	587.4	605.2	619.1	706.4	656.9	31.47	27.88

$$[\text{HCl}]_\alpha = \alpha[\text{HCl}]_f \tag{2}$$

which, once the logarithm of the inverse of the equation is found, gives

$$\text{pH}_\alpha = \text{pH}_f - \log \alpha \tag{3}$$

On the other hand, the height of the curve with respect to pH_0 is given by the equation

$$Y_\alpha = (\text{pH}_0 - \text{pH}_\alpha)/K \tag{4}$$

which, by substituting in eq. (3), regrouping, and making $\text{pH}_0 = 7$, gives eq. (1).

When it is used to determine the E_a for the dehydrochlorination, this method may be considered to be Barton's[14] differential thermal analysis method. In this case, the reaction is taken to be of 0 order:

$$\frac{\partial \alpha}{\partial t} = A \exp\left(\frac{-E_a}{RT}\right) \tag{5}$$

In eq. (5), α is the degree of conversion, A is the collision coefficient of the

TABLE IV

Temperatures at which Different Grades of Conversion (α) Appear in the PVC + 7.5% Epoxol 7-4 Dynamic Dehydrochlorination Curves at Different Heating Rates (Hr) and Calculated Activation Energy and Parameter C of Eq. (11)

	Temperature, °K						
α	Hr = 2.5°K/min	5°K/min	10°K/min	20°K/min	40°K/min	E_a, kcal/mole	C, %
0.005	539.5	549.5	569.3	586.0	597.3	28.80	27.80
0.01	540.8	550.7	570.0	587.4	598.0	78.82	27.83
0.015	541.6	551.4	570.6	588.3	598.9	29.08	28.03
0.02	541.9	551.5	571.1	588.7	601.5	28.35	27.35
0.05	543.7	553.3	572.2	592.7	604.1	27.83	26.79
0.10	545.8	555.4	573.7	593.4	608.7	27.61	26.51
0.15	547.6	557.4	575.1	596.4	613.6	26.73	26.54
0.20	549.2	559.3	576.5	599.0	617.8	26.04	24.94
0.50	565.4	578.0	602.7	618.2	638.9	26.33	24.42
0.75	583.6	601.6	615.2	630.9	661.0	28.32	25.41

Arrhenius equation, R is the general gas constant, E_a is the activation energy, T is the temperature, and t is the time. The heating rate may be expressed as

$$Hr = \frac{\partial T}{\partial \tau} \qquad (6)$$

which, by substituting in eq. (5) and regrouping, gives

$$\partial \alpha = \frac{A}{Hr} \exp\left(\frac{-E_a}{RT}\right) \partial T \qquad (7)$$

Integrating between T_0 and T_α gives

$$\alpha = \left(\frac{A}{Hr}\right) T_\alpha^2 \exp\left(\frac{-E_a}{RT_\alpha}\right) - \left(\frac{A}{Hr}\right) T_0^2 \exp\left(\frac{-E_a}{RT_0}\right) \qquad (8)$$

Disregarding the last term gives for two heating rates (Hr_A and Hr_B), at the same α,

$$\frac{\alpha = (A/Hr_A)T_{A\alpha}^2 \exp\left(-E_a/RT_{\alpha A}\right)}{\alpha = (A/Hr_B)T_{B\alpha}^2 \exp\left(-E_a/RT_{\alpha B}\right)} \qquad (9)$$

