Study of the Stabilization of Polyvinyl Chloride) by Using Model Molecules. VI. Mechanism of Reactions of Aminocrotonate Esters

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Study of the Stabilization of Poly(vinyl Chloride) by Using Model Molecules. VI. Mechanism of Reactions of Aminocrotonate Esters

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ABSTRACT

The mechanism of reaction of the β-aminocrotonate of butanediol (βACB) with 4-chloro-2-hexene (4C2H), a model compound for the allylic chlorine in poly(vinyl chloride), was studied in THF or dichloroethane at 60°C by gas and liquid chromatography. The reaction, which needs $ZnCl_2$ as a catalyst, leads to substitution products through the primary amine group and the hydrogen atom of the trisubstituted double bond. βACB reacts with HCl to give NH_4Cl and a set of complex organic products. NH_4Cl and the substitution products are able to complex $ZnCl_2$, inhibiting its catalytic activity. In combination with other stabilizers, βACB strongly induces the substitution reaction versus the dehydrochlorination. In the polymer at 190°C, it increases very much the time of action of the stabilizers; it acts as an HCl acceptor but also it may be substituted on the polymer even without catalysts. Synergistic effects are observed with epoxy compounds or indole derivatives.

INTRODUCTION

Aminocrotonate esters have long been used as secondary stabilizers in PVC [1]. However, the mechanism of their action has never been elucidated.

The purpose of this paper is to establish the basis of the reaction of such compounds with the weakest structure of PVC under conditions of thermal degradation, i.e., allylic chlorine atoms, either alone or in the presence of other additives of the so-called zinc-calcium formulation for rigid PVC. As in the previous papers of this series [2-6], we have used 4-chloro-2-hexene (4C2H) in solution, either in dichloroethane (DCE) or tetrahydrofuran (THF), as a model compound for allylic chlorine atoms present at the end of growing polyene sequences during PVC degradation.

We previously established [2] that the thermal degradation of 4C2H in solution in the range of 40-80°C is essentially a reversible reaction obeying an ionic mechanism and is catalyzed by a charge-transfer complex between HCl and the hexadiene products of the reaction. All the compounds complexing HCl more strongly than hexadiene, like THF, pyridine, or phosphine compounds, inhibit the pure thermal degradation under these conditions. Zinc chloride is a powerful catalyst of the degradation [3], which is then observed in THF as well as in DCE, although at a lower rate. As the reaction is first-order versus both 4C2H and $ZnCl_2$, the rate-determining step is the formation of an intermediate carbocation, the counteranion being $ZnCl_3^-$. It has also been shown that, in DCE and in the presence of HCl, $ZnCl_2$ is a catalyst for the polymerization of diene through a cationic mechanism.

Zinc stearate reacts rather slowly with 4C2H in THF; the rate accelerates progressively due to the formation of $ZnCl_2$, which is a strong catalyst for the esterification reaction, as well as for the degradation reaction, the former being favored [4]. The esterification by calcium stearate is also catalyzed by zinc chloride. In both cases, the reaction is first-order with respect to 4C2H and $ZnCl_2$ but the rate is independent of the concentration of the stearate. It may therefore be concluded that the same intermediate carbocation is involved, with which the stearates undergo nucleophilic reaction. However, the rate constant is sixteen times greater in the case of zinc stearate. This fact may be explained on assuming that the catalytic action of zinc chloride is partly inhibited by calcium stearate through the formation of a complex. The synergistic effect between zinc and calcium stearate has been studied in more detail [4]. It is generally explained [7, 8] by an exchange reaction between calcium stearate and zinc chloride which restores zinc stearate and gives calcium chloride, which is inactive. A careful study of this exchange reaction in the total absence of water and other impurities has shown that it is

indeed limited and reversible. The limit of the reaction corresponds to the formation of a mixture of three kinds of rather stable complexes: the first one is $CaCl_2 \cdot 2ZnCl_2$; the second one involves both stearates with the same stoichiometry (already described by Onozuka [7]); the third is a mixed 1:2 complex of $ZnCl_2$ with calcium stearate. It has been proved that, in this complex, the catalytic action of zinc chloride is drastically reduced. It is to be noted that in the presence of an excess of HCl the ester formed is not stable and one gets hexadiene again, and stearic acid.

Epoxy compounds react with 4C2H through an etherification reaction which is again catalyzed by $ZnCl_2$ [5]. This reaction has already been described by Anderson and MacKenzie [9] in the case of the barium-cadmium formulation. However, the reaction is first-order with respect to the three components. Here, too, there is a secondary polymerization reaction of the epoxy compound catalyzed by $ZnCl_2$, which is partly engaged. For this reason, its catalytic activity decreases progressively. Here, too, the ether is destroyed in the presence of an excess of HCl, and one receives hexadiene again. There is a definite synergistic effect between epoxy and calcium stearate, in the presence of $ZnCl_2$ as catalyst, it concerns both etherification and esterification as well as degradation. Between esterification by metal carboxylates and etherification by epoxy compounds, the competition is in favor of esterification.

Some studies have been made of the degradation of 4C2H in the presence of phosphines or phosphite. Phosphines, as well as other organic bases such as pyridine, essentially act as powerful complexing agents for both HCl and $ZnCl_2$. With phosphites, and chiefly with alkylphosphites, a substitution reaction catalyzed again by $ZnCl_2$ occurs, giving phosphonate ester. Again here the phosphonate ester is not stable in the presence of an excess of HCl. There is no synergistic effect between phosphite and metal carboxylates in the conditions we chose, and the competition for esterification reactions is again strongly in favor of metal carboxylates. Finally, the behavior of α-phenylindole as secondary stabilizer has been studied [6]. A substitution reaction involving the hydrogen atom on the unsubstituted carbon atom of the double bond of the heterocycle has been observed, as well as the fixation of 4C2H residue on the aromatic rings. The proton of the NH group is involved only in complexation with either HCl or $ZnCl_2$, both of which act as catalysts for the substitution reaction. It is to be noted that these reactions lead to the formation of HCl which is not fixed. On the other hand, the product of the substitution reaction is not sensitive to HCl, so that the stabilization reaction is definite. But α-phenylindole is not a powerful inhibitor of the degradation reaction, so that it cannot be used alone. Other stabilizers are necessary, mainly metal carboxylates. Owing to the formation of HCl from α-phenylindole, degradation is observed at

the end of the reaction if the total amount of the other stabilizers (metal carboxylates, epoxy compounds and phosphites) is lower than the amount of 4C2H.

It has been proved in most of the above studies that the conclusions drawn from the results concerning model compounds are valid for PVC at working temperature. The degradation behavior in the Brabender Plastograph at 190°C is similar to that of the model compound at 60°C, for instance, versus the relative concentration of the different stabilizers. The only exception is the case of the phosphite, where zinc chloride is reacted and neutralized at high temperature. It is to be noted also that reversibility of the degradation reaction becomes negligible at high temperature, due to a difference of about 7 kcal/mole between the activation energy of the direct and reverse reactions.

The behavior of aminocrotonate esters might be expected to be similar to that of the α-phenylindole. However, the results presented in this paper show that mostly the NH_2 group is involved and that a number of secondary reactions occur.

EXPERIMENTAL

Materials

The β-aminocrotonate of butanediol 1-4 (βACB) is a commercial product (Stabilizer S420, Sapchim-Fournier-Cimag). The preparation of 4C2H has already been described previously [2]. The solvents were carefully dried and distilled before use. Zinc chloride was purified by sublimation.

Chromatography

Gas chromatographic analyses were used to follow the consumption of 4C2H and the formation of hexadiene [2]. Liquid chromatography is used to prove the condensation of βACB on 4C2H [6].

Product Identification

Product identification was mostly by IR spectroscopy.