Upon regrouping one obtains

$$\frac{Hr_A}{T_{\alpha A}^2} = \frac{Hr_B}{T_{\alpha B}^2} \exp\left(\frac{E_a}{RT_{B\alpha}}\right) \exp\left(\frac{-E_a}{RT_{A\alpha}}\right) \qquad (10)$$
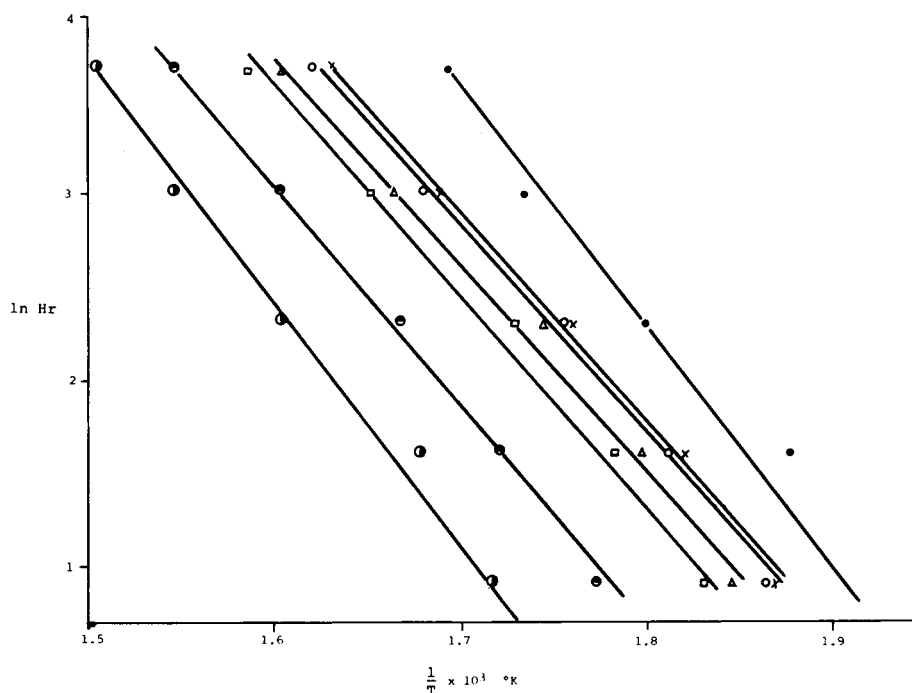
Fig. 2. Graph of ln Hr vs. $1/T$ ($^\circ K^{-1}$) for PVC dehydrochlorination under dynamic conditions at different grades of conversion: ($\bullet$) $\alpha = 0.001$; (X) $\alpha = 0.01$; (O) $\alpha = 0.02$; ($\triangle$) $\alpha = 0.1$; ($\square$) $\alpha = 0.2$; ($\ominus$) $\alpha = 0.5$; ($\mathbf{o}$) $\alpha = 0.75$.
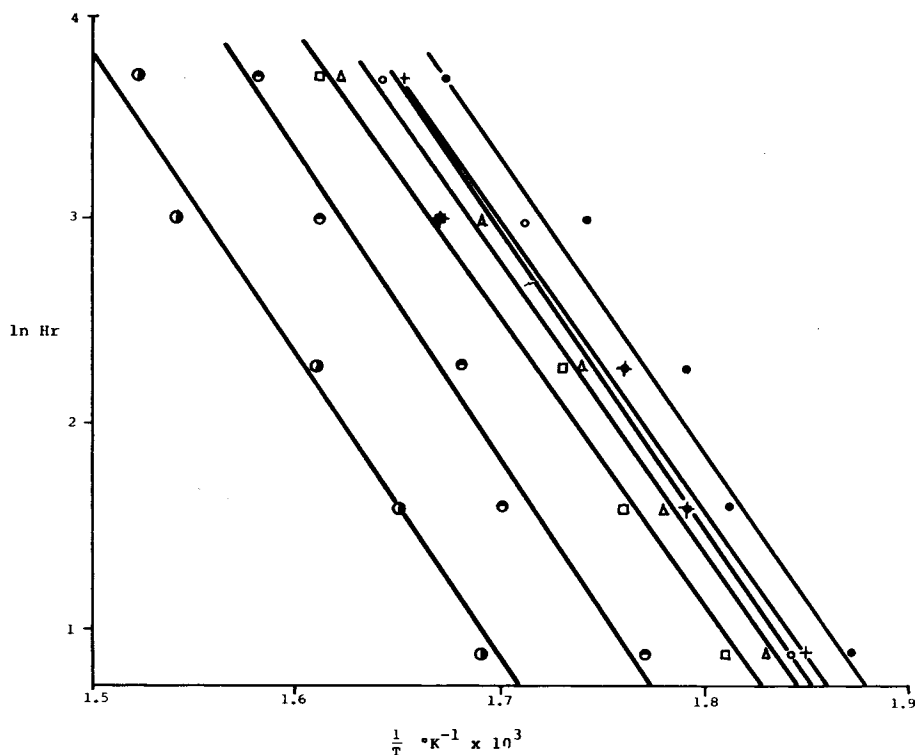
Fig. 3. Graph of ln Hr vs. $1/T$ (°K^{-1}) for PVC dehydrochlorination + 2.5% Epoxol 7-4, under dynamic conditions at different grades of conversion: (●) $\alpha = 0.001$; (X) $\alpha = 0.01$; (O) $\alpha = 0.02$; (△) $\alpha = 0.1$; (□) $\alpha = 0.2$; (◐) $\alpha = 0.5$; (◑) $\alpha = 0.75$.

considering Hr_B and $T_{\alpha B}$ as reference constants and disregarding the term $T_{\alpha A}^2$ on the left side of the expression,

$$Hr = C \exp\left(\frac{-E_a}{RT}\right) \tag{11}$$

is obtained, and therefore the graphs of ln Hr versus $1/T$ for each α are straight; from their slope the E_a was calculated.