RESULTS AND DISCUSSION

Products of Reaction

In both THF and DCE the reaction between 4C2H and βACB only takes place in the presence of ZnCl₂. The solution, initially clear (THF) or slightly opalescent (DCE), gradually becomes yellow and, in most cases, heterogeneous, with a white precipitate. Figure 1 shows a typical liquid chromatogram of the solution, showing the gradual consumption of βACB and 4C2H and the formation of at least one condensation product (and possibly two) of higher molecular weight. Infrared spectra of the products at the end of the reaction show that the $-NH_2$ groups of βACB (two bands at 3300 and 3440 cm^{-1}) have been replaced by a secondary amine group (only one broad band at 3440 cm^{-1}). In another part of the spectrum, the activated ethylenic CH group (characteristic band at about 790 cm^{-1}) has disappeared
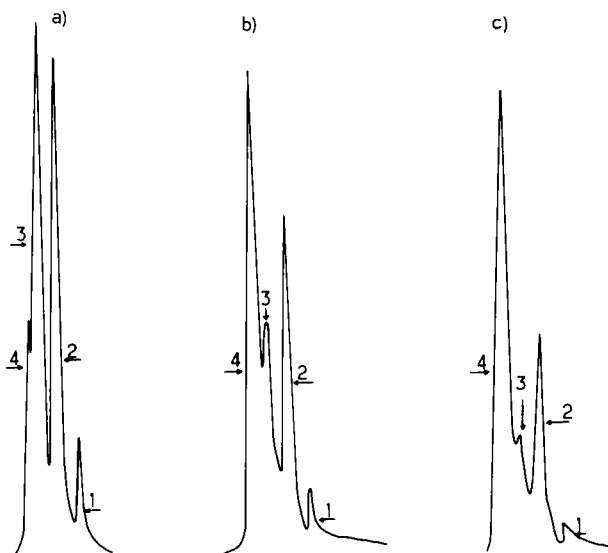
FIG. 1. Liquid chromatograms of the reaction medium in THF at various times t: (a) t = 0; (b) t = 15 min; (c) t = 40 min. The peaks are: (1) 4-chloro-2-hexene; (2) ZnCl₂; (3) butanediol β-aminocrotonate; (4) condensation product.

(Fig. 2, spectra a and b). When catalyzed by $ZnCl_2$, two successive substitution reactions probably take place [Eqs. (1) and (2)].

$$\left[\begin{array}{c} CH_3-C=C-C-O-(CH_2)_2- \\ \;\;\;\;\;|\;\;\;|\;\;\; || \\ \;\;\;\;NH_2\;\;H\;\;O \end{array}\right]_2 + 2CH_3-CH=CH-\overset{\overset{\displaystyle Cl}{|}}{CH}-CH_2-CH_3$$

$$\longrightarrow \left[\begin{array}{c} \;\;\;\;\;\;\;\overset{\overset{\displaystyle H}{|}}{} \\ CH_3-C=C-C-O-(CH_2)_2- \\ \;\;\;\;\;|\;\;\;\;\;\; || \\ \;\;\;\;NH\;\;\;\;\;O \\ \;\;\;\;| \end{array}\right]_2 + 2HCl$$

$$CH_3-CH_2-CH-CH=CH-CH_3$$

I   (1)
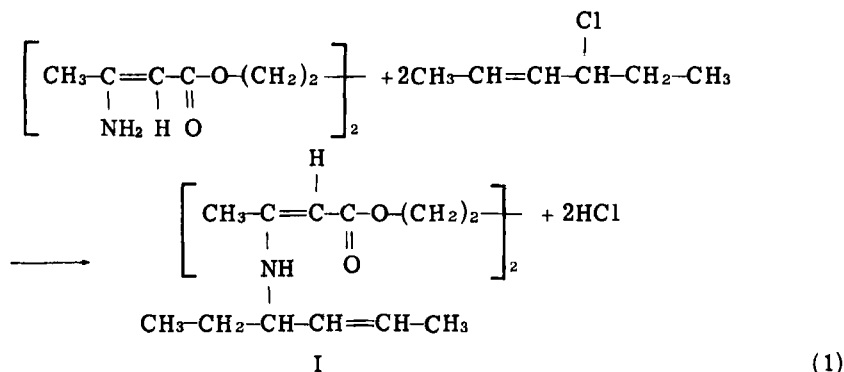
The new structure I then formed,

$$(R-NH-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-\overset{C}{\underset{||}{}}-O-CH_2-)$$
$$O$$
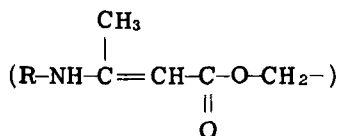
presents some analogy with α-phenylindole
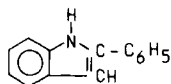
In the previous paper [6] it was shown that this product easily reacts with 4C2H through its ethylenic hydrogen atom. So, owing to the disappearance of the band characteristic of this C–H band, a similar reaction (2) may take place. In this case, the two condensation reactions give rise to the formation of HCl.

The reaction between dry HCl and βACB in dichloroethane has been studied independently at 60°C. The first product is the βACB chlorohydrate, a yellowish solid insoluble in water as well as in THF or DCE. The infrared spectrum of this product is given in Fig. 2c. It may be seen that the hydrogen bonding between the NH_2 and C=O groups of βACB has been eliminated, the C=O stretching vibration

$$\text{Cl}$$
$$|$$
$$\text{I} + 2\text{CH}_3\text{-CH}=\text{CH-CH-CH}_2\,\text{CH}_3$$

$$\longrightarrow \quad \left[\begin{array}{c} \text{CH}_3\text{-CH}_2\text{-CH-CH}=\text{CH-CH}_3 \\[4pt] \text{CH}_3\text{-C}=\text{C-C-O(CH}_2)_2 \\[-2pt] \quad | \quad\quad\; \| \\ \text{NH} \quad\; \text{O} \end{array} \right]_2 + 2\text{HCl}$$

$$|$$
$$\text{CH}_3\text{CH}_2\text{-CH-CH}=\text{CH-CH}_3 \tag{2}$$
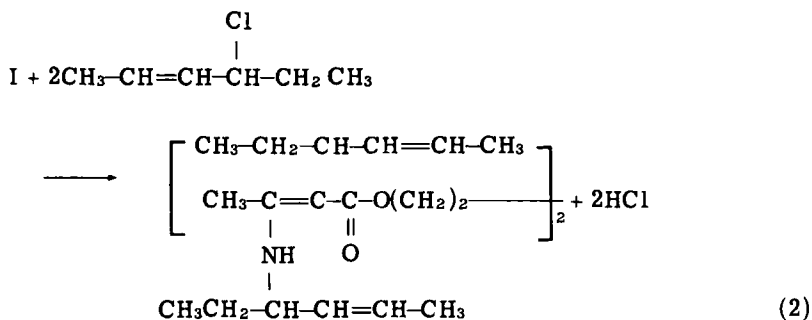
being shifted from 1600 to 1730 cm^{-1}. Another band appears at 650 cm^{-1}, which might be assigned to a C–Cl bond, which results from the addition of HCl to the double bond. This reaction is limited, because the band characteristic of the ethylenic C–H group (790 cm^{-1}) does not disappear. Upon further reaction, NH$_4$Cl is formed. In DCE the yield is limited to 20%, but in THF it can reach 85%. The organic part is a mixture; on heating under vacuum one can get Cl(CH$_2$)$_4$OH which may be identified from its infrared spectrum with

FIG. 2. Infrared spectra of (a) butanediol β-aminocrotonate (b) of its reaction product with 4C2H, and (c) of its chlorohydrate.

an OH band (3400 cm^{-1}), the CH$_2$ stretching bands at 2780-2950 cm^{-1}, and the CCl band at 650 cm^{-1}. The presence of this product shows the splitting of the ester group by HCl. Most probably, the reaction is as shown in Eq. (3).

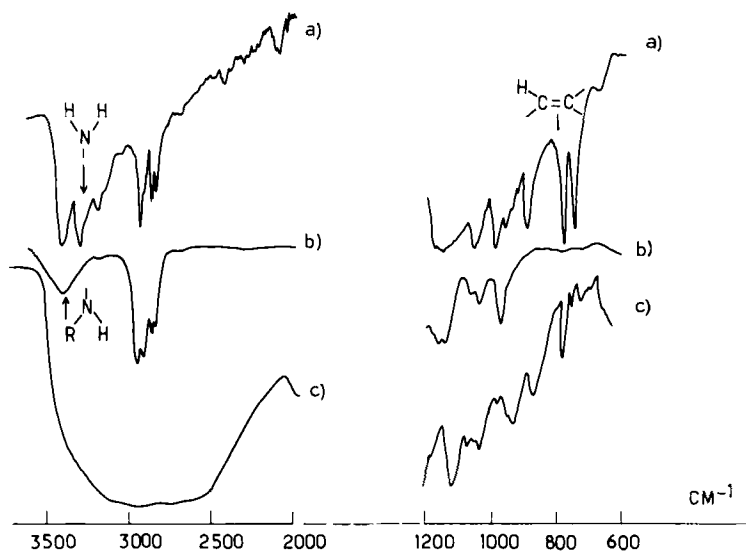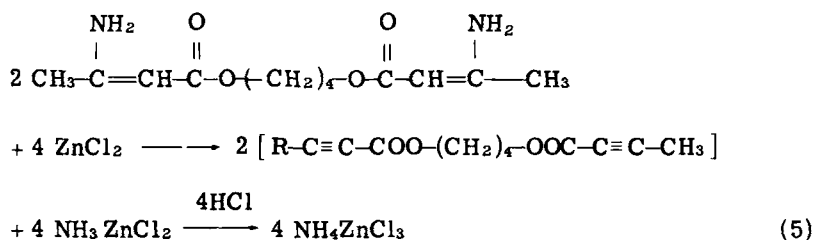$$\text{HCl} + \left[\begin{array}{c} \text{CH}_3\text{--C}\text{=}\text{CH--C--O}\text{(--CH}_2\text{--)}_{2} \\ | \qquad || \\ \text{NH}_2 \qquad \text{O} \end{array} \right]_2$$

$$\longrightarrow \ 2\ \text{CH}_3\text{--C} \overset{\diagup\ \text{NH}\ \diagdown}{\underset{\diagdown\ \text{CH}\ \diagup}{}} \text{C}\text{=}\text{O} + \text{Cl(CH}_2)_4\text{OH} + \text{H}_2\text{O} \qquad (3)$$

The lactam probably leads to oligomers, as suggested by the infrared spectrum of the organic residue.

Zinc chloride also reacts with βACB. It first forms a complex through the NH$_2$ group and then an NH$_3$$-$ZnCl$_2$ complex is formed. The reaction is much more rapid in the presence of water; in that case, an insoluble solid compound is separated, having a formula ZnCl$_2$·6ZnO·6H$_2$O [10]. It must be mentioned also that ZnCl$_2$ forms a complex with NH$_4$Cl which results from the reaction of HCl and βACB.

The corresponding reaction might be as shown in Eqs. (4) and (5).

$$\begin{array}{cccc} \text{NH}_2 & \text{O} & \text{O} & \text{NH}_2 \\ | & || & || & | \\ \text{CH}_3\text{--C}\text{=}\text{CH--C--O}\text{(--CH}_2)_4 & \text{--O--C--CH}\text{=}\text{C---CH}_3 \end{array}$$

$$\begin{array}{cc} & \text{O} \qquad\qquad\qquad \text{O} \\ 2\ \text{ZnCl}_2 & || \qquad\qquad\qquad || \\ + 2\text{HCl} \xrightarrow{\hspace{1cm}} \text{CH}_3\text{--C}\text{=}\text{C--C--O--(CH}_2)_4\text{--O--C--CH}\text{=}\text{C---CH}_3 \\ & | \qquad\qquad\qquad\qquad\qquad | \\ & \text{Cl} \qquad\qquad\qquad\qquad \text{Cl} \end{array}$$

$$+\ 2\text{NH}_3\text{ZnCl}_2 \xrightarrow{\ 2\ \text{HCl}\ } 2\ \text{NH}_4\text{ZnCl}_3 \qquad\qquad (4)$$

The ZnCl$_2$ engaged in these complexes has probably lost its catalytic activity. For that reason, a rather large amount of zinc chloride is necessary to promote a complete reaction between 4C2H and βACB. Typical results reported in Table 1 illustrate this point. They show that a ratio ZnCl$_2$/βACB greater than 1 is necessary for a complete

$$2 \ CH_3-C=CH-\overset{\overset{NH_2}{|}}{C}-\overset{\overset{O}{||}}{C}-O+CH_2)_4-O-\overset{\overset{O}{||}}{C}-\overset{\overset{NH_2}{|}}{C}-CH=C-CH_3$$

$$+ \ 4 \ ZnCl_2 \longrightarrow 2 \left[R-C \equiv C-COO-(CH_2)_4-OOC-C \equiv C-CH_3 \right]$$

$$+ \ 4 \ NH_3 \ ZnCl_2 \xrightarrow{\ 4HCl\ } 4 \ NH_4ZnCl_3 \tag{5}$$

reaction. A first reaction needs a ratio larger than 1.5, so that one may suggest that reaction (5) is the most probable one inhibiting the catalytic action of $ZnCl_2$.

Kinetic Study

Typical kinetic curves of the consumption of 4C2H versus time are illustrated in Fig. 3, relative to experiments at 60°C in THF, in the presence of zinc chloride in limited amount. It may be seen that the reaction rapidly reaches a limit which is dependent mainly on the amounts of $ZnCl_2$ and βACB. The reaction mostly corresponds to a substitution reaction and the amount of hexadiene obtained is always very low. From the measurement of the initial rate, the law (6) is deduced.

$$V_0 = 2.0 \times 10^{-2} \ [4C2H] \ [\beta ACB] \ [ZnCl_2] \tag{6}$$

The reaction is first-order with respect to $ZnCl_2$ as well as to each one of the other two reactants. The rate-determining step then involves three species. We suggest a preliminary complexation of $ZnCl_2$ by the two NH_2 groups of βACB. The complex formed in that way would attack the Cl atoms of 4C2H leading to a polarization of the C–Cl bond towards the formation of an intermediate but unstable carbocation. The stabilization involves the elimination of one HCl molecule and the substitution of the hexenyl group on the nitrogen atom. The residual $ZnCl_2$ remains complexed by one NH_2 group and more strongly by the newly formed NH group. This new complex may react readily with another 4C2H molecule for a substitution on the second nitrogen atom. The product of the reaction may promote the substitution of two further 4C2H molecules on the ethylenic groups with again elimination of HCl. It is interesting to note the analogy with the reaction with α-phenylindole. In this case [6], the kinetic law was the same and also the rate constant had the same value. The overall scheme might be as shown in scheme 1.

TABLE 1. Results of Reaction between β-Aminocrotonate of Butanediol and 4-Chloro-2-hexene in the Presence of $ZnCl_2$ at 60°C in THF Solution