Tables I to IV show the temperatures at the different α values for each heating rate. For each one: the E_a and C of eq. (11) were calculated using linear regression and Figures 2 to 5. The resulting correlation coefficient was 0.99. For each formulation the average and standard deviation for each parameter was obtained. Table V shows that the results are consistent as the standard deviations are between 1.9% for C of PVC without stabilizer and 7.1% for the E_a of PVC with 5% stabilizer. It is noteworthy that the E_a of the PVC dehydrochlorination (22.6 kcal/mole) rises an average 24.5% to remain constant when the stabilizer is added. It is also known[11] that the dehydrochlorination rate does not change on addition of this type of stabilizer. This means that the epoxy derivative reacts in the labile sites of dehydrochlorination, producing initiation in more stable sites. The reaction continues by a zipper-type mechanism once it is initiated. This, in addition to the fact that the reaction is carried out in mass and is ther-
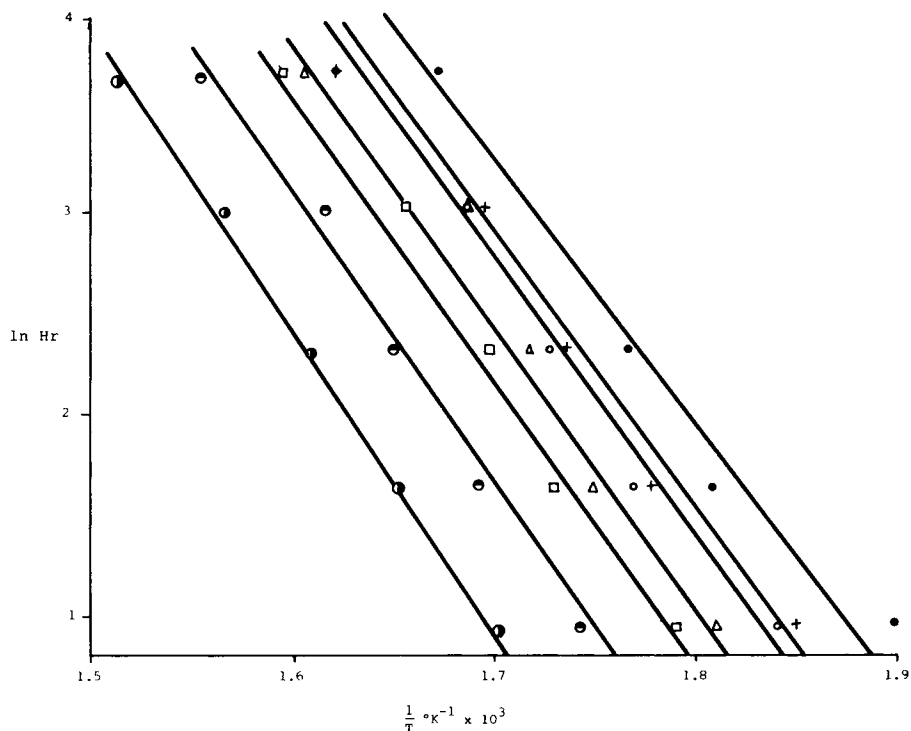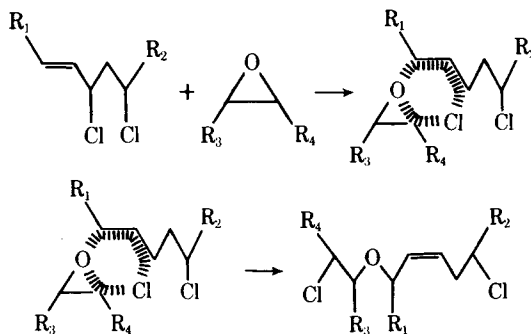
Fig. 4. Graph of ln Hr vs. $1/T$ (°K^{-1}) for PVC dehydrochlorination + 5% Epoxol 7-4, under dynamic conditions at different grades of conversion: (●) α = 0.001; (X) α = 0.01; (O) α = 0.02; (△) α = 0.1; (□) α = 0.2; (◑) α = 0.5; (◐) α = 0.75.

TABLE V
Averages and Standard Deviations of Calculated Activation Energies and Parameter C of Eq.
(11) for PVC Dehydrochlorination Stabilized with Different Concentrations of Epoxol 7-4

C, %	$E_a + \sigma$, kcal/mole	$C \pm \sigma$, kcal/mole
0	22.61 ± 0.78	21.87 ± 0.42
2.5	28.08 ± 1.45	26.66 ± 0.92
5	28.65 ± 2.04	26.95 ± 1.20
7.5	27.79 ± 1.08	26.51 ± 1.27

mally catalyzed, leads to the supposition that the epoxy attacks the double bonds (structural abnormalities which have chlorine atoms in the allylic position) by an arranged mechanism:
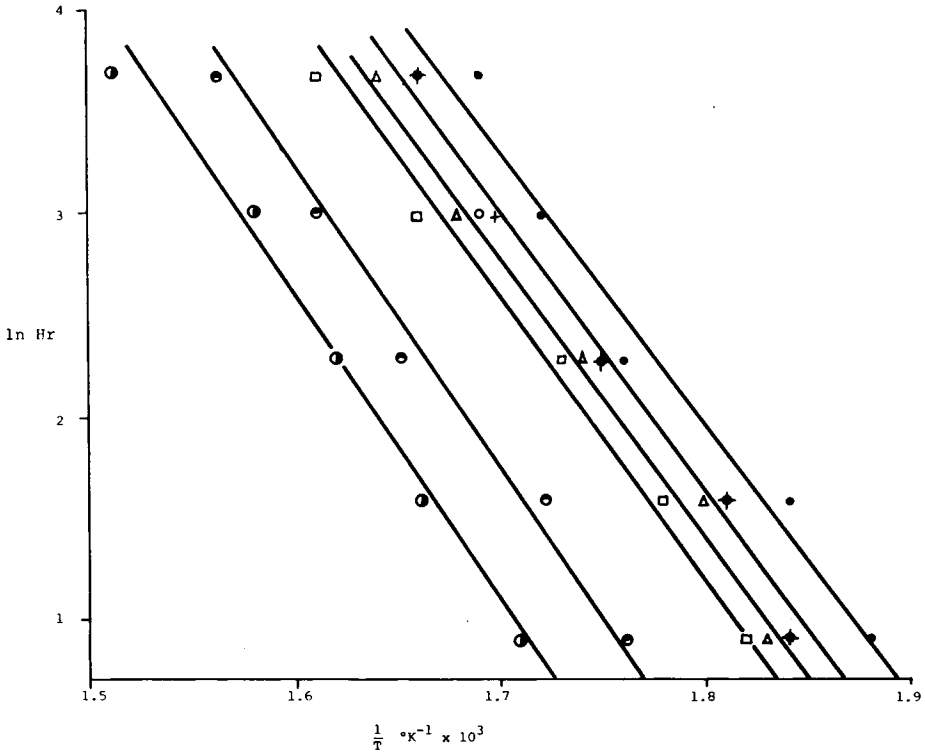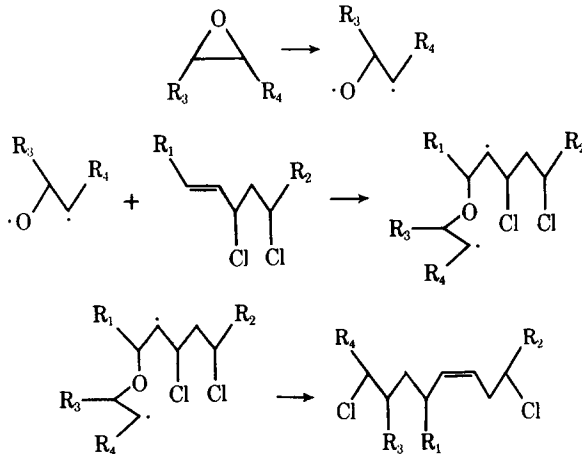
Fig. 5. Graph of ln Hr vs. $1/T$ ($°K^{-1}$) for PVC dehydrochlorination + 7.5% Epoxol 7-4, under dynamic conditions at different grades of conversion: (●) $\alpha = 0.001$; (X) $\alpha = 0.01$; (O) $\alpha = 0.02$; (△) $\alpha = 0.1$; (□) $\alpha = 0.2$; (◒) $\alpha = 0.5$; (◐) $\alpha = 0.75$.

or through free radicals,

in such a way that even though the product contains double bonds it does not have allylic chlorine atoms (which makes it more stable), thus increasing the E_a. As the quantity of double bonds present in the original polymer is very low, small quantities of stabilizers are sufficient to increase the E_a, and larger quantities do not affect this kinetic parameter.

CONCLUSIONS

The dynamic pH technique is useful for determining the E_a of PVC dehydrochlorination and formulations, using the Barton[14] method. The calculations are simple and can be done for a single reaction conversion degree. The results obtained here offer the possibility of elucidating the action mechanism of epoxy derivatives in PVC stabilization and suggest the study of the reaction, in mass and thermally catalyzed, from such model compounds as 4,6-dichloro-2-heptene and 2-epoxybutane, or 4-chloro-2-hexene and 2-epoxybutane.

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