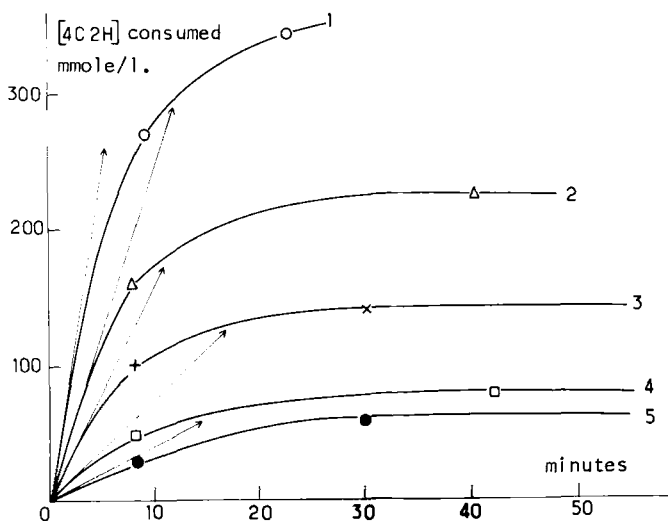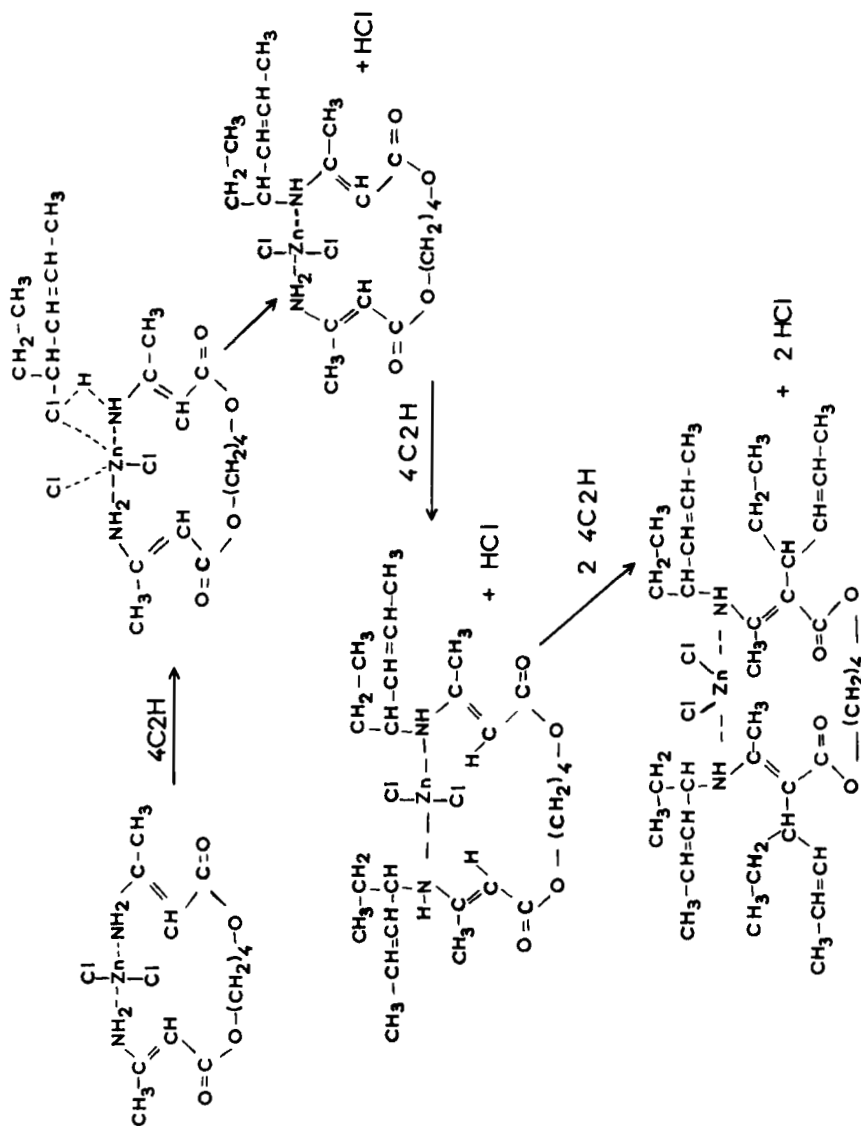| 4C2H (mmole/liter)	βACB (mmole/liter)	$ZnCl_2$ (mmole/liter)	Reaction time (min)	Yield (% relative to 4C2H)	
				Hexadiene	Substitution product
450	240	100	400	1	24
450	230	230	400	4.5	62
450	230	345	400	5	95
450	230	460	40	6.5	93.5

FIG. 3. Consumption of 4-chloro-2-hexene (4C2H) by reaction with butanediol β-aminocrotonate (βACB) in THF at 60°C in the presence of zinc chloride: (1) 4C2H 480 mmole/liter, βACB, 280 mmole/liter, ZnCl$_2$, 200 mmole/liter, (2) 4C2H, 660 mmole/liter, βACB, 280 mmole/liter, ZnCl$_2$, 100 mmole/liter, (3) 4C2H, 430 mmole/liter, βACB, 280 mmole/liter, ZnCl$_2$, 100 mmole/liter, (4) 4C2H, 425 mmole/liter, βACB, 280 mmole/liter, ZnCl$_2$, 50 mmole/liter, (5) 4C2H, 340 mmole/liter, βACB, 100 mmole/liter ZnCl$_2$, 100 mmole/liter.

The complexation of ZnCl$_2$ will obviously favor the four successive steps of substitution within the same molecule and this fact might explain why, in the liquid chromatogram, there is no indication of several reaction products (Fig. 1). It is possible also that the strong complexation by the reacted molecule tends to prevent the ZnCl$_2$ molecule from catalyzing other reactions. This possible fact, as well as the formation of NH$_4$ZnCl$_3$, might explain why the reaction tends to stop, except in the presence of a very high amount of ZnCl$_2$.

The kinetic law is different in DCE solution. The shape of the kinetic curve of consumption of 4C2H is not changed (Fig. 4) and after a high initial rate, a leveling off is observed. However the expression for the initial rate is now:

$$V_0 = 7.2 \times 10^{-3} [4C2H][ZnCl_2] \tag{7}$$

Scheme 1.

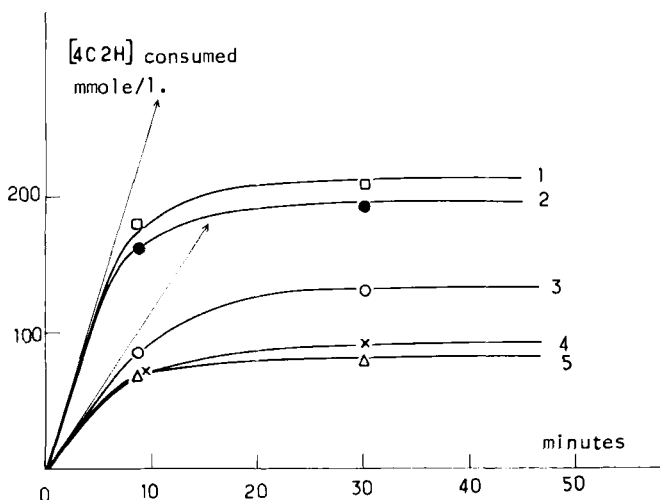FIG. 4. Consumption of 4-chloro-2-hexene by reaction with butanediol β-aminocrotonate (βACB) in dichloroethane (DCE) at 60°C in the presence of zinc chloride: (1) 4C2H, 600 mmole/liter, βACB, 200 mmole/liter, ZnCl₂, 100 mmole/liter; (2) 4C2H, 280 mmole/liter, βACB, 200 mmole/liter, ZnCl₂, 200 mmole/liter; (3) 4C2H, 300 mmole/liter, βACB, 200 mmole/liter, ZnCl₂, 100 mmole/liter; (4) 4C2H, 270 mmole/liter, βACB, 300 mmole/liter, ZnCl₂, 100 mmole/liter; (5) 4C2H, 280 mmole/liter, βACB, 100 mmole/liter, ZnCl₂, 100 mmole/liter.

The reaction is zero order with respect to βACB and first order with respect to ZnCl₂ and 4C2H. Another fact is that the formation of hexadiene through a dehydrochlorination of 4C2H is not at all negligible. Some typical results of dehydrochlorination are shown in Fig. 5. The kinetic law for dehydrochlorination is given in Eq. (8):

$$V_D = 5 \times 10^{-3} \, [4C2H] \, [ZnCl_2]/[\beta ACB] \qquad (8)$$

In this case it seems that the rate-determining step is the formation of an allylic carbocation through the attack of 4C2H by ZnCl₂. A similar situation has been observed in the catalytic dehydrochlorination of 4C2H by ZnCl₂ without additives [3], or for the substitution reaction of either zinc carboxylate [4] or alkyl phosphite [3] or etherification by epoxy compounds [5]. The complexation of ZnCl₂ by βACB probably occurs again, and reactions between the carbocation and the
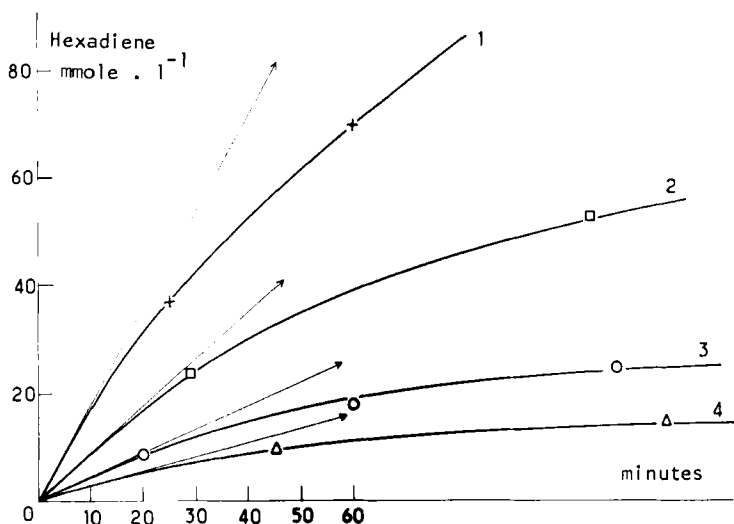
FIG. 5. Dehydrochlorination of 4-chloro-2-hexene (4C2H) in the presence of $ZnCl_2$ and butanediol β-aminocrotonate (βACB) in dichloroethane (DCE) at 60°C: (1) 4C2H, 590 mmole/liter, βACB, 200 mmole/liter, $ZnCl_2$, 200 mmole; (2) 4C2H, 600 mmole/liter, βACB, 200 mmole/liter, $ZnCl_2$, 100 mmole/liter; (3) 4C2H, 290 mmole/liter, βACB, 200 mmole/liter, $ZnCl_2$, 100 mmole/liter; (4) 4C2H, 260 mmole/liter, βACB, 300 mmole/liter, $ZnCl_2$, 100 mmole/liter.

free or complexed βACB molecules are both possible. The final products seem to be the same, so that we favor the second possibility. Anyway, the competition between dehydrochlorination and substitution is less in favor of the latter, although it remains dominant. The product of substitution, because of its complexing power to $ZnCl_2$, is able to inhibit the dehydrochlorination. A few experiments, illustrated in Fig. 6 prove that fact.

Stabilization of Poly(vinyl Chloride) (PVC)

Some differences between the behavior of βACB versus the model compounds and PVC are to be expected, because it is well known, as cited by Nass [1], that aminocrotonate esters are able to stabilize PVC to thermal degradation without the help of any organometallic additive. Indeed, βACB reacts with HCl, and this is a stabilizing action; but we suspect that when the temperature rises from 60 to 190°C direct reaction of βACB with PVC may take place, without the help of any catalyst like $ZnCl_2$.
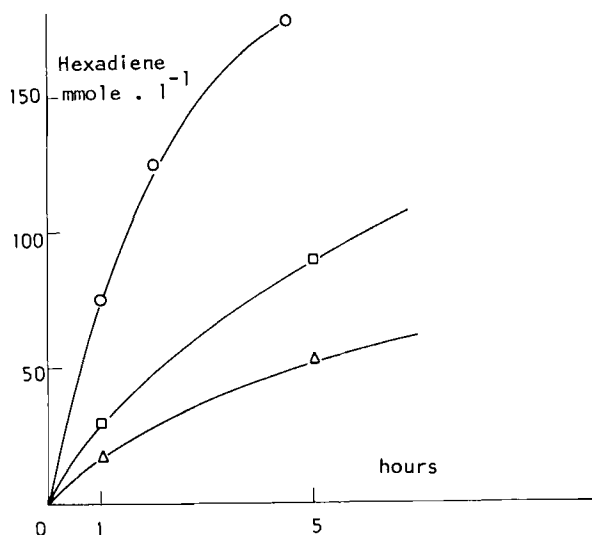
FIG. 6. Dehydrochlorination of 4C2H (420 mmole/liter) by $ZnCl_2$ (40 mmole) in the presence of the organic product of substitution of βACB and 4C2H. The amount of the product is ($\circ$) 0; ($\square$) 40; or ($\triangle$) 80 mmole/liter.

Experiments have been carried out in a Brabender Plastograph at 190°C with a mixture of 30 g of PVC and 9 g of dioctyl phthalate. Typical plastograms are illustrated in Fig. 7. After the gelation peak, a second peak is visible which corresponds to the total consumption of the stabilizer. The interval between the two peaks is the time of action of the stabilizer T_A, which is a measure of either a chemical (substitution or HCl neutralization) or a physical (lubricant) activity, or both. As shown in Fig. 8, the T_A for βACB is, on a mole basis, greater than that of any one of the pure organic components of a stabilizer formulation. The comparison with α-phenylindole is interesting because in both cases HCl is formed after a substitution reaction but βACB is able to neutralize it.

An analysis of the reaction products after T_A has been performed. The solid black product was dissolved in THF and then precipitated with water to separate the polymer. The liquid phase was then evaporated and the solid washed with THF. The solid was then dissolved in water. The solid residue is the chlorhydrate of βACB, and in the liquid phase there is NH_4Cl. The products obtained, on the basis of βACB, are about 20% chlorhydrate, 20% NH_4Cl, and 20% oligomers.
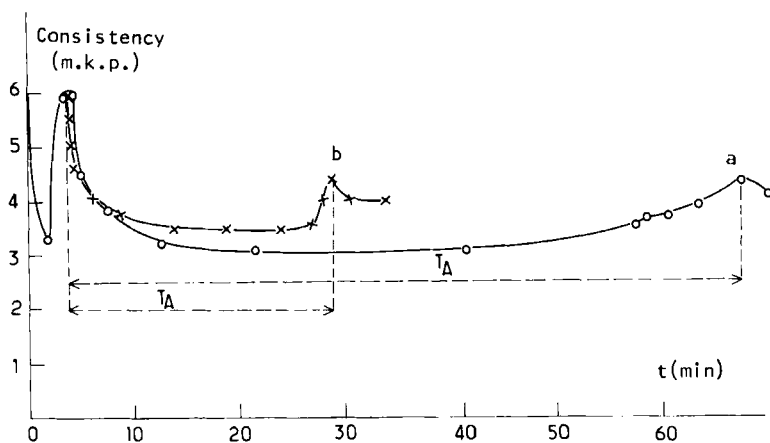
FIG. 7. Plastogram of PVC (30 g), DOP (9 g) and (a) βACB (2 g) or (b) βACB (0.4 g), zinc stearate (0.4 g), and calcium stearate (0.4 g).
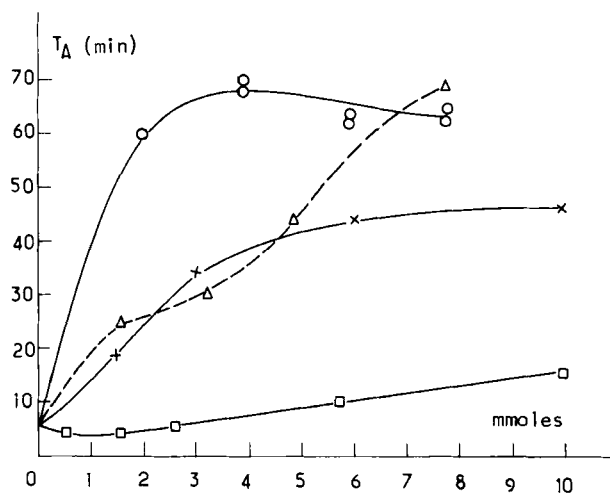

FIG. 8. Action time T_A of various molar amounts of stabilizer (in Brabender Plastograph): (○) βACB; (×) α-phenylindole, (□) zinc stearate; (△) calcium stearate.

Thus a large fraction of βACB has been fixed onto the polymer. The chlorhydrate and also surprisingly NH₄Cl seem to have a lubricant action, because they can increase T_A of the pure polymer.

β-Aminocrotonate in Conjunction with Other Stabilizers

Although it has been pointed out that βACB may be used alone, in practice it is now usually used as a secondary stabilizer in the calcium-zinc formulation, possibly together with other organic compounds. Studies have been carried out either with the model compound 4C2H or with PVC in the Brabender plastograph. In the latter case, organic mixtures of βACB and epoxidized soyabean oil (ESO) or βACB and α-phenylindole, without any zinc compound, have been studied. The results, illustrated in Figs. 9 and 10 show that in both cases true synergistic effects are observed. βACB alone is, as expected, more efficient than any of the two other components but mixtures give in both cases a very much higher efficiency. A number of typical results obtained in the study of 4C2H are reported in

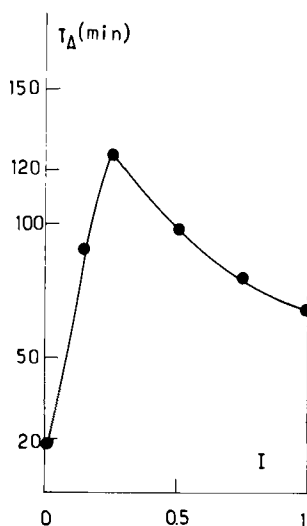FIG. 9. Action time T_A of a mixture of βACB and epoxidized soyabean oil (ESO) as a function of the ratio: $I = \beta$ACB$/(\beta$ACB + ESO). Total molar amount of organic stabilizer, 0.004 mole for 30 g of PVC plasticized with 9 g of DOP in a Brabender Plastograph.
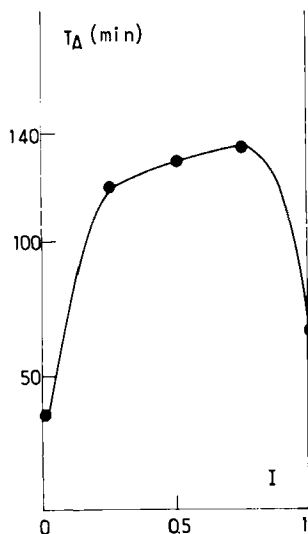
FIG. 10. Action time T_A of a mixture of βACB and α-phenylindole (αPhI) as a function of the ratio: $I = \beta ACB/(\beta ACB + \alpha PhI)$. Total molar amount of organic stabilizer, 0.0028 mole for 30 g of PVC and 9 g of DOP in a Brabender plastograph.

Table 2. The presence of zinc compounds is always necessary for the reaction to take place, and either $ZnCl_2$ or zinc stearate, $Zn(OCOR)_2$, have been used. A number of general conclusions can be drawn.

The reaction may be blocked by βACB if the molar ratio of βACB to zinc compound is higher than 1. Rapid reactions need very high amount of zinc compounds.

βACB is very efficient in favoring the substitution reaction versus the dehydrochlorination reaction. High yields in dehydrochlorination are observed mostly when zinc chloride is used in very high amounts and also if the total amount of stabilizer is higher than the amount of 4C2H, kept constant at 450 mmole/liter in all the experiments. It must be recalled here that the substitution products from the calcium or zinc stearates from epoxy compounds or from phosphites are sensitive to an excess of HCl, so that the substitution reaction may possibly be retrograded in favor of the dehydrochlorination. In this respect, the combination of βACB and α-phenylindole (which gives substitution products insensitive to HCl) is very efficient in limiting dehydrochlorination.

The comparison of the various costabilizers used in conjunction

TABLE 2. Reaction of 4C2H (450 mmole/liter) in THF at 60°C with Combination of Stabilizers

No.	βACB (mmole/ liter)	ZnCl$_2$ (mmole/ liter)	Costabilizer[a]			Reaction time (min)	Dehydro- chlorination (%)	Substi- tution (%)
			Zn(OCOR)$_2$ (mmole/ liter)	Type	Amount (mmole/ liter)			
1	50	–	180	–	–	75	20	80
2	80	–	80	–	–	∞	11.1	61
3	100	–	180	–	–	60	11.2	88.8
4	118	–	118	–	–	300	8	92
5	180	–	50	–	–	∞	5	40
6	180	–	180	–	–	40	5.7	94.3
7	50	270	–	Ca(OCOR)$_2$	180	350	8	92
8	80	300	–	"	80	230	70	30
9	80	400	–	"	80	185	71	29
10	115	130	–	"	115	320	9.4	90.6
11	115	270	–	"	115	130	9.0	91
12	115	400	–	"	115	25	6.5	93.5
13	180	270	–	"	50	285	15	85
14	50	200	–	C4H8O	390	35	13.6	86.4
15	80	200	–	"	200	400	35	65

(continued)

TABLE 2 (continued)

No.	βACB (mmole/ liter)	ZnCl$_2$ (mmole/ liter)	Zn(OCOR)$_2$ (mmole/ liter)	Costabilizer[a]		Reaction time (min)	Dehydro-chlorination (%)	Substitution (%)
				Type	Amount (mmole/ liter)			
16	115	200	–	C4H8O	260	80	13.3	86.7
17	180	200	–	"	130	120	13.2	86.8
18	35		35	C4H8O	320	∞	6.8	57.2
19	35		160	"	70	50	20	80
20	56		56	"	230	150	7.5	92.5
21	56		115	"	112	45	8	92
22	77		77	"	150	180	15	85
23	115		56	"	112	∞	7.6	58.4
24	160		35	"	70	∞	0	40
25	50	390	–	P(OBu)$_3$	300	400	80	20
26	65	390	–	"	115	400	70	30
27	115	130	–	"	230	500	12.5	57.5
28	115	260	–	"	230	500	52	48
29	115	390	–	"	230	170	28	72
30	115	390	–	"	470	600	10	90
31	175	390	–	"	115	170	20	80

32	33	–	100	P(OBu)$_3$	195	200	25	75
33	65	–	100	"	130	150	15	85
34	98	–	100	"	65	400	6	94
35	98	–	100	"	195	100	3.5	96.5
36	50	200	–	αPhI	180	150	30	70
37	50	400	–	"	180	110	34	66
38	115	200	–	"	115	420	32	68
39	115	400	–	"	115	70	32	68
40	180	200	–	"	50	∞	9.1	60.9
41	180	400	–	"	50	45	34	66
42	35	–	35	αPhI	160	∞	0	32
43	35	–	160	"	35	180	60	40
44	56	–	56	"	115	∞	0	41
45	56	–	115	"	56	∞	16.8	67.2
46	60	–	170	"	170	120	6	94
47	60	–	230	"	170	120	8.4	91.6
48	77	–	77	"	77	∞	6.2	55.8
49	115	–	56	"	56	∞	0	40
50	115	–	115	"	115	120	6	94
51	115	–	230	"	115	100	6	94

(continued)

TABLE 2 (continued)

No.	βACB (mmole/ liter)	ZnCl$_2$ (mmole/ liter)	Zn(OCOR)$_2$ (mmole/ liter)	Costabilizer[a]		Reaction time (min)	Dehydro- chlorination (%)	Substi- tution (%)
				Type	Amount (mmole/ liter)			
52	160	-	35	αPhI	35	8	0	30
53	170	-	170	"	170	100	6	94
54	170	-	230	"	60	90	6	94

[a]Ca(OCOR)$_2$: calcium stearate; Zn(OCOR)$_2$: zinc stearate; C4H8O: epoxy-1,2-butane, P(OBu)$_3$: n-butyl phosphite; αPhI: α-phenylindole.
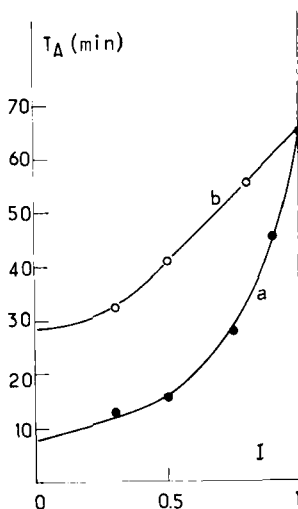
FIG. 11. Influence of the ratio $\beta ACB/(\beta ACB + stearate)$ on the action time T_A in the case of (●) zinc stearate or (○) calcium stearate for mixtures of PVC (30 g) DOP (9 g) and stabilizer (2.86 mmole) in a Brabender plastograph at 190°C.

with βACB show that their ability to limit the dehydrochlorination is a direct function of their ability to neutralize HCl. In this respect stearate and epoxy compounds are superior to the phosphites.

When a costabilizer is present to react with HCl more rapidly than βACB, then up to four molecules of 4C2H may be reacted with βACB (Table 2).

Experiments with polymers in the Brabender plastograph have been also carried out in some cases. Typical results are shown in Figs. 11 and 12 for the system with zinc and calcium stearate in binary (Fig. 11) or ternary (Fig. 12) formulations. The presence of βACB increases the efficiency of the system, but no true synergistic effect is observed.

The presence of zinc compounds increases the yield of substitution products from βACB, because the yield of organic products from βACB typically decreases from about 20% in the absence of zinc compound to about 4% in its presence. However, NH$_4$Cl as well as the βACB hydrochloride are present in rather high yield (15-20% and 25-30%, respectively). In Figs. 13 and 14 are shown the results of experiments with ternary systems of βACB, zinc stearate, and either ESO or αPI. In both cases, it may be seen that, in the presence of a fixed amount of zinc stearate, βACB is not so much superior
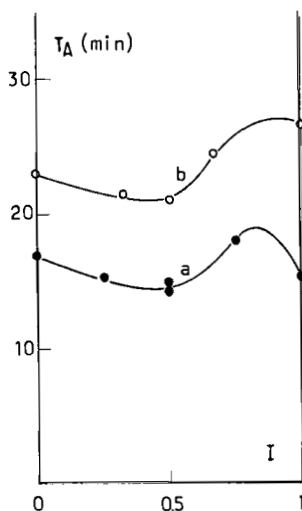
FIG. 12. Influence of $I = \beta ACB/[\beta ACB + Ca(OCOR)_2]$ on T_A in the Brabender plastograph at 190°C for ternary systems of zinc and calcium stearate, βACB: (•) zinc stearate = 1.4 mmole; βACB + $Ca(OCOR)_2$ = 1.4 mmole; (○) zinc stearate = 0.7 mmole; βACB + $Ca(OCOR)_2$ = 2.1 mmole.

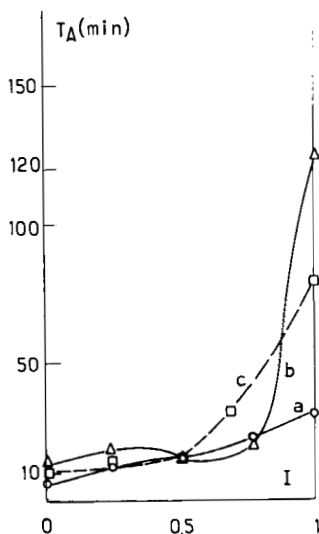FIG. 13. Influence of I on T_A in the Brabender plastograph at 190°C for ternary system: zinc stearate, βACB, epoxidized oil ESO at total concentration of the stabilizer of 4 mmole: (○) $Zn(OCOR)_2$ = 1.33 mmole, $I = \beta ACB/(\beta ACB + ESO)$; (△) βACB = 1.33 mmole, $I = ESO/$ $[ESO + Zn(OCOR)_2]$; (▢) ESO = 1.33 mmole, $I = \beta ACB/[\beta ACB + Zn(OCOR)_2]$.

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T_A (min)

FIG. 14. Influence of I on T_A in the Brabender Plastograph at 190°C for ternary system: zinc stearate (Zn(OCOR)₂), βACB, and α-phenylindole (αPhI) at total concentration of stabilizer of 2.8 mmole; (□) βACB = 1.4 mmole, I = αPhI/[αP + Zn(OCOR)₂]; (△) α PhI = 1.4 mmole, I = βACB/[βACB + Zn(OCOR)₂]; (○) Zn(OCOR)₂ = 1.4 mmole, I = βACB/(βACB + αPhI).

to the organic compound. No true synergistic effect is observed, and the action time increases chiefly when the amount of zinc stearate decreases.

CONCLUSIONS

βACB is a very powerful component of a stabilization formulation but gives rise to a variety of reactions. It is a good HCl acceptor, but it may also be substituted for the allylic chlorine either by its primary amine groups or by its hydrogen atom of the trisubstituted double bonds. It is able to complex ZnCl₂ and inhibits its catalytic activity; the same is true for amonium hydrochloride which results from its reaction with HCl.

ACKNOWLEDGMENTS

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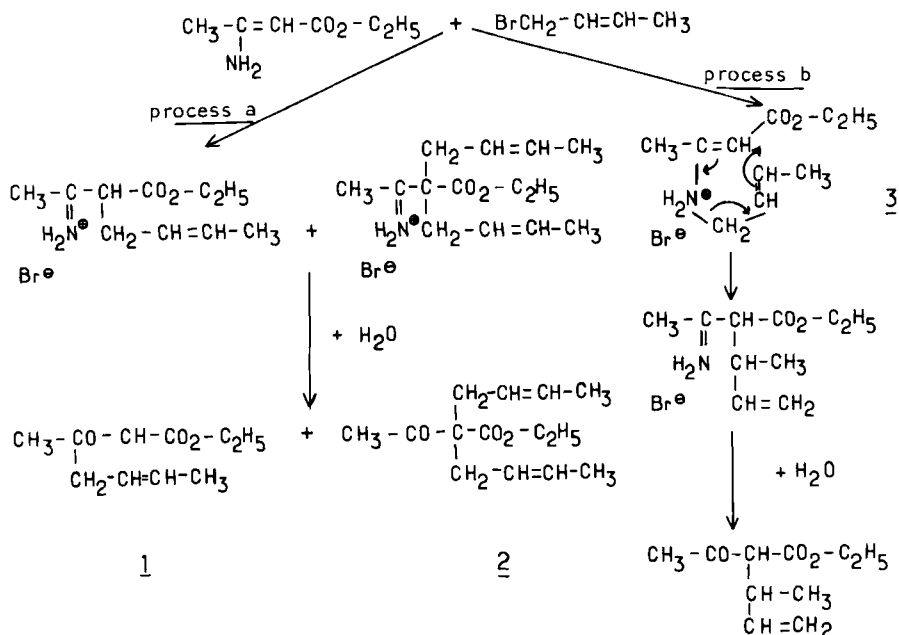   New York, 1970, Vol. 12, pp. 725-768.
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DISCUSSION

Mr. P. de Cointet (CREP, Sisteron, France): I would like to com-
ment on one aspect of the topic of Dr. Hoang related to the stabilizing
action of β-aminocrotonate types compounds. In our laboratory we
have worked to get a thermal stabilizer for PVC better than the
butanediol β-aminocrotonate. Our results (Eur. Polym. J., in press)
are consistent with those just presented by Dr. Hoang.

As Dr. Hoang pointed out, we have not found any report in the
literature on the stabilizing action of β-aminocrotonates. Therefore
we suggested that an alkyl β-aminocrotonate reacts with the allylic
chlorine of a degradated PVC unit as an enamine with allylic halide
(A. C. Cook, Enamines, Dekker, New York, 1969). Thus two mech-
anisms are equally possible [K. C. Brannock and R. D. Burpitt, J.
Org. Chem., 26, 3576 (1961)]: direct C-alkylation or N-alkylation
accompanied by a rearrangement.

In order to study the reaction process we have worked on the
reaction of ethyl β-aminocrotonate and 1-bromo 2-butene. Two
different compounds may be obtained according to the process con-
sidered (Scheme 2). It should be noted that the mixture was hydrolyzed
in order to simplify the purification and identification of the constitu-
ents. The ethyl α-butenylacetoacetate(1) and its α,α-disubstituted

$$CH_3-C=CH-CO_2-C_2H_5 \quad + \quad BrCH_2-CH=CH-CH_3$$
$$\underset{NH_2}{|}$$

process a   process b

$$\overset{CO_2-C_2H_5}{}$$

$$CH_2-CH=CH-CH_3 \qquad CH_3-C=CH$$

$$CH_3-\underset{\underset{H_2N^\oplus}{\|}}{C}-\underset{\underset{CH_2-CH=CH-CH_3}{|}}{CH}-CO_2-C_2H_5 \qquad CH_3-\underset{\underset{H_2N^\bullet}{\|}}{C}-\underset{\underset{CH_2-CH=CH-CH_3}{|}}{C}-CO_2-C_2H_5 \qquad H_2N^\bullet \overset{CH-CH_3}{\underset{Br^\ominus}{\overset{|}{C}H}} \quad 3$$

$$Br^\ominus \qquad\qquad Br^\ominus \qquad\qquad Br^\ominus \quad CH_2$$

+ H₂O

$$CH_3-C-CH-CO_2-C_2H_5$$
$$\underset{H_2N}{\|} \underset{CH-CH_3}{|}$$
$$Br^\ominus \quad CH=CH_2$$

$$CH_3-\underset{\underset{CH_2-CH=CH-CH_3}{|}}{CO}-CH-CO_2-C_2H_5 \quad + \quad CH_3-CO-\underset{\underset{CH_2-CH=CH-CH_3}{|}}{\overset{CH_2-CH=CH-CH_3}{|}}C-CO_2-C_2H_5$$

+ H₂O

$$CH_3-CO-\underset{\underset{CH=CH_2}{\underset{|}{CH-CH_3}}}{CH}-CO_2-C_2H_5$$

1   2

Scheme 2.

homolog (2) were identified and isolated in 36% yield. The recovery of these two molecules shows clearly that the direct C-alkylation was operative (process a).

We must emphasize that it was not possible to detect the N-alkylated derivative (3) obtained by an N-alkylation reaction without any C-alkylation rearrangement, since the mixture was hydrolyzed.

On the other hand, the analysis of the stabilizing effect of β-aminocrotonic acid derivatives synthesized by us corroborates the suggested mechanism. Thus structural modifications disadvantaging direct C-alkylation induce a decrease of stabilizing action. N-substitution is such a case (compounds 4), since the reaction is oriented towards an N-alkylation [G. Stork et al. J. Amer. Chem. Soc., 85, 207 (1963)], on the one hand and the rate of direct C-alkylation is decreased on the other hand (C. Egliton and M. C. Whiting, J. Chem. Soc., 1953, 3052). The same behavior is shown for an α-substitution (compound 5), since the steric hindrance of the active site is increased.

By contrast, structural modifications favoring the direct C-alkylation lead to β-aminocrotonic acid derivatives exhibiting a clear stabilizing effect. Thus for β-aminocrotonanilides 6 (Table 3) we have found a correlation between their stabilizing action S and the electronic

TABLE 3.

$$CH_3 - \underset{\underset{NH_2}{|}}{C} = CH - CO - NH - \underset{Y}{\overset{}{\bigcirc}} - X$$

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Compound	-X	-Y	Stabilizing power S	σ^-	Solubility x in octanol (g/liter)
6-a	-OH	-H	38	-0.37	0.2
6-b	$-O-C_2H_5$	-H	40	-0.24	1.9
6-c	$-O-CH_3$	-H	41	-0.27	0.8
6-d	-H	-H	44	0.00	2.1
6-e	$-CO_2-C_2H_5$	-H	60	0.68	0.3
6-f	$-CO_2-C_4H_9$	-H	61	0.67	1.7
6-g	-Cl	-H	60	0.23	26.3
6-h	$-SO_2NH_2$	-H	35	0.91	1.7×10^{-4}
6-i	-Cl	-Cl	63	0.60	16.3
Butanediol -amino- crotonate			53		

$$CH_3 \underset{\underset{R^1 \diagdown \diagup R^2}{N}}{\overset{}{-\!-\!-}} C \!=\! CH\!-\!CO_2R \qquad\qquad CH_3 \underset{\underset{\underset{CH_3}{|}}{\underset{CH_2}{|}}}{\overset{}{-\!-\!-}} C \!=\! \underset{NH_2}{\overset{}{C}} \underset{}{-\!-\!-} CO_2-C_2H_5$$

$$\underline{4} \qquad\qquad\qquad\qquad \underline{5}$$

R = alkyl R^1, R^2 = H, alkyl, aryl . . .

constant $\sigma-$ [C. Hansch, E. D. Deutsch, and R. N. Smith, J. Amer. Chem. Soc., <u>87</u>, 2738 (1965)] of the X and Y phenyl branched substituents:

$$\log S = 1.648833(\pm 0.5060 \times 10^{-2}) + 0.3039 \times 10^{-2} \ (\pm 0.422 \times 10^{-3})x$$
$$- 0.46 \times 10^{-4} \ (\pm 0.2 \times 10^{-5}) \ (1/x) + 0.186520 \ (\pm 0.9241 \times 10^{-2})\sigma$$
$$R^2 = 0.9936, \text{ Test } F < 1\%.$$

We must point out that another parameter x has been introduced which corresponds to the liposolubility of β-aminocrotonanilide and takes into account the PVC-stabilizer compatibility.

An electroattractive group favoring the delocalization of the amide nitrogen doublet towards the phenyl ring increases the electroattractive power of the C=O group. Thus the migration of enamine residue π electrons and therefore the direct C-alkylation is favored.

In conclusion our results are consistent with those of Dr. Hoang, but it seems to us that the stabilizing action of β-aminocrotonate types compounds is due mainly to a direct C-alkylation.

Dr. Tran Van Hoang: Our results are little different from those of Mr. de Cointet, because firstly, the products used are not the same: ethyl-β-aminocrotonate instead of butanediol β-aminocrotonate (βACB) and 1-bromo-2-butene instead of 4-chloro-2-hexene (4C2H), which is a more typically unstable model compound of PVC. Secondly, we have used a Lewis catalyst, ZnCl₂.

In solvents of different electronic constant such as tetrahydrofuran and 1,2 dichloroethane, at mild temperature of 60° C the reaction between βACB and 4C2H takes place only in the presence of ZnCl₂, and the mechanism is first N-alkylation accompanied by C-alkylation.
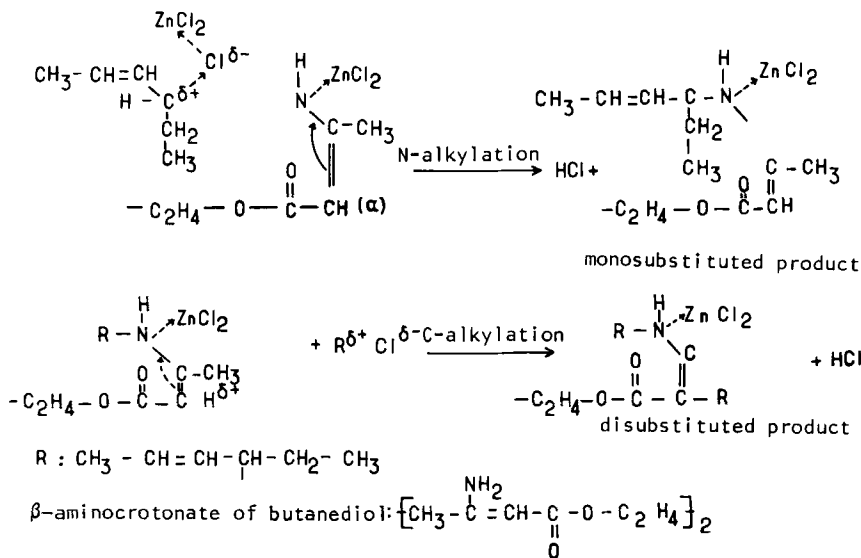
According to Mr. de Cointet, the increase of the electroattractive power of the C=O group can delocalize the amide nitrogen doublet towards αC to favor C-alkylation. In our case, the $ZnCl_2$ coordinates the free electron doublet of nitrogen atom, displacing the π electron to the latter, so that the αC of βACB cannot attack nucleophilly the carbocation of the intermediate compound of $(4C2H + ZnCl_2)$ [Eur. Polym. J., 12, 337 (1976)]. Consequently, there is no direct C-alkylation. After the evolution of HCl and N-alkylation, this mono-substituted product which has a structure similar to that of α-phenyl-indole [Eur. Polym. J., 12, 357 (1976)] gives, after a C-alkylation, a disubstituted product.

Dr. A. Guyot (Centre National de la Recherche Scientifique, Villeurbanne, France): I agree that there is a great deal of difference in the conditions used, but I think a better characterization of the final products will be necessary in order to clarify the differences between the two systems.